heterotactic triads to peak D is extremely small. Thus, peaks C and D for these copolymers are essentially made up of purely MMV triad tacticities, and the relative intensities of C to D are independent of the reactivity ratios. For samples 7 and 8, peak C is less than peak D, while for samples 9 and 10, peak D is less than peak C. At lower polymerization temperatures, peak C increases at the expense of D; therefore, C must correspond to the more sterically favored tacticity, namely, MMV (SS). Peak D contains the MMV (IS) contribution.

Experimentally, the relative amount of MMV triads in peaks C, D, and E may be obtained from the slopes and intercepts obtained from Figure 4. A distribution very close to the experimental distribution may be obtained when the triads are grouped and arranged as shown in Table V.

It is not possible to determine within our experimental accuracy which of the MMV (IS) and MMV (II) triads contributes to peaks D and E exactly. We have established, however, that the MMV (SI) peak is shifted upfield from MMV (SS). Thus, we tentatively assign MMV (IS) to peak D and MMV (II) to peak E. Table V summarizes all the sequence distribution and tacticity assignments made.

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Copolymerization with Depropagation. VII.[1a] Coisotacticities in the Free-Radical Copolymerization of α-Methylstyrene and Methyl Methacrylate between Their Ceiling Temperatures

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ABSTRACT: Nuclear magnetic resonance spectra have been studied for copolymers of α-methylstyrene and methyl methacrylate polymerized at temperatures from 0 to 147°. Analysis of the methoxy resonance patterns in terms of a previously published reversible copolymerization model yielded information on the coisotacticities of the copolymers. From an Arrhenius plot, the difference in enthalpy of activation for a coisotactic placement relative to that for a cosyndiotactic placement, $\Delta(\Delta H^{\ddagger})$, was determined to be 1.8 ± 0.5 kcal/mol, while $\Delta(\Delta S^{\ddagger})$ was found to be 3.6 ± 1.4 eu.

The monomers α-methylstyrene and methyl methacrylate have relatively low ceiling temperatures of 61 and 164°, respectively.[2] Therefore, the effects of depropagation must be considered when copolymerizations involving these monomers are conducted at about 100° or higher. In a previous paper,[3] we showed that the effect of reaction temperature on the copolymer composition curve could be interpreted quantitatively in terms of the kinetics for the dyad reversible copolymerization model.[4] In this paper, we report studies on the nmr spectra of the copolymers formed under conditions where depropagation occurs. We have analyzed the methoxy resonance patterns of the copolymers by applying our reversible copolymerization model[3] and have determined, according to the scheme proposed by Ito and Yamashita,[5] the coisotacticities of copolymers prepared at various temperatures.

Experimental Section

Free radical copolymerizations were carried out in bulk by the procedures described in the previous paper.[3] Nmr spectra (60 MHz) of copolymers in CCl_4 solution (10 wt % or less polymer) were measured at 90%. Copolymer compositions were determined from the proportions of aromatic proton resonance observed in the spectra. The methoxy resonance patterns were evaluated in the standard manner.[6] Resonance areas were determined by planimetry.

Results and Discussion

The methoxy proton resonance of α-methylstyrene-(S)-methyl methacrylate (M) copolymers is observed as two or three resonances occurring over the δ 3.0–4.0 ppm range. According to the interpretation of Ito and Yamashita,[5] the resonance observed at 3.3–3.9 ppm (designated X) is due to methoxy protons centered in *all* MM*M triads and in (SM*M + MM*S) and SMS triads having *only* racemic (cosyndiotactic) M–S placements. The resonance observed at 2.9–3.3 ppm (designated Y) is attributed to methoxy protons centered in (SM*M + MM*S) and SM*S triads having *one* meso (coisotactic) M–S placement. The methoxy proton resonance observed at the highest field area, 2.5–2.9 ppm (designated Z), is attributed to methoxy protons centered in SMS triads having *two* meso (coisotactic) M–S placements. If σ represents the probability that a given M–S placement is meso (coisotactic) and if P_{MS} represents the conditional probability that an M unit is followed by an S unit in the copolymer, the fractions of methoxy resonance observed in

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(1) (a) Part VI: M. Izu and K. F. O'Driscoll, *Polym. J.*, **1**, 27 (1970); (b) on leave from the Department of Hydrocarbon Chemistry, Kyoto University, Kyoto, Japan; (c) University of Waterloo; (d) University of Akron.

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X, Y, and Z areas (F_X, F_Y, and F_Z, respectively) may be expressed as

$$F_X = (1 - \sigma P_{MS})^2 \tag{1}$$

$$F_Y = 2\sigma P_{MS}(1 - \sigma P_{MS}) \tag{2}$$

$$F_Z = (\sigma P_{MS})^2 \tag{3}$$

If P_{MS} and F_X, F_Y, or F_Z are known, σ can be evaluated for a copolymer. It is important to note that P_{MS} *is a real quantity which can only be predicted by a correct kinetic scheme.* Ito and Yamashita determined σ values using P_{MS} values calculated by assuming the irreversible terminal copolymerization model. However, we have shown that an irreversible model was inadequate to interpret the copolymer composition curves of the α-methylstyrene–MMA system at temperatures above 100° due to the occurrence of depropagation reactions. It proved possible to interpret the copolymer composition curves in terms of the following reversible terminal copolymerization model.

$$\sim\!\!\sim M^* + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sim\!\!\sim MM^*$$

$$\sim\!\!\sim M^* + S \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \sim\!\!\sim MS^*$$

$$\sim\!\!\sim S^* + M \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \sim\!\!\sim SM^*$$

$$\sim\!\!\sim S^* + S \underset{k_8}{\overset{k_7}{\rightleftharpoons}} \sim\!\!\sim SS^*$$

We determine P_{MM} ($\equiv\epsilon$) and P_{SS} ($\equiv\eta$) as the roots of the following nonlinear simultaneous equations, which can be solved numerically if the values of the rate constants are given.[4]

$$k_4\epsilon(1 - \eta)[k_3[S] + k_6(1 - \epsilon)] = [k_5[M] + k_4(1 - \eta)] \times [\epsilon(k_1[M] + k_2 + k_3[S]) - (k_1[M] + \epsilon^3 k_2)] \tag{4}$$

$$k_6\eta(1 - \epsilon)[k_5[M] + k_4(1 - \eta)] = [k_3[S] + k_6(1 - \epsilon)] \times [\eta(k_5[M] + k_8 + k_7[S]) - (k_7[S] + \eta^2 k_8)] \tag{5}$$

We calculated P_{MS} ($=1 - P_{MM}$) using the rate constants estimated in the previous paper.[3] We then used P_{MS} in eq 1 and 2 to calculate σ for each sample from measured F_X and F_Y values. The results at 60 and 114° are summarized in Tables I and II.

Spectra of copolymers prepared at 147° were also examined. The proportion of the methoxy resonance observed in the Y area was below 9% in all spectra. Because of the low styrene contents of these copolymers, it was a reasonable approximation to estimate σ from the fraction of methoxy resonance occurring in the Y area by use of eq 6, where x is the mole fraction of styrene in the copolymer.

$$\sigma = F_Y(1 - x)/2x \tag{6}$$

By using this approach, σ was found to be approximately 0.47 for copolymers prepared at 147° (Table III).

TABLE I
EVALUATION OF σ FROM METHOXY RESONANCE PATTERNS OF COPOLYMERS PREPARED AT 60°

f_s[a]	F_s[b]	F_X[c]	F_Y[c]	P_{MS}	σ_1[d]	σ_2[e]	$\bar{\sigma}$[f]
0.656	0.502	0.649	0.271	0.749	0.26	0.22	0.24
0.550	0.471	0.691	0.285	0.673	0.25	0.26	0.25
0.449	0.406	0.712	0.240	0.591	0.26	0.24	0.25
0.352	0.362	0.775	0.222	0.500	0.24	0.25	0.25
0.259	0.287	0.774	0.176	0.399	0.30	0.24	0.27
0.169	0.215	0.860	0.114	0.274	0.27	0.22	0.24
0.083	0.112	0.896	0.081	0.152	0.36	0.28	0.32

[a] Mole fraction of α-methylstyrene in the monomer feed. [b] Mole fraction of α-methylstyrene unit in the copolymer. [c] The average of two measurements. F_X and F_Y values are considered reliable to within ±0.02. [d] Coisotacticity calculated from F_X using eq 1. [e] Coisotacticity calculated from F_Y using eq 2. [f] The average of σ_1 and σ_2. The average (±standard deviation) of $\bar{\sigma}$ was 0.26 (±0.03).

TABLE II
EVALUATION OF σ FROM METHOXY RESONANCE PATTERNS OF COPOLYMERS PREPARED AT 114°

f_s	D_s	F_X[a]	F_Y[a]	P_{MS}	σ_1	σ_2	$\bar{\sigma}$[b]
0.880	0.390	0.611	0.282	0.516	0.42	0.33	0.37
0.765	0.366	0.632	0.261	0.450	0.40	0.34	0.37
0.550	0.310	0.771	0.223	0.338	0.36	0.38	0.37
0.449	0.274	0.789	0.205	0.285	0.39	0.41	0.40
0.352	0.229	0.817	0.169	0.231	0.42	0.40	0.41
0.259	0.180	0.825	0.156	0.177	0.52	0.48	0.50

[a] The average of two measurements. F_X and F_Y values are considered reliable to within ±0.02. [b] The average of $\bar{\sigma}$ (±standard deviation) was 0.40 (±0.04).

TABLE III
EVALUATION OF σ FROM METHOXY RESONANCE PATTERNS OF COPOLYMERS PREPARED AT 147°

f_s	F_s	F_X	F_Y	σ
0.656	0.096	0.918	0.082	0.47
0.352	0.089	0.921	0.079	0.49
0.169	0.080	0.935	0.065	0.44

TABLE IV
COMPARISON OF COISOTACTICITY PARAMETERS

	Coisotacticity (σ)	
Temp, °C	This paper	Ito, *et al.*[a]
0	—	0.21 ± 0.03
60	0.26 ± 0.03	0.27 ± 0.03
100	(0.31[b])	0.25 ± 0.03
114	0.40 ± 0.04	(0.20[c])
147	0.47	

[a] Reference 5b. [b] The data reported by Ito, *et al.*,[5b] were reanalyzed using P_{MS} values predicted with our model. [c] Evaluated by analyzing our data according to Ito and Yamashita's graphical method[5a] (which assumes the irreversible terminal copolymerization model).

Table IV compares σ values determined by us with those determined by Ito and Yamashita.[5b] The results agree well for copolymers prepared at 60° but disagree for copolymers prepared at higher temperatures. Our results show that the coisotacticity (σ) increases with temperature, whereas the results of Ito and Yamashita suggest that it decreases above 60°. Since it is likely that the randomness of stereospecific addition will increase with temperature, our results seem to be more plausible. The value of σ at 100° obtained by Ito and Yamashita must be revised because it is based on an inadequate model for the copolymerization. The effect of the temperature on the coisotacticity parameter σ may be expressed by the following equations.

$$-RT \ln \frac{\sigma}{1 - \sigma} = \Delta(\Delta G^{\ddagger}) = \Delta G_{i}^{\ddagger} - \Delta G_{s}^{\ddagger} \qquad (7)$$

$$-\frac{d \ln [\sigma/(1 - \sigma)]}{d(1/T)} = \frac{\Delta(\Delta H^{\ddagger})}{R} \qquad (8)$$

Here, $\Delta G_i^{\ddagger}$ and $\Delta G_s^{\ddagger}$ express the free energes of activation for coisotactic and cosyndiotactic additions, respectively. An Arrhenius plot of the data in Table IV enables us to estimate the values of $\Delta(\Delta H^{\ddagger})$ as 1.8 ± 0.5 kcal/mol and $\Delta(\Delta S^{\ddagger})$ as 3.6 ± 1.4 eu (Figure 1). These may be compared with the values of $\Delta(\Delta H^{\ddagger}) = 1.07$ and $\Delta(\Delta S^{\ddagger}) = 1$ eu obtained by Fox and Schnecko[7] for homopolymerization of MMA. Elias and Goldi have collected a number of other values showing the temperature dependencies of tacticities in various homopolymerizations.[8]

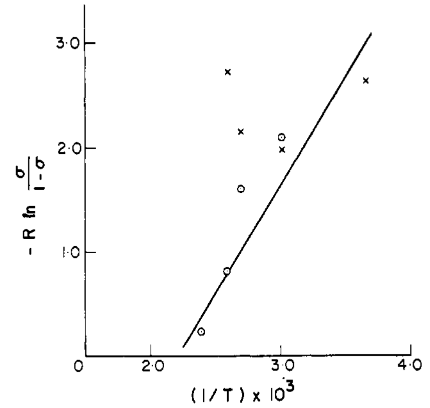

Figure 1. An Arrhenius plot of the data in Table IV: ⊙, our analysis; ×, analysis of Ito and Yamashita.

It is important to recognize that the reasonable value of temperature dependence of σ is dependent on *both* the nmr assignments *and* the reversible kinetic scheme (including its parameters). An irreversible treatment of the kinetic scheme yields an unrealistic temperature dependence of σ, as is seen in the third column of Table IV. While this cannot be taken as proof of the validity of the reversible treatment,[3] it does tend to further confirm it. As Berger and Kuntz[9] pointed out a number of years ago, sequence distribution analysis is superior to composition analysis for discriminating between alternate kinetic schemes in copolymerization.

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Highly Stereoelective Polymerization Processes[1]

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ABSTRACT: The initiator resulting from the reaction of diethylzinc with (*R*)-(−)-3,3-dimethyl-1,2-diol is a highly stereoelective system for the polymerization of propylene sulfide. Starting from racemic mixture, monomers of optical purities up to 90% could be obtained using this system. An equation linking the conversion and the optical activity of unreacted monomer has been established. The ratio, $r = \Sigma K_{iR}/\Sigma K_{iS}$, of rate constants for the consumption of the two antipodes was found equal to 3.5. It was also shown that the optical purity of a pure enantiomer of propylene sulfide has a higher value than the one previously obtained by direct synthesis. This polymerization process can be used as a method of preparation of enantiomers of high optical purity and also in order to determine their absolute optical purity.

We have reported recently[2] that products of reaction between diethylzinc and substituted optically active 1,2-diols are very suitable initiators for stereoelective polymerization of propylene sulfide. In a stereoelective process, as defined by Pino,[3] there is a preferential polymerization of one of the enantiomers of a racemic monomer. In the present work we report more detailed data concerning the use of one of these initiators resulting from the reaction between diethylzinc and (*R*)-(−)-3,3-dimethyl-1,2-butanediol.

The polymerization of racemic propylene sulfide by this initiator at different conversions produces a dextrorotatory polymer (in C_6H_6 or $CHCl_3$ solution); unreacted monomer is levorotatory (neat value). This corresponds to a preferential consumption of the *R* monomer over the *S* monomer. It was established previously that the *S* monomer is levorotatory.[4]

Experimental Section

The preparation of the standard initiator was carried out in toluene solution at room temperature by treating diethylzinc with the glycol with a molar ratio 1:1.2. The polymerization proceeds in this case in an apparently homogeneous medium. At the end of the polymerization, unreacted monomer and solvent are evaporated under vacuum and the distillate is fractionated through a spinning-band column, giving the pure monomer. The polymer is dissolved in benzene, separated from remaining initiator by centrifugation, and then precipitated in an excess of methanol. Another technique of preparation of the initiator was also used: after allowing diethylzinc and glycol to react for 2 hr in toluene solution, the solvent was evaporated and the catalyst dried 2 hr under vacuum. Then a

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