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George B. Butler<sup>a</sup>; Choon H. Do<sup>a</sup>; Michael C. Zerner<sup>a</sup>

<sup>a</sup> Department of Chemistry, Center for Macromolecular Science and Engineering University of Florida, Gainesville, Florida

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## THE STEREOCHEMISTRY OF STYRENE–MALEIC ANHYDRIDE COPOLYMERS: $^{13}\text{C}$ -NMR STUDY AND PVCILO AND INDO/1 CALCULATIONS

GEORGE B. BUTLER,\* CHOON H. DO, and MICHAEL C. ZERNER

Department of Chemistry and Center for Macromolecular Science  
and Engineering  
University of Florida  
Gainesville, Florida 32611

### ABSTRACT

The stereochemistry of alternating copolymers of styrene (ST) with maleic anhydride (MA) was examined by  $^{13}\text{C}$ -NMR spectroscopy, and the stabilization energies and the most stable geometries of complexes and adducts between ST and MA were calculated by the PVCILO program and by INDO/1. The methine and carbonyl carbon atoms of the MA portion and the quaternary carbon atom of the ST portion reveal different stereochemistries due to various polymerization conditions, suggesting that the donor-acceptor complex may participate in the copolymerization. The complex postulated according to the Diels-Alder geometry was more stable than that according to [2+2] cycloaddition geometry. It is believed that the stabilization energy is so great that the copolymerization occurs spontaneously via forming a donor-acceptor complex and adducts. The geometries of 1:1 adducts formed by *endo* and *exo* approaches in the Diels-Alder geometry mode were also calculated.

## 1. INTRODUCTION

The copolymer between styrene (ST) and maleic anhydride (MA) is a typical example of an alternating copolymer. Since Mayo et al. studied this copolymer [1, 2], its structure and kinetics have been studied and reviewed by many research groups [3-17]. The copolymer shows a strong tendency toward alternation and does not follow the classical termination mechanism in which the reaction of a growing free radical is determined by the terminal monomer unit alone. As a consequence, the mechanism of the alternation has been explained by the participation of a donor-acceptor complex (DA) [5-9] and by the penultimate copolymerization model [9, 10]. The formation of the DA was confirmed by NMR, and the equilibrium constant determined as 0.33 L/mol with  $\Delta H = -1.5$  kcal/mol [5], although the presence of a DA is not a sufficient condition to validate copolymerization via the donor-acceptor complex mechanism.

The copolymerization occurs spontaneously even in the absence of a radical initiator [18], and it is assumed that the Diels-Alder adduct between ST and MA, bicyclo[4.4.0]deca-1,7,9-triene 4,5-dicarboxylic anhydride initiates the copolymerization [16, 18], similar to the thermal homopolymerization of ST [19]. The stereochemistry of the copolymer was examined by  $^{13}\text{C}$ -NMR spectroscopy [13-15], and the effect of the stereochemistry of the DA on the copolymer was also discussed [6]. Hill et al. employed  $^{13}\text{C}$  NMR to determine the sequence distribution of the ST-MA copolymer [13, 14]. Raetzsch et al. tried to explain the configuration of the copolymer by  $^{13}\text{C}$ -NMR spectra [15].

We believe that not only may the alternating copolymerization occur by participation of the DA, but also the resulting alternating copolymer may possess the same degree of regio- and stereoregularity due to the DA. Furthermore, since the copolymerization can occur in the absence of a radical initiator, we were interested in comparing the stereochemistry of the copolymers prepared with and without a radical initiator by  $^{13}\text{C}$ -NMR spectroscopy. We have also compared the effects of solvents and temperature on the stereochemistry by  $^{13}\text{C}$ -NMR spectroscopy because the solvents and temperature affect the concentration of DA and, consequently, the stereochemistry of the copolymer. Solvents and temperature change [DA] by 1) lowering [DA] at a lower concentration of monomers and higher temperature, and 2) forming solvent-donor (or acceptor) monomer complexes. The effects of solvents on the copolymerization kinetics and the equilibrium constants of the solvent-donor (or acceptor) monomer complexes have been studied previously [11]. In addition, since the PVCIO electronic structure method [20-22] is well

suited to calculating the stabilization energy and the geometry of the DA [23], we extend the calculations to the ST-MA complex here. The geometries of the adducts were further refined by optimizing all geometric parameters by the INDO/1 method [24, 25].

## 2. EXPERIMENTAL SECTION

### 2.1. Materials

Styrene (Aldrich, 99%) was distilled just before use. Maleic anhydride (Aldrich, 99%) and maleic-2,3- $d_2$  anhydride (Merck, 98 atom% D) were recrystallized from chloroform. AIBN was recrystallized from methanol. Methylene chloride was dried over calcium hydride. Toluene and hexanes were distilled over sodium.

### 2.2. Copolymerization

Copolymers were prepared under varied conditions: with and without initiator (AIBN), with and without solvent (methylene chloride), and at different polymerization temperatures (Table 1). A general procedure is as follows: Appropriate amounts of monomers, AIBN, and methylene chloride were added to a polymerization tube, and the tube was sealed under vacuum after removing oxygen by several freeze and thaw cycles. The tube was then placed in a water bath and shaken for a specified time. The copolymer was precipitated by pouring the solution into dried toluene. After the copolymer was washed successively with toluene and hexanes, it was dried under vacuum at room temperature.

The procedure for the photoinitiated polymerization is as follows: Appropriate amounts of AIBN (with 3 mL methylene chloride) and styrene (with 3 mL methylene chloride) were placed in break-seal tubes separately and degassed and sealed as described above. After connecting these tubes to a three-neck quartz tube, the maleic anhydride in 4 mL methylene chloride was placed in the tube and degassed and sealed. The seal between the styrene and AIBN compartments was then broken, the contents mixed, and the tube quickly immersed in a 10°C bath. The tube was then irradiated with a 350-W long-wave UV lamp for a specified period. Precipitation and drying of the copolymer were carried out as described above.

### 2.3. NMR Spectroscopy

NMR spectra were recorded on a Varian 200-XL NMR spectrometer at ambient temperature with acetone- $d_6$  as solvent. Heterocorrelated  $^1\text{H}$ - $^{13}\text{C}$

TABLE 1. Copolymerization of Styrene with Maleic Anhydride

Expt.	ST, mL	MA, g	AIBN, mg	CH <sub>2</sub> Cl <sub>2</sub> , mL	Polymerization temperature, °C	Polymerization time, h	Yield, g (%)
1	2.30	1.96	None	None	20-21	24	0.43 (11)
2	1.15	1.02 <sup>a</sup>	None	None	20-21	24	0.70 (34)
3	2.30	1.96	None	10	20-21	24	0.052 (1.3)
4	2.30	1.96	None	10	60	8.7	0.091 (2.2)
5	2.30	1.96	30	10	60	0.17	0.50 (12)
6	2.30	2.04 <sup>a</sup>	30	10	60	0.17	0.74 (18)
7 <sup>b</sup>	1.15	1.02 <sup>a</sup>	30	10	-10	1.0	0.17 (8.3)
8 <sup>b</sup>	2.30	1.96	30	10	-10	1.0	0.22 (5.4)

<sup>a</sup>Deuterated MA.<sup>b</sup>Photoinitiated polymerization.

2D spectra and attached proton test (APT) were also performed to assign the peaks of the NMR spectra.

### 3. CALCULATION

#### 3.1. Geometric Parameters of ST and MA

The geometric parameters of ST were obtained from *ab initio* calculation at the STO-3G level [26]. The geometric parameters of MA were obtained from the crystal structure [27].

#### 3.2. The Geometry of ST-MA Complex

[2+2] Cycloaddition and [2+4] Diels-Alder addition geometries were considered in the PVCILO calculation. In the case of [2+2] cycloaddition geometry, the two planes of MA and ST were placed parallel to cause overlap of the C–C double bonds, and the distance between the two planes was altered. In the [2+4] Diels-Alder addition case, the plane of MA was moved parallel after overlapping the C–C double bonds and fixing the vertical distance of the two planes. The stabilization energy ( $\Delta E$ ) was calculated from the energy difference between the energy of ST-MA complex,  $E_{\text{ST-MA}}$ , and the energies of ST ( $E_{\text{ST}} = -39\,472.538$  kcal/mol) and MA ( $E_{\text{MA}} = -53\,403.207$  kcal/mol).  $\Delta E = E_{\text{ST-MA}} - (E_{\text{ST}} + E_{\text{MA}})$ .

#### 3.3. The Geometry of Adducts

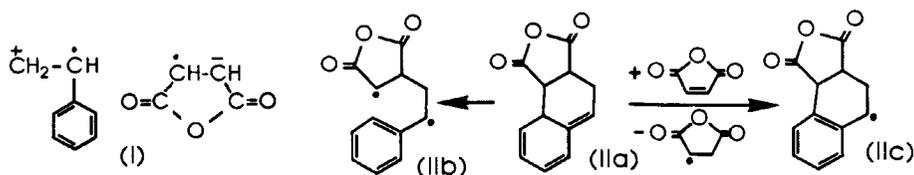
First, two best [2+4] Diels-Alder addition geometries possessing the highest stabilization energies, one from *endo* and another from *exo* additions, were obtained from the PVCILO calculations on ST-MA complex. Then these initial geometries were used to calculate the geometries of *endo* and *exo* adducts by the INDO/1 method using a gradient optimization technique [24, 25].

## 4. RESULTS AND DISCUSSION

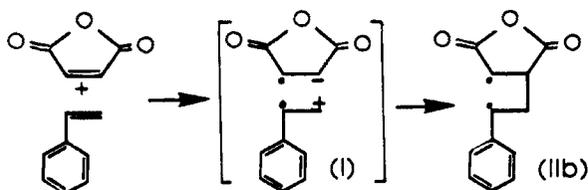
### 4.1. Copolymerization

The results of the copolymerization are summarized in Table 1. ST copolymerized easily with MA by a radical-initiated polymerization (Expt. 3 and 4, copolymer insoluble in methylene chloride started to appear even dur-

ing the degassing step), and copolymerization occurred even in the absence of a radical initiator (Expt. 1 and 2). The yield of the copolymer obtained without use of a radical initiator increased as the concentration of monomers increased, i.e., without solvent. According to the  $^1\text{H-NMR}$  spectrum, the composition ratio of ST and MA is 1:1. This strongly suggests that ST and MA interact with each other to form a radical which initiates the copolymerization. We therefore speculate that the radical might be generated by 1) ST-MA complex (I) as suggested by Mayo et al. [2] or 2) a Diels-Alder adduct intermediate (II) as suggested by Raetzsch et al. [16].

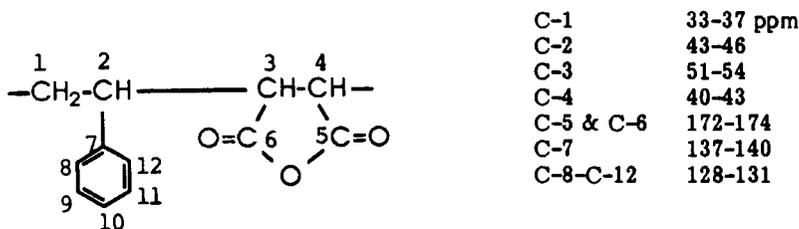


Structure IIb may also be formed by interaction between the C—C double bonds of ST and MA, probably via I, similar to the case where donor and acceptor molecules form a tetramethylene diradical as studied by Hall et al. [28].



The stabilization energies of the complexes of ST with MA for Diels-Alder addition and [2+2] cycloaddition geometries will be discussed later. Spontaneous copolymerization without an initiator indicates that the ST-MA complex plays a role in the initiation, but it does not necessarily mean that DA participates in the propagating step. Nevertheless, the radicals or the ions postulated do not lead to either ionic homopolymerization of ST or MA or cyclization of ST and MA, as for other DA's [28]. Therefore, we may assume that the zwitterionic intermediate (I) is involved only insignificantly and that the radicals and DA participate in the copolymerization. The participation of DA in the propagating step may result in a regio- and stereoregular copolymer because 1) the interaction between ST and MA may result in a specific spatial arrangement of the DA, and 2) the opening mode of the double bonds of ST





the carbon atoms of the main chain (C-1 to C-4), the carbonyl carbon atoms (C-5 and C-6) of the MA portion, and the quaternary carbon atom (C-7) of the benzene ring.

The shape of the peak for the methylene carbon atom (C-1) of the styrene portion (Fig. 2) is similar to that reported by Barron et al. [14], according to whom it represents the presence of MA-ST-MA triad sequences and consequently suggests that this copolymer is alternating. This peak also shows a multiplet (a-e) related to the fine structure of the copolymer. The ratios of peak heights, especially Peaks *c* and *d*, change as the methods of the copolymerization are varied. Photoinitiated copolymerization (Fig. 2a) gives a more distinct fine structure than radical polymerization (Figs. 2b-e), and this trend continues in the other peaks, too. This result indicates that lowering the polymerization temperature increases [DA] and consequently enhances the stereoregularity of the copolymer although we cannot rule out the possibility that the difference in the fine structures of the peaks comes from the difference in the monomer sequences. Comparison of the peak obtained from the copolymer prepared by radical-initiated copolymerization with AIBN (Fig. 2b) with one obtained without AIBN (Fig. 2d) shows that the peak shapes are very similar. As the copolymerization time was increased from 3 to 8.7 h, Peak *a* increased slightly (Fig. 2c). The copolymer obtained without initiator and without solvent shows the same peak shape as the copolymer obtained by conventional radical copolymerization (Fig. 2b vs Fig. 2c). This result indicates that the same mechanism, radical copolymerization, was operating in both cases.

The peaks for C-2 and C-4 are partially overlapped and appear around 40-46 ppm (Fig. 3). We used deuterated MA in the copolymerization instead of MA and examined the copolymer by an APT experiment in order to separate these two peaks. Due to the deuterium, the peak of the methine carbon atoms (C-3 and C-4) of the deuterated MA shows the opposite direction from the methine carbon atoms of MA (Fig. 4). From this experiment we can assign the peaks for C-2 and C-4. The relative height of C-4 over C-2 is reduced in Fig. 4(b) compared to Fig. 4(a). It is a result of nuclear Overhauser enhance-

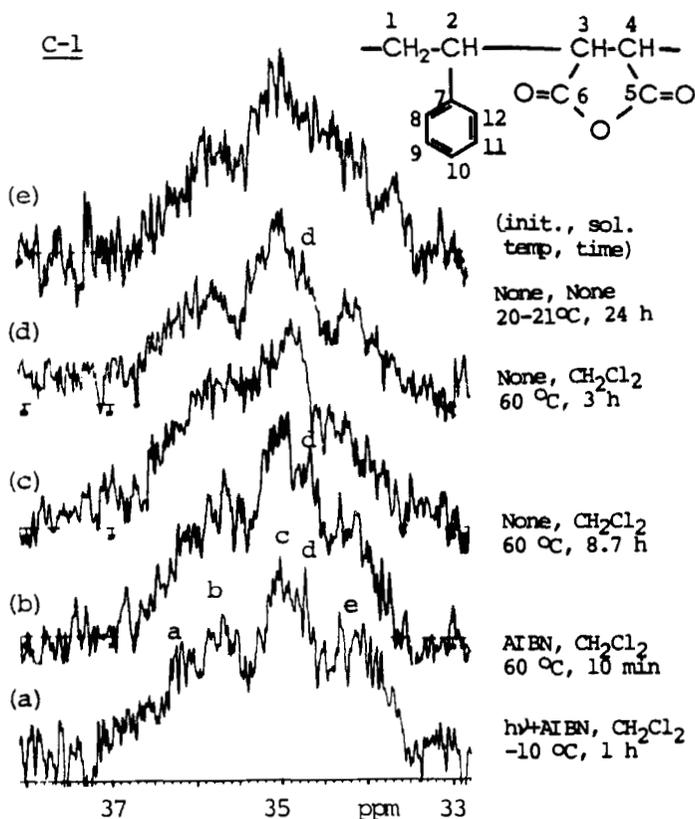


FIG. 2. <sup>13</sup>C-NMR spectra of methylene carbon atom (C-1).

ment of the C-2 peak. The α-carbon atom of the styrene portion (C-2) appears around 43-46 ppm and shows two main peaks. It does not show a significant difference among the different polymerization methods.

The C-4 carbon atom shows *erythro* (*cis*) and *threo* (*trans*) stereochemistry of the 2,3-dialkylsuccinyl anhydride unit in the MA-olefin copolymers ( $\delta_{cis} - \delta_{trans} = -1.2$  ppm) [15]. The C-4 peak shows two sharp spikes (3 ppm apart) in the MA-ethyl vinyl ether (EVE) copolymer (our unpublished data), and we speculate that the two peaks represent a kind of *meso* and racemic configuration between the ring of MA and the ethoxy group. The C-4 peak here apparently shows a strong spike, *c*, and a small one, *d*. Consequently, the appearance

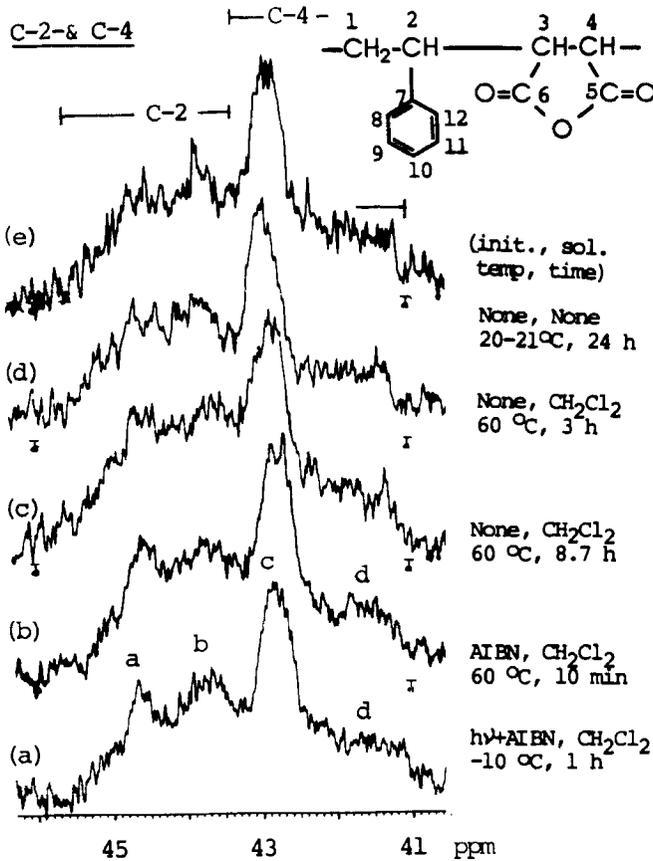


FIG. 3.  $^{13}\text{C}$ -NMR spectra of C-2 and C-4.

of the strong peak in the ST-MA copolymer suggests that either *meso* or racemic, probably *meso*, configurations might be dominant because of the interaction between ST and MA. Careful examination of the C-4 peak may reveal that the double bond of MA might be opened by a *trans*-opening in the ST-MA copolymer. This anticipation is based on the observation of the C-4 peak of the MA-EVE copolymer where the double bond of MA was opened mainly by *trans*-opening, and also on a theory that the formation of a ST-MA complex will restrict the rotation of the MA molecule.

The peak for C-3 shows fine structure (*a* and *b* in Fig. 5) which can be

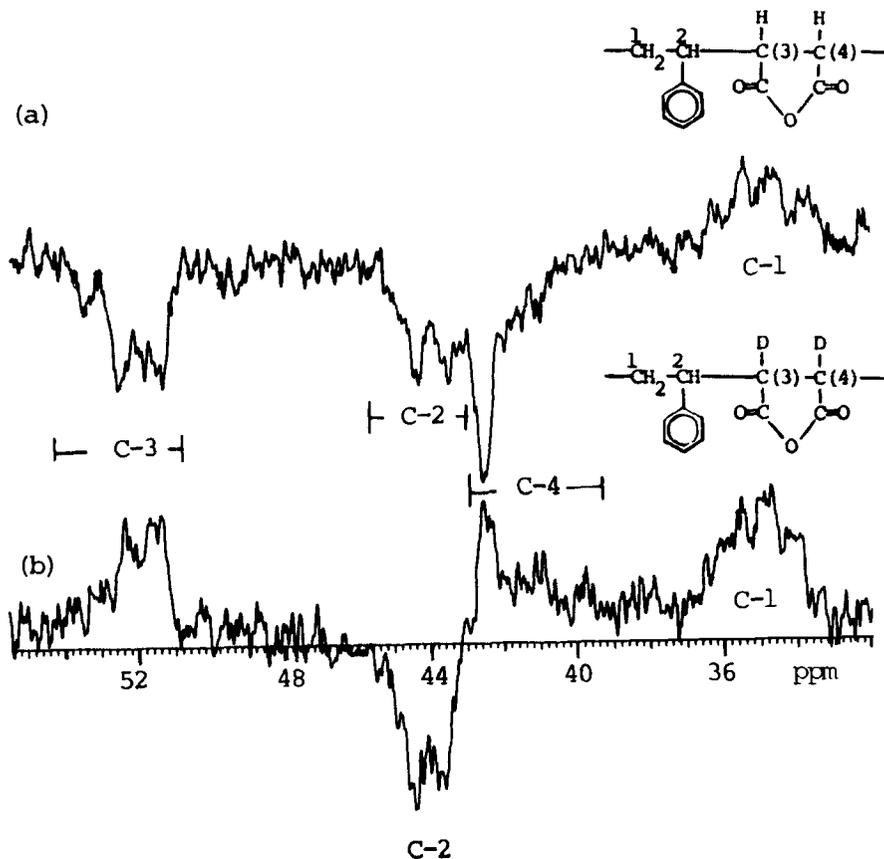


FIG. 4. APT experiment of (a) ST-MA and (b) ST-deuterated MA copolymers.

related to *erythro* and *threo* configurations of the MA portion or related to the tacticity of the copolymer. Although we are unable to assign the peaks of the fine structure, the shape of the peaks differ according to the copolymerization conditions. It therefore supports that they possess a different stereochemistry in the copolymer structure.

The peaks for the carbonyl carbon atoms, C-5 and C-6, are shown in Fig. 6. The C-6 peak may appear downfield relative to C-5 because C-6 is close to the

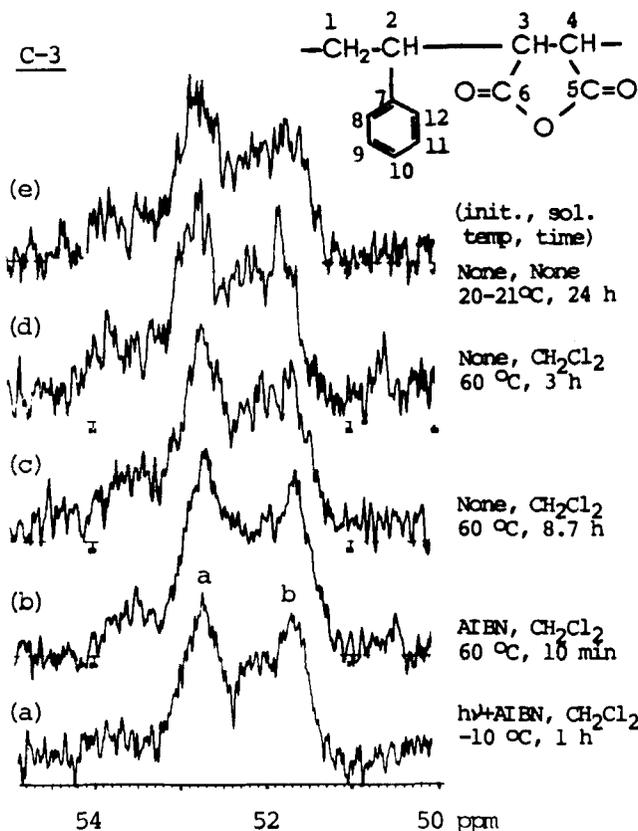


FIG. 5.  $^{13}\text{C}$ -NMR spectra of C-3.

methine carbon atom of ST and C-5 is close to the methylene carbon atom of ST. Figure 6 shows that there are more than four peaks of slightly different shapes according to the copolymerization conditions.

The quaternary carbon atom (C-7) of the benzene ring shows at least a quartet splitting (Fig. 7). Peaks *c* and *d* are stronger than Peaks *a* and *b*, and this indicates that a specific configuration may prevail although we are uncertain how to assign the peaks correctly. It is also notable that the relative height of Peak *d* to *c* varies from Fig. 7(a) to Fig. 7(e). Splitting of this carbon atom was also observed in other ST copolymers, such as the ST-acrylo-

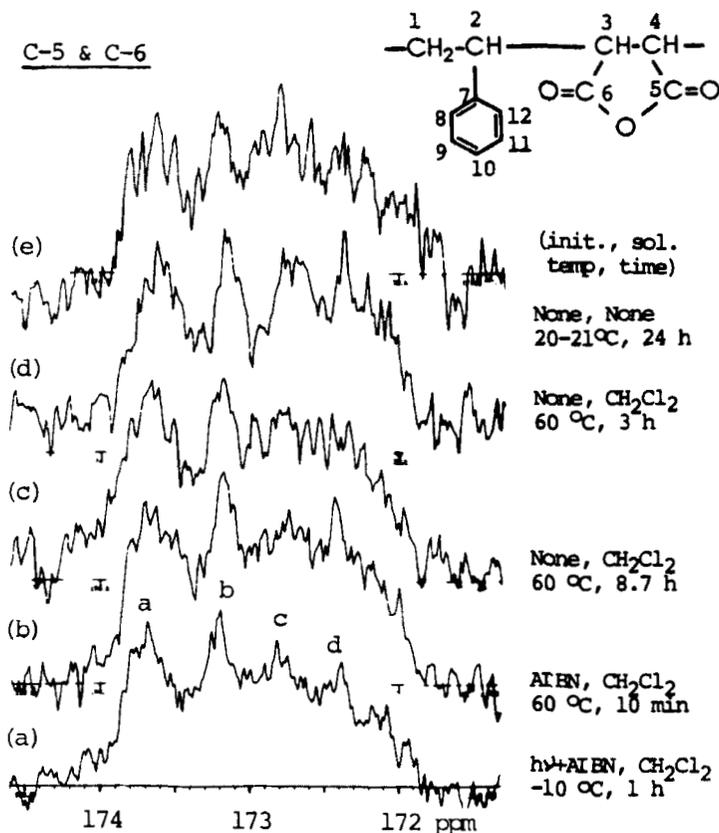


FIG. 6. <sup>13</sup>C-NMR spectra of the carbonyl carbon atoms (C-5 and C-6) of the MA portion in ST-MA copolymers.

nitrile [30] and ST-methyl methacrylate [31] copolymers, although the splitting was not correlated with the microstructure of the copolymer.

The <sup>13</sup>C-NMR spectra of the quaternary carbon atom (C-7) of the benzene ring, the carbonyl carbon atoms (C-5 and C-6), and methine carbon atom (C-4) of the MA portion reveal some evidence for the stereoregularity of the copolymers. A further examination of these carbon atoms may yield a better understanding of the stereochemistry of the copolymer and the copolymerization mechanism between ST and MA.

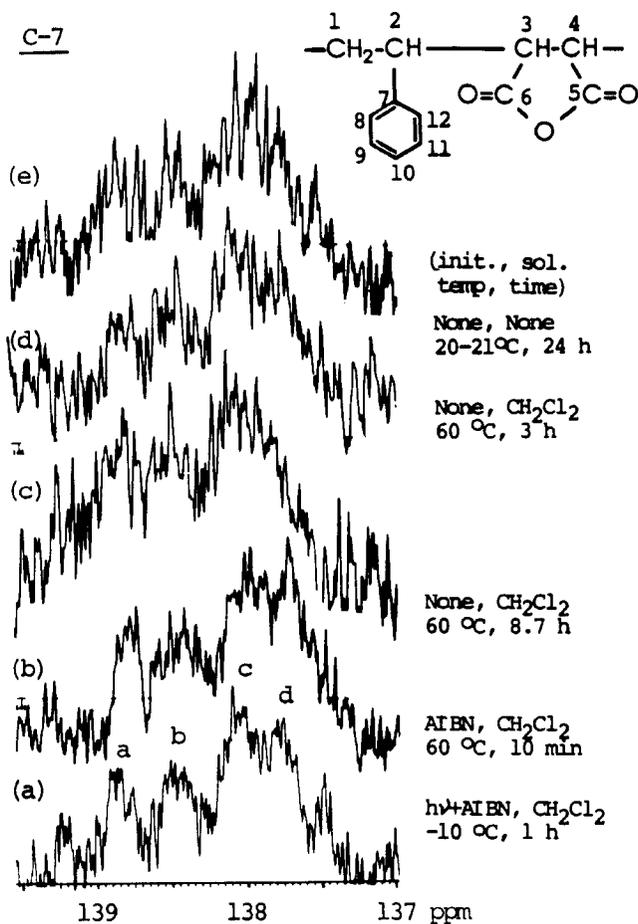


FIG. 7.  $^{13}\text{C}$ -NMR spectra of the quaternary carbon atom of the benzene ring in ST-MA copolymers.

#### 4.3. The Stabilization Energy of the Complexes

Since the DA participates in the copolymerization between ST and MA, its geometry may affect the stereochemistry of the copolymer. Therefore, we calculated the stable geometry of 1:1 ST-MA complexes and their stable energies for the cases of [2+2] cycloaddition and [2+4] Diels-Alder addition approaches.

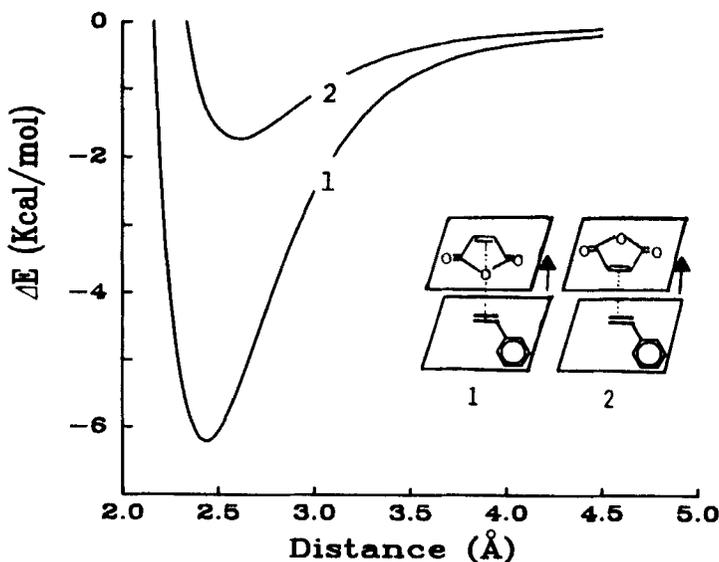


FIG. 8. The stabilization energy and the [2+2] cycloaddition geometries of ST-MA complex.

Two [2+2] cycloaddition geometries of ST-MA complex were considered: The ring of MA was located on the same side as the benzene ring of ST and on the opposite side of the benzene ring of ST (Fig. 8).  $\Delta E$  was calculated to be  $-6.2$  kcal/mol at  $2.4$  Å and  $-1.9$  kcal/mol at  $2.6$  Å when the two rings were located on the same side and opposite side, respectively. This result indicates that the ST-MA complex is more stable when the two rings are located on the same side and further implies that this geometry may be maintained in the copolymer if the DA participates in the copolymerization.

In the case of the Diels-Alder geometry (Fig. 9), the complex of *endo* geometry ( $\Delta E = -48$  kcal/mol) is more stable than that of the *exo* geometry ( $\Delta E = -39$  kcal/mol), as expected from general concepts of Diels-Alder reactions. In addition, the results reveal that the Diels-Alder geometries are more stable than the [2+2] cycloaddition geometries. Therefore, the ST-MA complex may exist predominantly in the Diels-Alder geometry forms. These stabilization energies are quite high compared to  $\Delta H$  estimated from the NMR study ( $-1.5$  kcal/mol) [5]. Consequently, we believe that these high stabilization energies produce Diels-Alder adducts and radicals which will eventually lead to spontaneous copolymerization although this calculation does not sup-

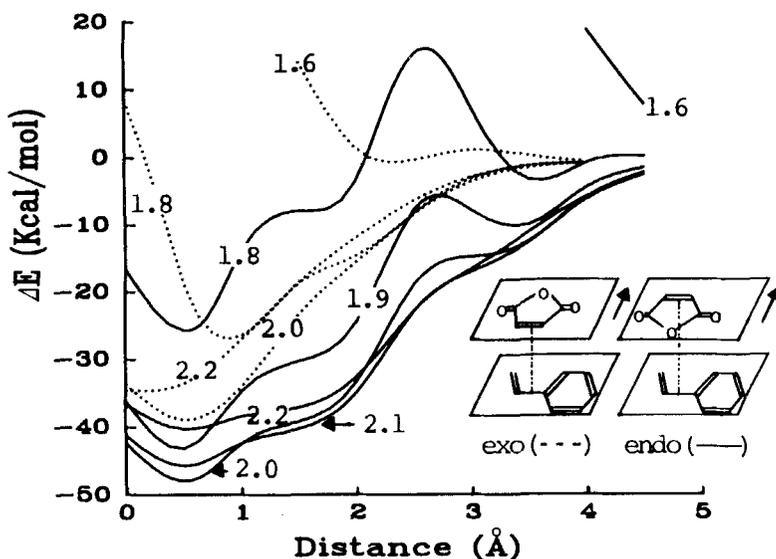


FIG. 9. The stabilization energy and the Diels-Alder geometries of ST-MA complex. The numbers on the curves show the vertical distances between the two planes.

ply the information on the intermediate (transition) state. The distance (2.06 Å) that we calculate between the double bond of MA and the single bond of ST in *endo* geometry is likely to be short. The geometry, however, gives us an idea of the stabilization of the ST-MA complex. The DA complex has a maximum stabilization when the  $\pi$  orbitals of ST and MA are delocalized uniformly in the entire complex (Fig. 10).

#### 4.4. The Geometries of Diels-Alder Adducts

Although the 1:1 (IIa and IIc, the formation of IIa by *exo* rather than *endo* approach is shown for the convenience of observation) and the 1:2 (IVa and IVb) adducts between ST and MA have been reported [32-34], the 1:1 adduct, IIa, is only postulated and has not been isolated. Because we, like other researchers, believe that IIa is an important intermediate in the copolymerization, we calculated its possible geometries. The geometry of a ST-MA adduct formed by the *exo* addition is shown in Fig. 11, and the geometric parameters are listed in Table 2. The plane of ST is tilted about

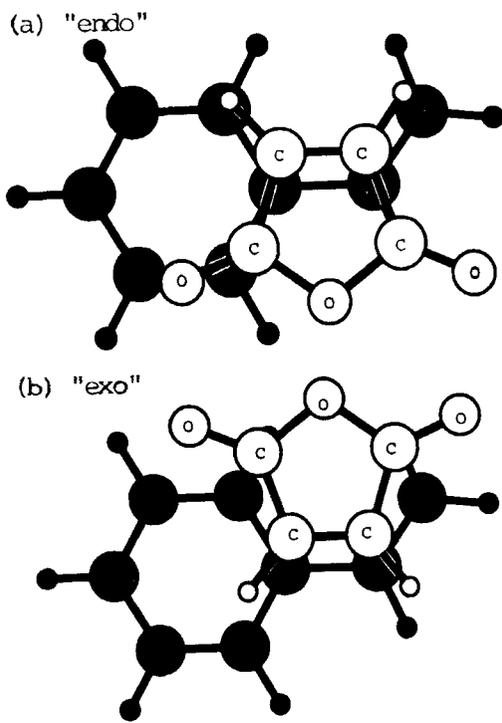


FIG. 10. Top views of ST-MA complex: (a) *endo* and (b) *exo* complexes in Diels-Alder approaches.

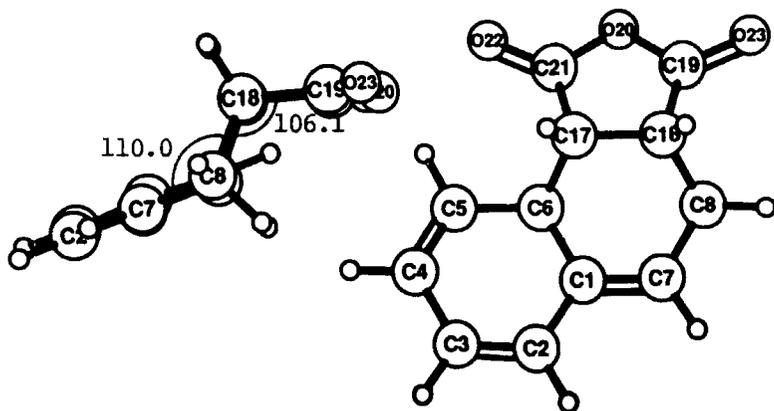


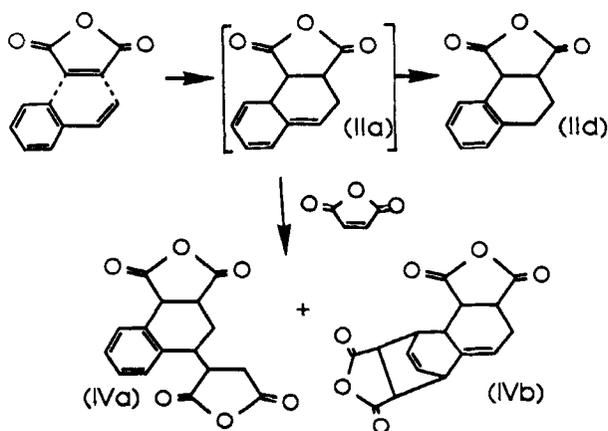
FIG. 11. The geometry of *exo* Diels-Alder adducts from ST and MA.

TABLE 2. Structural Data on the *Exo* Adduct between ST and MA

<u>Nearest-Neighbor Interatomic Distance, Å</u>			
C(1)–C(2)	1.4519	C(5)–H(15)	1.0979
C(2)=C(3)	1.3511	C(6)–H(16)	1.1110
C(3)–C(4)	1.4466	C(6)–C(17)	1.5079
C(4)=C(5)	1.3484	C(8)–C(18)	1.5020
C(5)–C(6)	1.4877	C(17)–C(18)	1.5065
C(1)=C(7)	1.3575	C(18)–C(19)	1.4732
C(7)–C(8)	1.4716	C(19)–O(20)	1.3751
C(8)–H(9)	1.1020	C(17)–O(21)	1.4741
C(8)–H(10)	1.1058	O(20)–C(21)	1.3740
C(7)–H(11)	1.0957	C(21)=O(22)	1.2754
C(2)–H(12)	1.0962	C(19)=O(23)	1.2751
C(3)–H(13)	1.0958	C(18)–H(24)	1.1027
C(4)–H(14)	1.0952	C(17)–H(25)	1.1036
<u>Nearest-Neighbor Bond Angle, degree</u>			
C(2)C(1)C(6)	118.61	C(7)C(8)H(10)	109.12
C(2)C(1)C(7)	124.53	C(7)C(8)C(18)	109.97
C(6)C(1)C(7)	116.79	H(9)C(8)H(10)	105.65
C(1)C(2)C(3)	121.57	H(9)C(8)C(18)	110.80
C(1)C(2)H(12)	117.00	H(10)C(8)C(18)	109.17
C(3)C(2)H(12)	121.42	C(6)C(17)C(18)	114.46
C(2)C(3)C(4)	121.06	C(6)C(17)C(21)	104.87
C(2)C(3)H(13)	121.20	C(6)C(17)H(25)	110.15
C(4)C(3)H(13)	117.74	C(18)C(17)C(21)	103.65
C(3)C(4)C(5)	120.14	C(18)C(17)H(25)	112.68

TABLE 2 (continued)

Nearest-Neighbor Bond Angle, degree (continued)			
C(3)C(4)H(14)	118.03	C(21)C(17)H(25)	110.53
C(5)C(4)H(14)	121.83	C(8)C(18)C(17)	115.09
C(4)C(5)C(6)	122.95	C(8)C(18)C(19)	106.12
C(4)C(5)H(15)	121.93	C(8)C(18)H(24)	109.08
C(6)C(5)H(15)	115.12	C(17)C(18)C(19)	103.24
C(1)C(6)C(5)	115.57	C(20)C(19)O(23)	115.88
C(1)C(6)H(16)	107.47	C(19)O(20)C(21)	105.74
C(1)C(6)C(17)	109.76	C(17)C(21)O(20)	113.42
C(5)C(6)H(16)	106.12	C(17)C(21)O(22)	130.46
C(5)C(6)C(7)	110.94	O(20)C(21)O(22)	116.08
H(16)C(6)C(17)	106.46	C(17)C(18)H(24)	112.82
C(1)C(7)C(8)	120.15	C(19)C(18)H(24)	110.08
C(1)C(7)H(11)	122.08	C(18)C(19)O(20)	113.70
C(8)C(7)H(11)	117.74	C(18)C(19)O(23)	130.39
C(7)C(8)H(9)	112.02		



$4^\circ$  to the plane of MA or vice versa. The bond between the C-6 and C-17 carbon atoms is long (1.5079 Å), and this bond would be broken to initiate or propagate the copolymerization because the hydrogen atom attached to the C-6 is labile.

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