dependence of the monomer reactivity ratios may be written as

$$\ln r_1 = \frac{\Delta S^{\dagger}_{11} - \Delta S^{\dagger}_{12}}{R} - \frac{\Delta H^{\dagger}_{11} - \Delta H^{\dagger}_{12}}{RT}$$

$$\ln r_2 = \frac{\Delta S^{\dagger}_{22} - \Delta S^{\dagger}_{21}}{R} - \frac{\Delta H^{\dagger}_{22} - \Delta H^{\dagger}_{21}}{RT}$$

where $\Delta S^{\dagger}$ represents the entropy of activation and $\Delta H^{\dagger}$ the enthalpy of activation. For our ACOST/MMA copolymerization system, the differences in the entropy of activation are $\Delta S^{\dagger}_{11} - \Delta S^{\dagger}_{12} = 13.3$ J/(K·mol) and $\Delta S^{\dagger}_{22} - \Delta S^{\dagger}_{21} = 1.27$ J/(K·mol). The difference between the two values is relatively large, though smaller than in the case with the MVL/ST copolymerization (39.7 vs −12.9 J/(K·mol)), which suggests that the steric effect cannot be neglected in the ACOST/MMA copolymerization. Accordingly, we conclude that the calculated Q–e values have little meaning.

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References and Notes

(1) Ueda, M.; Ito, H. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 89.
(2) Giese, B.; Meister, J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 178.
(3) Ito, H.; Renaldo, A. F.; Ueda, M. *Macromolecules* **1989**, *22*, 45.
(4) Marvel, C. S.; Moon, N. S. *J. Am. Chem. Soc.* **1940**, *62*, 45.
(5) Chapin, E. C.; Ham, G. E.; Mills, C. L. *J. Polym. Sci.* **1949**, *4*, 597.
(6) Haas, H. C.; Schuler, N. W.; MacDonald, R. B. *J. Polym. Sci., Part A-1* **1969**, *7*, 3440.
(7) Monthéard, J. P.; Camps, M.; Seytre, G.; Guillet, J.; Dubois, J. C. *Angew. Makromol. Chem.* **1978**, *72*, 45.
(8) Sahraoui, Z.; David, J.-C.; Camps, M.; Monthéard, J.-P.; Vergnaud, J.-M. *C. R. Seances Acad. Sci., Ser. C* **1978**, 683.
(9) Monthéard, J.-P.; Camps, M.; Kawaye, S.; Pham, Q. T.; Seytre, G. *Makromol. Chem.* **1982**, *183*, 1191.
(10) Monthéard, J.-P.; Camps, M.; Belfkira, A.; Steffan, G.; Lucas, J. M. *Polym. Commun.* **1984**, *25*, 337.
(11) Monthéard, J.-P.; Camps, M.; Belfkira, A.; Chatzopoulos, M.; Granger, R.; Jorat, L.; Noyel, G. *Makromol. Chem.* **1985**, *186*, 1519.
(12) Tsuruta, T.; Chikanishi, K. *Makromol. Chem.* **1965**, *81*, 198.
(13) Yuki, H.; Hatada, K.; Niinomi, T.; Hashimoto, M.; Ohshima, T. *Polym. J.* **1971**, *2*, 629.
(14) Ito, H.; Ueda, M. *Macromolecules*, preceding paper in this issue.
(15) Noyce, D. S.; Pollack, R. M. *J. Am. Chem. Soc.* **1969**, *91*, 119.
(16) House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 3310.
(17) Lüssi, V. H. *Makromol. Chem.* **1967**, *103*, 68.
(18) Ueda, M.; Takahashi, M.; Imai, Y.; Pittman, C. U., Jr. *Macromolecules* **1983**, *16*, 1300.
(19) Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Wiley: New York, 1975; p II-452.
(20) Bywater, S. *Trans. Faraday Soc.* **1955**, *12*, 61.
(21) Joshi, R. M. *J. Polym. Sci.* **1962**, *56*, 313.
(22) Joshi, R. M. *Makromol. Chem.* **1963**, *66*, 115.
(23) Lüssi, H. *Chimia* **1966**, *20*, 379.
(24) Roberts, D. E.; Walton, W. W.; Jessup, R. S. *J. Res. Natl. Bur. Stand.* **1947**, *38*, 627.
(25) Daiton, F. S.; Evans, D. M.; Hoare, F. E.; Melia, T. P. *Polymer* **1962**, *3*, 286.
(26) Roberts, D. E.; Jessup, R. S. *J. Res. Natl. Bur. Stand.* **1951**, *46*, 11.
(27) Worsfold, D. J.; Bywater, S. *J. Polym. Sci.* **1957**, *26*, 299.
(28) McCormick, H. W. *J. Polym. Sci.* **1957**, *25*, 488.
(29) Iwatsuki, S.; Itoh, T.; Higuchi, T.; Enomoto, K. *Macromolecules* **1988**, *21*, 1571.
(30) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McCraw-Hill: New York, 1969.
(31) Herman, J. J.; Teyssié, Ph. *Macromolecules* **1978**, *11*, 839.
(32) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594.
(33) Wittmer, P. *Makromol. Chem.* **1967**, *103*, 188.
(34) Wittmer, P. In *Multicomponent Polymer Systems*; Advances in Chemistry 99; American Chemical Society: Washington, DC, 1970; p 140.
(35) Ueda, M.; Suzuki, T.; Takahashi, M.; Li, Z. B.; Koyama, K.; Pittman, C. U., Jr. *Macromolecules* **1986**, *19*, 558.
(36) Lowry, G. G. *J. Polym. Sci.* **1960**, *42*, 463.
(37) Joshi, R. M.; Zwolinski, B. J. In *Vinyl Polymerization*; Ham, G. E., Ed.; Marcel Dekker: New York, 1967; Vol. 1, Chapter 8.
(38) Meyer, V. *J. Polym. Sci., Part A-1* **1967**, *5*, 1289.

On the Kinetic Model for the Radical Copolymerization of Methyl Acrylate and Sulfur Dioxide

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ABSTRACT: Composition data for the copolymerization of sulfur dioxide and methyl acrylate at −78 and 0 °C were obtained and analyzed using a nonlinear least-squares optimization routine. In the model which was found to be adequate to describe experimental data the reactions of methyl acrylate addition to the growing chain are irreversible. Sulfur dioxide can be added only to the macroradicals having methyl acrylate as a terminal and a penultimate monomeric unit, and this reaction is highly reversible even at −78 °C. On the basis of the results obtained, several kinetic parameters are estimated and factors determining the reactivity of sulfur dioxide in propagation and depropagation reactions are discussed.

Introduction

The free-radical copolymerization of sulfur dioxide with many olefinic compounds leads to the formation of polysulfones having a regular alternating structure, which is independent of the monomer feed ratio.[1,2] In contrast, several vinyl monomers such as styrene,[3] vinyl chloride,[4] chloroprene,[5] acrylamide,[6] or alkyl acrylates[7] form polysul-

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fones of variable composition, which usually depends on the reaction temperature. For this type of nonalternating copolymerization Bovey et al.[8] proposed a kinetic scheme assuming the penultimate model and an equilibrium character of the propagation reactions in which a carbon–sulfur bond is formed.

$$\sim MM^{\bullet} + SO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \sim MMSO_2^{\bullet} \quad (1)$$

$$\sim MSO_2^{\bullet} + M \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \sim MSO_2M^{\bullet} \quad (2)$$

$$\sim SO_2M^{\bullet} + M \xrightarrow{k_3} \sim SO_2MM^{\bullet} \quad (3)$$

$$\sim MM^{\bullet} + M \xrightarrow{k_4} \sim MMM^{\bullet} \quad (4)$$

$$\sim SO_2M^{\bullet} + SO_2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \sim SO_2MSO_2^{\bullet} \quad (5)$$

An analytical solution of the kinetic scheme defined by eqs 1–5 is quite complex, and the parameters characterizing this type of copolymerization were not determined. Recently[7] we found that in the copolymers of alkyl acrylates with sulfur dioxide obtained at −78 °C or at higher temperature, the alternative SO_2MSO_2 triad does not appear and thus eq 5 can be omitted in the reaction sequence. For this case, with the steady-state assumption for $[MM^{\bullet}]$, $[MSO_2^{\bullet}]$, and $[SO_2M^{\bullet}]$, the copolymer composition can be described by the equation

$$\frac{d[M]}{d[SO_2]} = \bar{n} = \frac{2k_3[SO_2M^{\bullet}][M] + k_4[MM^{\bullet}][M]}{k_3[SO_2M^{\bullet}][M]} = 2 + r_{MM}\frac{[M]}{[SO_2]} + \frac{r_{MM}r'_{MSO_2}}{[SO_2]} + \frac{r_{MM}r'_{MSO_2}r'_{SO_2M}}{[SO_2][M]} \quad (6)$$

where

$$r_{MM} = \frac{k_4}{k_1};\quad r'_{MSO_2} = \frac{k_{-1}}{k_2};\quad r'_{SO_2M} = \frac{k_{-2}}{k_3}$$

In this paper we have tested the applicability of the above equation in the copolymerization of sulfur dioxide and methyl acrylate (M) carried out at −78 and 0 °C.

Experimental Section

The copolymerizations were carried out in bulk with *tert*-butyl hydroperoxide as initiator according to the method described previously.[9] The copolymer compositions were determined from the elemental analysis of carbon, hydrogen, and sulfur (the error of determination of the monomeric units contents is estimated as ca. 1.5%).

Results and Discussion

The results of copolymerizations are presented in Tables I and II. It can be noticed that the mole ratio of methyl acrylate monomeric units to SO_2 monomeric units in copolymers ($\bar{n}$) is always greater than 2 and increases with a rise of reaction temperature.

The composition data were analyzed according to eq 6 using the nonlinear least-squares optimization routine. The optimization was carried out for three cases. Case 1 was the completely general form for eq 6. Case 2 incorporated the assumption that $r'_{SO_2M} = 0$. Case 3 included the assumption that both reactions 1 and 2 are irreversible; i.e., $r'_{SO_2M} = r'_{MSO_2} = 0$. The results of calculations are summarized in Table III, where the values of parameters, sum of squares (SS), and standard errors (Sy) are shown.

Table I
Composition Data for the Copolymerization of Sulfur Dioxide with Methyl Acrylate (M) at −78 °C

[M] in monomer feed, mol·L^{-1}	[SO_2] in monomer feed, mol·L^{-1}	mole fractn of SO_2 in copolymer	M conversn, wt %
10.04	3.28	0.112	9.69
9.73	3.89	0.133	7.00
8.89	5.60	0.132	9.19
8.89	5.60	0.164	9.73
7.65	7.65	0.179	11.33
5.77	9.78	0.223	5.36
4.61	13.68	0.262	10.28
3.86	15.08	0.280	5.38
3.86	15.08	0.265	14.17
2.04	18.30	0.281	7.32
1.07	20.08	0.294	4.46
1.07	20.08	0.296	15.59
0.22	21.59	0.303	25.80

Table II
Composition Data for the Copolymerization of Sulfur Dioxide with Methyl Acrylate (M) at 0 °C

[M] in monomer feed, mol·L^{-1}	[SO_2] in monomer feed, mol·L^{-1}	mole fractn of SO_2 in copolymer	M conversn, wt %
10.26	2.05	0.018	22.90
9.48	3.16	0.024	13.00
9.13	3.65	0.026	15.30
8.67	4.33	0.030	5.70
8.01	5.34	0.033	11.80
7.06	7.06	0.036	11.10
5.91	8.86	0.071	7.60
5.15	10.32	0.088	5.90
4.10	12.37	0.086	9.00
3.45	13.69	0.093	12.90
1.86	16.74	0.106	4.00
0.97	18.41	0.126	7.10

Table III
Calculated Reactivity Ratios for the Copolymerization of Sulfur Dioxide with Methyl Acrylate (M)

	case 1: no restriction		case 2: $r'_{SO_2M} = 0$		case 3: $r'_{SO_2M} = r'_{MSO_2} = 0$	
	−78 °C	0 °C	−78 °C	0 °C	−78 °C	0 °C
r_{MM}	1.5489	3.9080	1.5082	3.9940	2.0241	44.6042
r'_{MSO_2}, L·mol^{-1}	3.5276	23.2193	3.8386	22.5568		
r'_{SO_2M}, L·mol^{-1}	0.0359	−0.0081				
SS[a]	0.0012	0.0006	0.0012	0.0006	0.0064	0.0112
Sy[b]	0.0111	0.0082	0.0106	0.0078	0.0231	0.0319

[a] $SS = \sum(Y_c - Y_e)^2$, where Y_c and Y_e are the calculated and experimental mole fractions in the polymer. [b] $Sy = [SS/(n-p)]^{0.5}$, where Sy is the standard error and n and p are the number of data points and variables in the model, respectively.

In case 1 positive values are obtained for r_{MM} and r'_{MSO_2}, while the value of r'_{SO_2M} is positive at −78 °C and negative at 0 °C, but in both cases very near to 0. The standard deviations are 1.11% and 0.82% for the copolymers obtained at −78 and 0 °C, respectively. Optimization of composition data with the assumption that r'_{SO_2M} is equal to 0 leads to slight changes in the values of r_{MM} and r'_{MSO_2} and a small decrease of the standard error. Optimization with the assumption that $r'_{MSO_2} = r'_{SO_2M} = 0$ leads to a significant increase of the r_{MM} values and standard error, especially for reactions carried out at 0 °C. This indicates that the model, in which depropagation reactions are excluded, is inadequate to describe the system studied.

The significance of the improvement in the fit of the higher order model to the experimental data is usually evaluated using the statistical F-test.[10] At the differ-

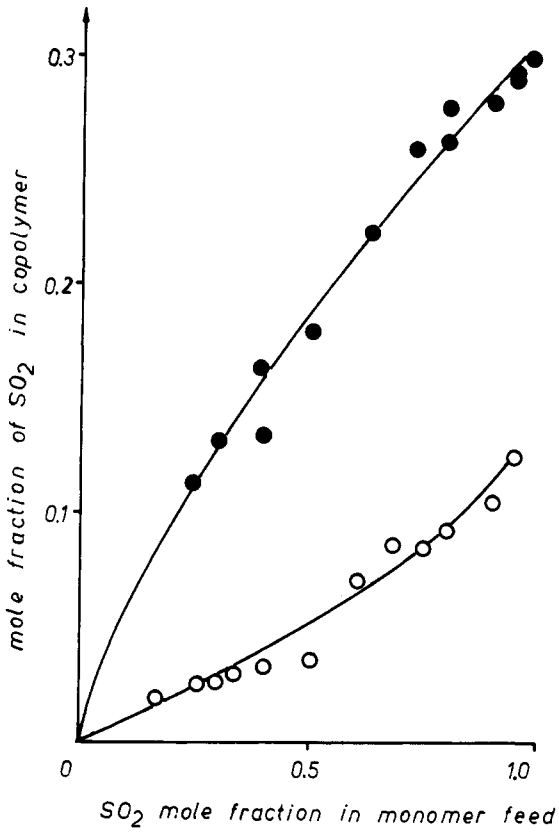


Figure 1. Composition diagram for the copolymerization of SO_2 and methyl acrylate. Experimental data at (●) −78 °C and (○) 0 °C. Theoretical curves (—) for case 2.

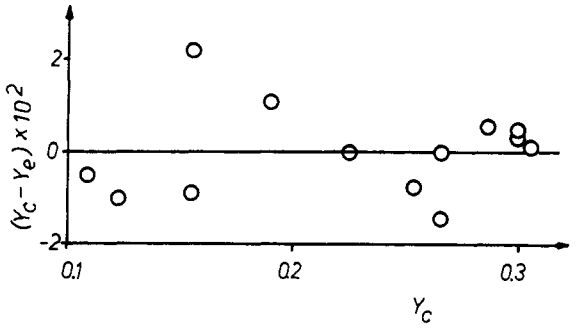


Figure 2. Difference between the calculated and experimental SO_2 content in the copolymer vs the calculated SO_2 content in the copolymer at −78 °C.

ences in the values of square sums obtained in this work, the number of experimental points, and the number of parameters in particular models, it can be found that case 2 provides a significant improvement over case 3 with probability higher than 99%. Case 1 does not provide improvement over case 2 since both cases afford practically the same sum of squares.

These results let us suggest that in the systems studied reaction 2 leading to the formation of $\sim SO_2M^\bullet$ radicals is practically irreversible whereas the depropagation of $\sim MSO_2^\bullet$ has a significant effect on the copolymer composition. Figure 1 presents the fit of the experimental data to the theoretical curves for case 2, which describes this situation. As can be seen from Figures 2 and 3, the differences between the discussed and computed results show a random pattern, and most of them are much smaller than the estimated uncertainity for the copolymer composition determination (errors in the values of the concentration of starting monomers may also be an important factor affecting the experimental precision in reactions involving SO_2).

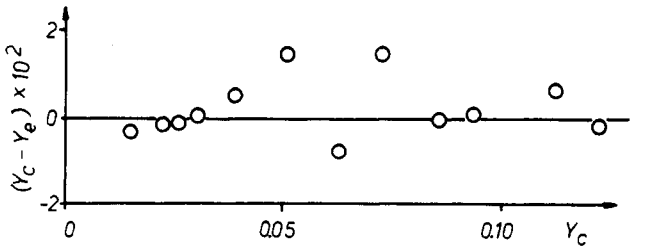


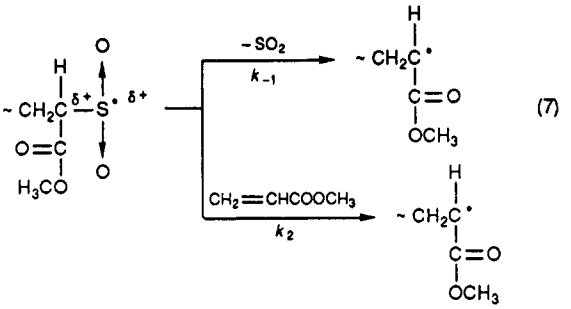
Figure 3. Difference between the calculated and experimental SO_2 content in the copolymer vs the calculated SO_2 content in the copolymer at 0 °C.

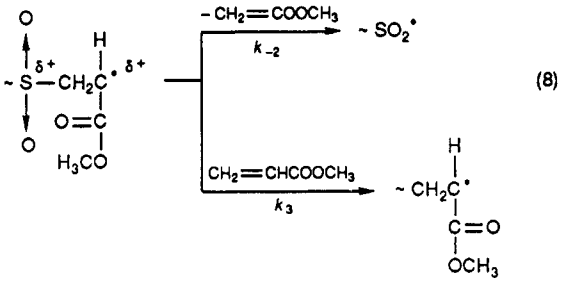
Table IV
Kinetic Parameters Estimated for Reactions 1 and 4

param	reaction 1	reaction 4[a]
k_p at −78 °C, L·mol^{-1}·s^{-1}	0.8	1.2
k_p at 0 °C, L·mol^{-1}·s^{-1}	49.1	196.0
E_a, kcal·mol^{-1}	5.6	7.1
A	0.15×10^7	1.0×10^7
ΔH^*, kcal·mol^{-1}	5.1	6.5
ΔS^*, cal·mol^{-1}·deg^{-1}	−32.0	−63.0

[a] Values taken from ref 11 or calculated on the basis of data published therein.

The various inclination of $\sim MSO_2^\bullet$ and $\sim SO_2M^\bullet$ radicals to depropagation results probably from the different dissociation energies of C–S bonds in these radicals.





The C–S bond in the $\sim MSO_2^\bullet$ radical is much weaker than that in the $SO_2M^\bullet$ radical due to the stronger polar and steric repulsion.

On the basis of the r'_{MSO_2} values, it can be estimated that at the 1 mol·L^{-1} concentration of methyl acrylate at −78 °C about 79% of $\sim MSO_2^\bullet$ radicals formed undergo depropagation and at 0 °C about 96%.

The reactivity ratio, r_{MM}, characterizes the relative reactivity of methyl acrylate and SO_2 in the addition to $\sim MM^\bullet$ macroradicals and can be correlated with the parameters Q and e of monomers according to the following relationship:

$$r_{MM} = \frac{Q_M}{Q_{SO_2}} \exp[-e_M(e_M - e_{SO_2})]$$

The e_{SO_2} value calculated from the published data on the dependence of the rate constant of *tert*-butyl radical addition to various monomers on their e parameter[11] is equal to 2.7. Considering this value and the typical

values for methyl acrylate, $e_M = 0.60$ and $Q_M = 0.42$, the average Q_{SO_2} value calculated from the data at -78 and 0 °C was found to be 0.67. Assuming that the rate constant of reaction 4 is equal to that of propagation in the homopolymerization of methyl acrylate, one can roughly estimate also other kinetic parameters characterizing the addition of SO_2 to $\sim MM^\bullet$ macroradicals (eq 1). As can be seen from Table IV this reaction is characterized by a lower Arrhenius activation energy (E_a) and lower value of the collision frequency factor (A) than the homopropagation of methyl acrylate. In terms of the active complex theory one can expect that the addition of SO_2 is connected with a lower enthalpy of activation ($\Delta H^\ddagger$) and a much larger entropy of activation ($\Delta S^\ddagger$), which indicates that the freedom of reagent movement in the active complex of the $\sim MM^\bullet$ macroradical with SO_2 is much less limited than that in the complex with methyl acrylate.

It should be noticed that also in other nonalternating copolymerizations of sulfur dioxide the occurrence of SO_2MSO_2 triads is not observed above a certain temperature. However, the number of experimental data available at present is insufficient for testing the applicability of eq 6 for the description of these systems.

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References and Notes

(1) Ivin, K. J.; Rose, J. B. In *Advances in Macromolecular Chemistry*; Pasika, W. M., Ed.; Academic Press: London, 1968; Vol. 1, p 335.
(2) Tokura, N. In *Encyclopedia of Polymer Science and Technology*; Mark, H., Ed.; Interscience: New York, 1968; Vol. 9; p 460.
(3) Barb, W. G. *Proc. R. Soc. London A* **1952**, *212*, 66, 177.
(4) Marvel, C. S.; Glavis, J. F. *J. Am. Chem. Soc.* **1938**, *60*, 2622.
(5) Hralak, F.; Blażek, J.; Webr, J. *Makromol. Chem.* **1966**, *97*, 81.
(6) Cais, R. E.; Stuk, G. J. *Polymer* **1977**, *19*, 179.
(7) Florjańczyk, Z.; Floriańczyk, T.; Zygadło, E. *Makromol. Chem.* **1989**, *190*, 677.
(8) Cais, R. E.; O'Donnell, J. H.; Bovey, F. A. *Macromolecules* **1977**, *10*, 254.
(9) Florjańczyk, Z.; Floriańczyk, T.; Kłopotek, B. B. *Makromol. Chem.* **1987**, *188*, 2811.
(10) Hill, D. J. T.; O'Donnell, J. H. *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 375.
(11) Kabanov, V. A. *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 193.
(12) Walling, C. *Free Radicals in Solution*; John Wiley and Sons Inc.: New York, 1957; Chapter 3, p 95.

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Isotactic-Specific Polymerization of Propene with Supported Catalysts in the Presence of Different Modifiers

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ABSTRACT: The behavior of several organic molecules in modifying the productivity and stereospecificity of two different supported Ziegler-Natta catalysts in the polymerization of propene has been investigated. Some correlation between the structure of the modifiers, the type of supported catalyst, and the polymerization results can be observed.

The "last generation" heterogeneous Ziegler-Natta catalysts for isotactic-specific polymerization of propene are rather complex systems consisting of (a) a solid precatalyst obtained from $MgCl_2$, $TiCl_4$, and an organic Lewis base (often referred to as the "internal modifier") and (b) a cocatalyst solution containing an alkylaluminum and an organic Lewis base (the "external modifier").[1] The function of the external modifier is to increase the stereospecificity of the catalytic system, which otherwise produces a mixture of isotactic and more or less stereoirregular macromolecules. While a great variety of Lewis bases are able to increase the stereospecificity of the polymerization, only three classes of external modifier are known that allow one to obtain polypropylene with a high isotactic index (e.g., >95%) without impracticably depressing the polymer productivity. These classes are (1) the esters of aromatic carboxylic acids (e.g., ethyl benzoate), (2) some sterically hindered amines (e.g., 2,2,6,6-tetramethylpiperidine), and (3) the alkoxysilanes of general formula $R_nSi(OR')_{4-n}$.

A considerable effort, with special attention to the aromatic esters, has been devoted by several research groups toward clarifying the stereoregulation mechanism of these modifiers.[2] A widely accepted hypothesis suggests selective coordination of the Lewis base to the nonstereospecific active sites of the solid precatalyst as the explana-

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