# Two-Dimensional NMR Studies of the Cyclocopolymerization of Sulfur Dioxide and Diethyl Diallylmalonate

**Jui-Yi Tsai, Jing-Lan Zhou, Yahong Sun, Philip B. Shevlin**

*Department of Chemistry, Auburn University, Auburn, Alabama 36849-5312*

**ABSTRACT:** Two-dimensional NMR spectroscopic studies (HECTOR and NOESY) have confirmed that the copolymer of diethyl diallylmalonate with sulfur dioxide consists predominately of *cis*-linked cyclopentane rings. When the cyclopolymerization is carried out at 81°C in acetonitrile, the ratio of *cis* to *trans* linkages is 4.3 : 1. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3477–3480, 2004

**Key words:** two-dimensional NMR spectroscopy; sulfur dioxide copolymer; cyclopolymerization; diethyl diallylmalonate; polymer structure

The sulfonyl radical-mediated cyclization of 1,6-heptadienes has recently stimulated the interest of several research groups.[1] The intermediate 5-hexenyl radical undergoes 5-*exo* ring closure affording cyclopentane derivatives. An example is the free-radical addition of *p*-toluenesulfonyl bromide to diethyl diallylmalonate **1**



(1)
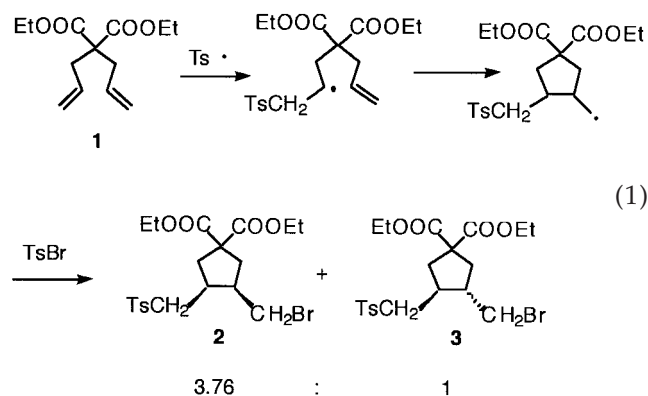
In this case, stereoelectronic factors favor the formation of the *cis* cyclized product **2** over the *trans* isomer **3** by a factor of 3.76 : 1 at 135°C.[2]

When carried out with equimolar amounts of $SO_2$ and **1** in the presence of an appropriate initiator, the reaction becomes an efficient cyclocopolymerization.[3]



(2)
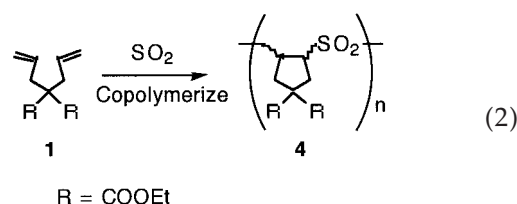
Recently, we reported NMR spectroscopic and mass spectral evidence that polymer[4] produced in this reaction is 1 : 1 copolymer, with linked five-membered rings. Although analogy with free-radical cyclizations of 5-hexenyl radicals indicates that **4** should have predominately *cis* linkages between the rings,[5] the amount of *trans* linkages, if any, is unknown. We now report the use of 2D NMR spectroscopy to address this problem.

Cyclocopolymerizations were carried out on equimolar mixtures of **1,** and $SO_2$ in acetonitrile, to which was added 2% AIBN. The solutions were degassed and heated at 81°C to effect the polymerizations in eq. 3.

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(3)
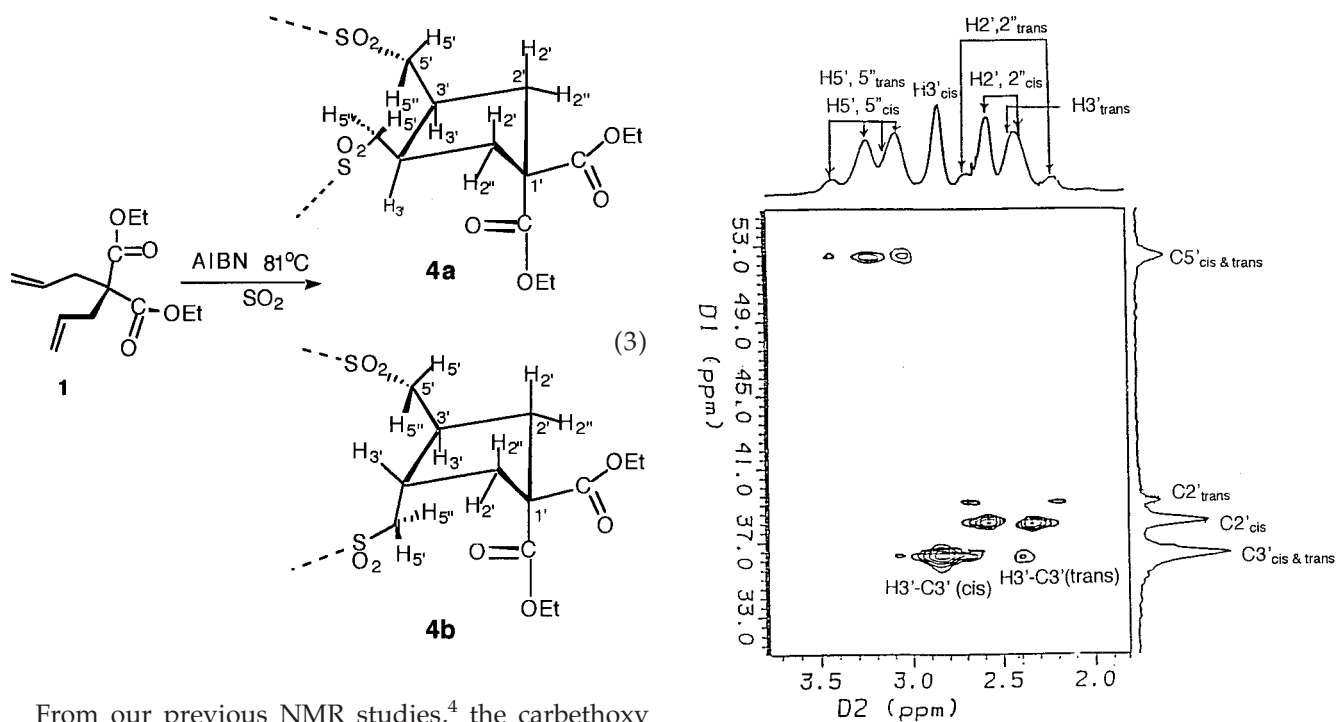
From our previous NMR studies,[4] the carbethoxy carbonyl groups are nonequivalent in the $^{13}$C-NMR
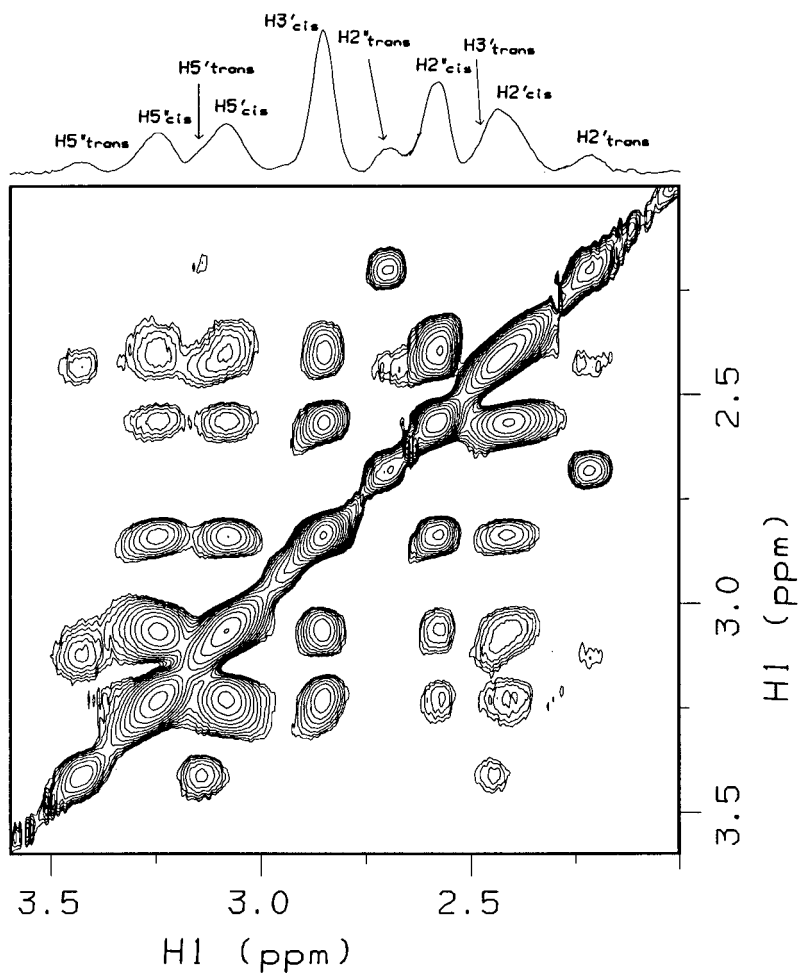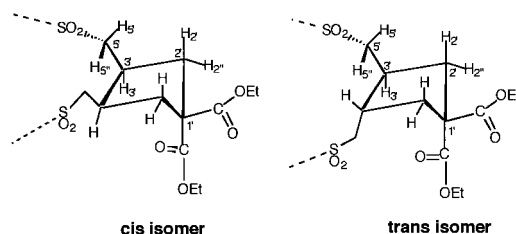
**Figure 1**    HECTOR NMR spectra of the copolymer **4a** and **4b**.



**Figure 2**    2D NOESY NMR spectra of the copolymer **4a** and **4b**. The carbethoxy groups were not shown.

cis isomer    trans isomer

**TABLE I**
**Relative NOE Intensities and Interproton Distance in the *cis* and *trans* Isomers of 4**

| | *cis* | | | *trans* | |
|---|---|---|---|---|---|
| Protons | NOE | Distances (Å) | Protons | NOE | Distances (Å) |
| 2′-2″ | 0.8784 | 1.77 | 2′-2″ | 0.7234 | 1.77 |
| 2′-3′ | 0.1665 | 3.09 | 2′-3′ | 0.1722 | 2.83 |
| 2′-5′ | 0.2558 | 2.81 | 2′-5′ | 0.2031 | 2.73 |
| 2′-5″ | 0.1394 | 3.76 | 2′-5″ | 0.0912 | 3.74 |
| 2″-3′ | 0.359 | 2.30 | 2″-3′ | 0.3094 | 2.26 |
| 2″-5′ | 0.1213 | 3.88 | 2″-5′ | 0.0529 | 3.83 |
| 2″-5″ | 0.0796 | 4.25 | 2″-5″ | 0.0306 | 4.28 |
| 3′-5′ | 0.2521 | 2.84 | 3′-5′ | 0.1106 | 3.10 |
| 3′-5″ | 0.2618 | 2.46 | 3′-5″ | 0.2276 | 2.56 |
| 5′-5″ | 1 | 1.75 | 5′-5″ | 1 | 1.75 |

NOE intensities were measured at 100 ms mixing time and are relative to 5′-5″ NOE = 1; all values are negative.

Distances were calculated with the program PCMODEL.[7]

spectra of **2,** absorbing at δ 171.7 and 172.0 ppm, while they are equivalent in **3,** absorbing at 171.4 ppm.[2] By analogy with the known stereochemistry of 5-hexenyl radical cyclizations[5] and with many other cyclopolymerizations,[6] it is reasonable to propose that copolymer **4** contains predominately *cis* linkages. If this is the case, we should see two $^{13}$C signals of equal intensity for this *cis* isomer and one less intense signal for the *trans* isomer. However, the $^{13}$C-NMR spectra of copolymer **4** shows two carbonyl signals with unequal intensities at δ 171.9 and 172.6 ppm and one is forced to conclude that one of the carbonyl peaks for the *cis*-linked polymer overlaps with the peak for the *trans*.[4]

To obtain the relative composition of the *cis/trans* linkages, the stereospecific $^1$H chemical shift assignments of the copolymer **4** were determined. The NMR studies were carried out on a Bruker 400 MHz NMR spectrometer. The polymer was dissolved in CDCl$_3$ with tetramethylsilane (TMS) as an internal reference. 2D $^1$H-$^{13}$C heteronuclear chemical-shift correlation (HECTOR) and 2D nuclear Overhauser and exchange spectroscopy (NOESY) experiments were performed. For the $^{13}$C-$^1$H HECTOR experiments, 128 $t_1$ increments were acquired with spectral widths of 5000 and 2000 Hz in the $^{13}$C and $^1$H domains, respectively. For the NOESY experiments, the mixing time was 100 ms and 256 $t_1$ increments were acquired. Data were weighted with 90° shifted sinebell functions in both dimensions previous to the Fourier transform.

In **4a,** protons H2′ and H2″ are pro-S and pro-R, and H5′ and H5″ are pro-R and pro-S, respectively. In **4b,** protons H2′ and H2″ are pro-S and pro-R, and H5′ and H5″ are pro-R and pro-S, respectively. It should be noted that there are two sets of enantiotopic protons for **4a** and two sets of homotopic protons for **4b**. The $^{13}$C-$^1$H-NMR HECTOR experiment in Figure 1 identifies the chemical shift for the protons attached to C2′ (H2′ and H2″), C3′ (H3′), and C5′ (H5′ and H5″). Figure 1 shows two H3′ chemical shifts correlated with the C3′ chemical shift. The major H3′-C3′ cross peak is assigned to the *cis* linkage and the minor peak corresponds to the *trans* linkage.

The NOESY NMR spectra of **4** were acquired with the principle aim of assigning the stereochemistry of H2′, H2″, H5′, and H5″ for the *cis* and *trans* links, respectively. The NOESY spectra is shown in Figure 2. The relative intensities of the NOE cross peaks for the *cis* and *trans* links in **4** and the interproton distances calculated by molecular mechanics[7] are shown in Table I. Because the NMR relaxation and NOEs depend on the inverse sixth power of the internuclear distances,[8,9] the NOE contribution of the interaction between protons can be neglected if the internuclear distance is greater than 4 Å. For example, the internuclear distance between H2′ and H2″ attached to the same carbon in **4a** is 1.77 Å, whereas the internuclear distance between H2′ and another enantiotopic H2″ attached to a different carbon is 4.29 Å by molecular mechanic calculation. Therefore, to simplify the NOE interaction analysis, we can omit the NOE interaction between H2′ and the H2″ that is attached to a different carbon. The same principle was applied to all NOE interac-

**TABLE II**
**The $^1$H Assignments for *cis*- and *trans*-Linked**
**Monomers in Copolymer 4**

| *Cis* | H2′ | H2″ | H5′ | H5″ | H3′ |
|---|---|---|---|---|---|
| δ (ppm) | 2.40 | 2.56 | 3.08 | 3.25 | 2.83 |
| *Trans* | H2′ | H2″ | H5′ | H5″ | H3′ |
| δ (ppm) | 2.20 | 2.65 | 3.12 | 3.42 | 2.42 |

tions for **4a.** The chemical shift of H3′$_{cis}$ has been assigned by the HECTOR experiment. Because there is a larger NOESY cross peak between H3′$_{cis}$ and H2″$_{cis}$ than between H3′$_{cis}$ and H2′$_{cis'}$, we can safely conclude that H2″$_{cis}$ is *cis* to H3′$_{cis'}$. Once the H2′$_{cis}$ and H2″$_{cis}$ are assigned, the fact that the NOESY interaction between H5′$_{cis}$ and H2′$_{cis}$ is greater than that between H5″$_{cis}$ and H2′$_{cis}$ means that we can also assign H5′$_{cis}$ and H5″$_{cis}$. For the *trans* linkages, the same strategy was applied and all the $^1$H chemical shifts for the *cis* and *trans* links are listed in Table II. By integration of the signals for H5″$_{cis}$ and H5″$_{trans}$ in **4** from a 1D $^1$H-NMR spectra, a *cis* : *trans* link ratio of 4.3 : 1 was determined.

The stereoselectivity observed in this cyclopolymerization fits well with the Beckwith stereoelectronic model of chair-like transition states (**TS**$_{cis}$ and **TS**$_{trans}$),[10] in which *cis* closure is favored by an electronic interaction between the radical center and a $\pi^*$ orbital of the alkene, while a steric interaction between the growing polymer chain and a carboethoxy group disfavors a *trans* closure.



**TS$_{cis}$**           **TS$_{trans}$**
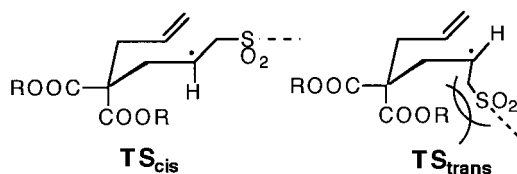
## CONCLUSION

These NMR studies indicate that the key step in the heptadiene-SO$_2$ cyclocopolymerization is a free-radical cyclization which gives predominately *cis* linkages in analogy to the well-studied cyclization of 5-hexenyl radicals. The protons and carbons in *cis* and *trans* linkages can be distinguished by using 2D NMR techniques.

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