Table II
3-^{13}C-Enriched Propene Polymerizations with Different Catalytic System

runs^{a,b,c,g}	catalytic systems	polymer yield, g
1^{d}	VCl_4–$Al(CH_3)_2Cl$–anisole	0.4
2^{d}	VCl_4–$Al(C_2H_5)_2Cl$–anisole	0.5
3^{e}	VCl_4–$Al(CH_3)_3$-$Zn(CH_3)_2$	0.2
4^{f}	δ-$TiCl_3$-$Al(CH_3)_3$-$Zn(CH_3)_2$	0.1

[a] 15 mL of toluene was used as solvent. [b] Polymerization time 24 h. [c] In all the runs 0.7 g of 30% enriched propene was employed. [d] [VCl_4 and anisole] 5×10^{-4} mol; [AlR_2Cl] 5×10^{-3} mol. [e] [VCl_4] 5×10^{-5} mol; [$Al(CH_3)_3$] 11×10^{-3} mol; [$Zn(CH_3)_2$] 5×10^{-3} mol. [f] [δ-$TiCl_3$] 3.2×10^{-3} mol; [$Al(CH_3)_3$] 11×10^{-3} mol; [$Zn(CH_3)_2$] 5×10^{-3} mol. [g] Runs 1, 2, and 3 were performed at −78 °C and run 4 at room temperature.

solutions (10% w/v) by adding 1% of hexamethyldisiloxane (HMD) as internal reference. An HX-90 Bruker spectrometer operating at 22.6_3 MHz in the PFT mode was used as described previously.[1]

References and Notes

(1) A. Zambelli and G. Gatti, *Macromolecules*, 11, 485 (1978).
(2) A. Zambelli, P. Locatelli, and G. Bajo, *Macromolecules*, preceding paper in this issue.
(3) A. Zambelli, G. Natta, and I. Pasquon, *J. Polym. Sci., Part C*, 4, 411 (1963).
(4) G. Natta, A. Zambelli, G. Lanzi, I. Pasquon, E. R. Mognaschi, A. L. Segre, and P. Centola, *Makromol. Chem.*, 81, 161 (1965).
(5) A. Zambelli, P. Locatelli, G. Bajo, and A. Bovey, *Macromolecules*, 8, 687 (1975).
(6) J. C. Randall, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 703 (1974).
(7) A. Zambelli, G. Gatti, C. Sacchi, W. O. Crain, Jr., and J. D. Roberts, *Macromolecules*, 4, 475 (1971).
(8) A. Zambelli, "NMR-Basic Principles and Progress", Vol. 4, Springer, Berlin, 1971.
(9) A. Zambelli and C. Tosi, *Adv. Polym. Sci.*, **15**, 38 (1974).
(10) A. Zambelli, C. Tosi, and C. Sacchi, *Macromolecules*, 5, 649 (1972).
(11) A. Zambelli, G. Bajo, and E. Rigamonti, *Makromol. Chem.*, 179, 1249 (1978).
(12) In the spectrum of 7′ methyl of 7′-^{13}C-enriched 2,4,6,7,9,-11,13-heptamethylheptadecane (the model compound of methyl carbons of monomer units in the considered tail-to-tail arrangement) 16 distinct resonances have been detected[1] due to the configurational effect on chemical shift of 7′ of all methyls six or less bonds distant from the considered one. In polymer spectra these peaks are less resolved. Therefore each of the peaks g to n in polymer spectra accounts for several uncompletely resolved resonances.
(13) The notation of ref 1 and 2 is used in this paper for configurational relationships of methyl carbons.
(14) No chain transfer via β-hydrogen abstraction is expected in these polymerizations due to the experimental conditions (see Experimental Section).
(15) T. Asakura, I. Ando, A. Nishioka, Y. Doi, and T. Keii, *Makromol. Chem.*, **178**, 791 (1977).
(16) G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti, and M. Peraldo, *Chim. Ind.* (*Milan*), **38**, 124 (1956).
(17) G. Mazzanti and P. Longi, *R. Ist. Lomb. Sci. Lett.*, **91**, 755 (1957).
(18) K. Ziegler, Italian Patent 567577 (Feb. 19, 1957).
(19) G. Natta, E. Giachetti, I. Pasquon, and G. Pajaro, *Chim. Ind.* (*Milan*), **42**, 1091 (1960).
(20) Unpublished data from our laboratory.

Comment on a Paper by Fong and Peterlin

BRUNO H. ZIMM

Department of Chemistry, University of California—San Diego, La Jolla, California 92093. *Received August 14, 1978*

Fong and Peterlin[1] have published a paper which contains some new results that they indicate are in contradiction to earlier work by this author.[2] The purpose of this note is to show that there is actually no contradiction, but that both procedures are correct, alternative methods of handling the same problem.

The discussion is concerned with the algebraic methods used to solve the eigenvalue and eigenvector problem of the Rouse–Bueche beads-springs dynamic-chain model with hydrodynamic interaction. The eigenvalue equation is usually written as

$$\mathbf{Q}^{-1}\mathbf{HAQ} = \Lambda \tag{1}$$

where **H** and **A** are two symmetric matrices, defined in the original papers, Λ is the diagonal matrix of the eigenvalues, and the columns of **Q** are the eigenvectors. Although **H** and **A** are symmetric, their product **HA** is not, so that the transformation **Q** is not orthogonal, that is, there are two sets of eigenvectors, the left-hand set, which are the rows of $\mathbf{Q}^{-1}$, and the right-hand set, which are the columns of **Q**. The question then arises as to how to normalize the length of these vectors, and it is here that Fong and Peterlin have made a choice different from the one that the author made earlier.

The author chose to normalize the right-hand eigenvectors so that their length was unity, leaving the length of the left-hand eigenvectors to be determined from the equation

$$\mathbf{Q}^{-1}\mathbf{Q} = \mathbf{I} \tag{2}$$

where **I** is the unit matrix. If we retain the notation **Q** for the matrix so normalized, and denote Fong and Peterlin's transformation matrix by **Q′**, the two are related through a diagonal matrix **B** as follows

$$\mathbf{Q}' = \mathbf{QB} \tag{3}$$

The diagonal element b_i of **B** multiplies the ith column of **Q**, that is, the ith right-hand eigenvector. Since the sum of the squares of the elements of the ith column of **Q** is unity, the corresponding sum of the squares of the ith column of **Q′** is b_i^2; that is, the length of Fong and Peterlin's eigenvectors is b_i.

In any case, we can define a matrix **M** or **M′** as

$$\mathbf{M} = \mathbf{Q}^{\mathrm{T}}\mathbf{AQ} \tag{4a}$$

$$\mathbf{M}' = \mathbf{Q}'^{\mathrm{T}}\mathbf{AQ}' \tag{4b}$$

It has been shown in eq 2 that **M** is diagonal, with elements μ_i. From eq 3 it follows that the diagonal elements, μ_i', of **M′** are

$$\mu_i' = b_i^2\mu_i \tag{5}$$

Fong and Peterlin show that their method leads to $\mu_i' = \lambda_i$ where λ_i is the ith eigenvalue of **HA**. Thus they have effectively chosen their normalization constants so that the lengths of their right-hand eigenvectors are

$$b_i = (\lambda_i/\mu_i)^{1/2} \tag{6}$$

Not recognizing that two different choices of the lengths had been made, Fong and Peterlin believed that their matrix **M′** should be the same as the author's matrix **M**. It clearly is not; hence the apparent contradiction. When we perceive, however, that the normalizations are different, the contradiction disappears.

Fong and Peterlin's procedure leads to formally simpler basic equations, since the matrices **M′** and Λ become identical. To accomplish this, they introduce a symmetric matrix **C**, such that

$$\mathbf{C}^2 = \mathbf{H} \tag{7}$$

Then they transform **HA** to **CAC**, which is symmetric as opposed to **HA**, and with the advantage that it can be efficiently diagonalized by widely available computer routines. Whether there is any fundamental gain in efficiency by this procedure is doubtful, however, since much additional computation has to be performed in evaluating **C** and in forming the product **CAC**. Lin and Schurr[3] have actually carried out such a scheme in the treatment of dynamic light scattering from the beads-springs model. However, they chose to symmetrize the problem by transforming **H** to $\mathbf{A}^{1/2}\mathbf{H}\mathbf{A}^{1/2}$, where $\mathbf{A}^{1/2}$ is a symmetric matrix such that

$$\mathbf{A}^{1/2}\mathbf{A}^{1/2} = \mathbf{A} \tag{8}$$

They calculate $\mathbf{A}^{1/2}$ by a trigonometric-series procedure.

On the other hand, Lodge and Wu[4] use a scheme in which they factor **A** as

$$\mathbf{L}^{\mathrm{T}}\mathbf{L} = \mathbf{A} \tag{9}$$

where **L** is a triangular (nonsymmetric) matrix which consists entirely of ones and zeros and has only two diagonals different from zero. They then transform **HA** to $\mathbf{LHL}^{\mathrm{T}}$, which is again symmetric, and diagonalize this. Since the elements of **L** are so simple, this would appear to be the fastest of the symmetrizing schemes for numerical computation; in fact, Fong and Peterlin chose to use it in their actual calculation of eigenvalues. For many purposes, for example, calculation of the dynamic viscosity, the eigenvalues are sufficient. However, in some cases the eigenvectors of HA are also needed (for example, in ref 5 and 6); however then their normalization constants will cancel out of the final results if used with a consistent definition of the matrix **M**. (Dr. Peterlin has, in fact, recognized this in his more recent paper.[6])

Acknowledgment. This work was aided by a grant from the National Institutes of Health, GM-11916.

References and Notes

(1) J. T. Fong and A. Peterlin, *J. Res. Natl. Bur. Stand., Sect. B*, **80**, 273 (1976).
(2) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).
(3) S.-C. Lin and J. M. Schurr, *Biopolymers*, **17**, 425 (1978).
(4) A. S. Lodge and Y.-J. Wu, *Rheol. Acta*, **10**, 539 (1971).
(5) B. H. Zimm, *Biophys. Chem.*, **1**, 279 (1947).
(6) A. Peterlin, *Croat. Chem. Acta*, **50**, 253 (1977).

Radical Copolymerization of Sulfur Dioxide and Styrene. 3.[1] Evidence for the Occurrence of the Depropagation of Growing Styryl Radicals

MASASHI IINO, HO HUU THOI, SUMIO SHIOYA, and MINORU MATSUDA*

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai, Japan.

Received September 13, 1978

One of the most characteristic features of the copolymerization of SO_2 with olefins is the low ceiling temperature[2,3] (the temperature above which the copolymerization does not occur). It has been proposed that two depropagations occur concurrently with propagation in the copolymerization of SO_2 and olefins:

$$\sim\!\!\sim CH_2CH(R)SO_2\cdot \rightarrow \sim\!\!\sim CH_2CH(R)\cdot + SO_2 \tag{1}$$

$$\sim\!\!\sim SO_2CH_2CH(R)\cdot \rightarrow \sim\!\!\sim SO_2\cdot + CH_2{=}CH(R) \tag{2}$$

In an earlier study,[4] we have investigated the depropagation of growing sulfonyl radicals, expressed by eq 1. The evidence for the occurrence of the latter depropagation, which consists of the elimination of an olefin molecule from a polymer radical containing the end group $\sim\!\!\sim SO_2CH_2CH(R)\cdot$, was reported by Bristow and Dainton.[5,6] They have shown by infrared spectroscopic measurement that, at a temperature near the ceiling temperature, the copolymerization of SO_2 with either *cis*- or *trans*-2-butene is accompanied by geometrical isomerization, which occurs via reaction 2. Nowadays it is well accepted that the depropagation[2] expressed by eq 2 occurs during copolymerization of SO_2 with olefins such as propylene, ethylene, butene, hexene, etc., in which, because the olefins do not homopropagate under conditions suitable for polysulfone formation, poly(olefin sulfone)'s having a regular alternating 1:1 composition are formed.[7]

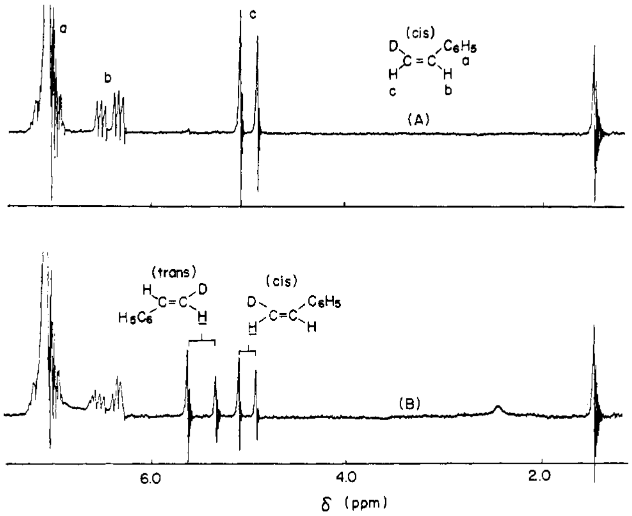

Figure 1. ^{1}H-NMR spectra of the reaction mixture: (a) before reaction, (b) after 120 min at reaction temperature 65 °C.

However, in the copolymerization of SO_2 with vinyl monomers such as styrene[8] and vinyl chloride,[9] in which polysulfones of variable composition are formed, evidence for the occurrence of depropagation of the growing radical endings has not been achieved so far. It is still a controversial problem. Walling[10] and Cais et al.[11,12] have assumed that this depropagation is involved in their proposed mechanisms for the SO_2–styrene copolymerization. The thermal decomposition of poly(styrene sulfone) at high temperature[13,14] (above 200 °C) to yield SO_2, styrene, and its dimer suggests the occurrence of this depropagation. In contrast, we have not taken into account this depropagation in our copolymerization model proposed for SO_2 and styrene[15] or vinyl chloride[16] copolymerization. Unlike olefins, the vinyl monomers can homopropagate; i.e., the $\sim\!\!\sim SO_2CH_2CH(R)\cdot$ radical can react further with vinyl monomers to produce the radical of structural formula $\sim\!\!\sim SO_2(CH_2CHR)_nCH_2CH(R)\cdot$, which is not expected to undergo depropagation over the range of copolymerization temperature investigated.

In the present paper, we report evidence for the occurrence of depropagation of the growing styryl radical by following the cis–trans isomerization of *cis*-β-deuteriostyrene by NMR during copolymerization with SO_2.

Experimental Section

cis-β-Deuteriostyrene was prepared from phenyldeuterioacetylene[17] by the method described in the literature.[18] The crude *cis*-β-deuteriostyrene was purified by preparative GLC (5 mm × 3 m column, GE-SE-30).

Polymerization was carried out in a NMR sample tube and stopped at times as desired by placing the tube in a precooled methanol bath. ^{1}H-NMR measurements were performed at room temperature and at 60 MHz. Polymerization rate was determined gravimetrically by carrying out the copolymerization of undeuterated styrene with SO_2 under the same experimental

0024-9297/79/2212-0160$01.00/0