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Stereoregulation in the Alternating Copolymerization Giving Highly Coheterotactic Poly(Methyl Methacrylate-*alt*-Styrene). Direct Determination of Coisotactic Parameters

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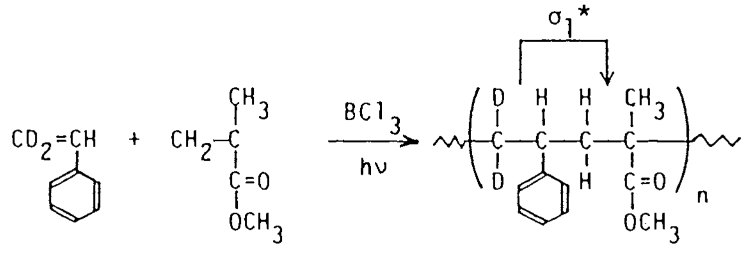
Coisotactic parameters of two steps in a propagating process, one from styrene (St) unit to methyl methacrylate (MMA) unit and the other from MMA unit to St unit, were experimentally determined in alternating copolymerization of MMA with St under the copolymerization conditions giving highly coheterotactic poly(MMA-*alt*-St). The former step resulted in highly syndiotactic addition and the latter, in highly isotactic addition.

Highly coheterotactic alternating copolymer has been successfully prepared by radical copolymerization of methyl methacrylate (MMA) with styrene (St) in the presence of boron trichloride excess to MMA at low temperature below -60 ℃.1) In order to make clear the stereoregulation mechanism to give the copolymer with the highest coheterotacticity ever reported, we have experimentally determined coisotactic parameters (Bovey's σ parameter : the probability of isotactic dyad addition) by carrying out the copolymerization of MMA and styrene-d_2 in which two methylene protons are solely deuterated. The results indicate that the propagating process from St unit to MMA unit is highly syndiotactic and that from MMA unit to St unit, highly isotactic.2)

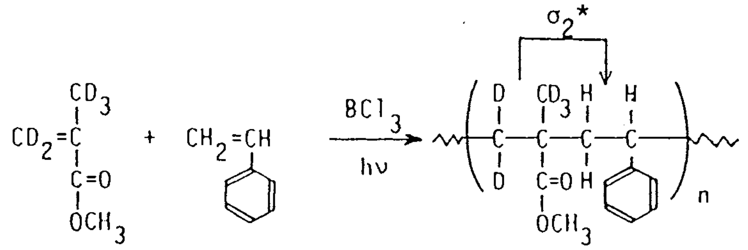
Methylene deuterated styrene ($C_6H_5CH{=}CD_2$, St-d_2) was synthesized by the dehydration of 1-phenylethanol-d_3 ($C_6H_5CHOHCD_3$), which was prepared from acetophenone-d_3 ($C_6H_5COCD_3$) by the reduction with $LiAlH_4$.3) Alternating copolymerization was carried out as previously reported.1) MMA-centered triad cotacticity (f_{SM}, f_{HM}, and f_{IM})4) and meso dyad content (P_m)4,5) were determined from ^{1}H NMR spectrum measured at 399.8 MHz and

St-centered one (f_{SS}, f_{HS}, and f_{IS}),[4)] from ^{13}C NMR spectrum measured at 22.5 MHz as previously reported.

Stereoregulation of alternating copolymerization involves two different steps. Coisotactic parameters of two steps in a propagating process, one from St unit to MMA unit and the other from MMA unit to St unit, have been defined as σ_1^* [6)] and σ_2^*, respectively. These parameters can be experimentally determined as follows. On a 400 MHz ^{1}H NMR spectrum of the alternating copolymer of MMA with St-d_2 the methylene proton peaks are originally derived from the methylene protons of MMA. Therefore, the meso dyad content (P_m) of the methylene proton of P(MMA-*alt*-St-d_2) gives directly the σ_1^* parameter, while that of P(MMA-d_5-*alt*-St) obtained by using a methylene-deuterated MMA (MMA-d_5) gives the σ_2^* parameter as shown in Eqs. 1 and 2. Since the synthesis of the deuterated MMA is more difficult than that of St-d_2, the σ_2^* parameter was determined by Eq. 3 using σ_1^* and the P_m of P(MMA-*alt*-St). K. Hatada et al. determined coisotactic parameters for the copolymers of MMA-d_8 with other methacrylates by examining a copolymerization of a large amount of MMA-d_8 with a trace of other methacrylate.[7)] In the present work, because of the

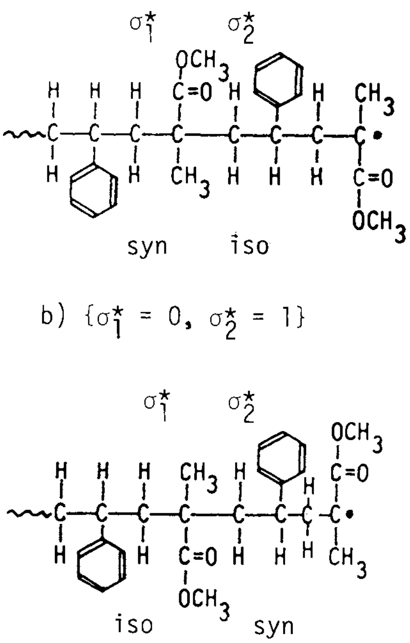


$\{P_m \text{ of P(MMA-}alt\text{-St-}d_2)\} \equiv \sigma_1^*$ (1)



$\{P_m \text{ of P(MMA-}d_5\text{-}alt\text{-St)}\} \equiv \sigma_2^*$ (2)

$$\{P_m \text{ of P(MMA-}alt\text{-St)}\} = \frac{\{P_m \text{ of P(MMA-}alt\text{-St-}d_2)\} + \{P_m \text{ of P(MMA-}d_5\text{-}alt\text{-St)}\}}{2} \equiv \frac{\sigma_1^* + \sigma_2^*}{2} \qquad (3)$$



b) $\{\sigma_1^* = 0,\ \sigma_2^* = 1\}$

a) $\{\sigma_1^* = 1,\ \sigma_2^* = 0\}$

Fig. 1. Two kinds of propagating processes to give coheterotactic poly(MMA-*alt*-St)s.

alternation both σ parameters can be determined directly without any assumption of polymerization mechanism.

There are two kinds of propagation processes a) and b) in Fig. 1 to give coheterotactic poly(MMA-*alt*-St)s. Although the alternating copolymers obtained by both processes can not be differentiated, the stereoregulation mechanism is opposite each other. Experimental determination of the σ parameters can reveal this difference.

Both poly(MMA-*alt*-St-d_2) (M_n=4.3 ×10^4, M_w/M_n=1.8)[8] and poly(MMA-*alt*-St) (M_n=5.0 ×10^4, M_w/M_n=2.3)[8] were synthesized under the same conditions to give the highly coheterotactic alternating copolymer. The MMA- and St-centered triad cotacticities of both copolymers are summarized in Table 1, which are coincident each other fairly well. Thus, the deuteration of methylene protons has not any effect on the stereoregulation in propagation. The methylene proton region of a ^{1}H NMR spectrum of poly(MMA-*alt*-St-d_2) is shown in Fig. 2 (a) as well as that of poly(MMA-*alt*-St) in (b). The racemo methylene peaks (r) of poly(MMA-*alt*-St-d_2) are dominant in Fig. 2 (a), while those of poly(MMA-*alt*-St) are comparable to the meso peaks (m) in Fig. 2 (b). The P_m values measured from these spectra are 9 and 46 mol%, respectively. Since the alternating regulation of these polymers was excellent based both on the absence of methoxyl proton peaks at δ=3.6 and 3.5[4] as shown in Fig. 2 and on 50 mol% of MMA content in copolymer (f_M), the coisotactic parameter σ_1^*, from St unit to MMA unit, was determined to be 0.09, and the σ_2^* was calculated to be 0.85 from Eq. 3.[9] Therefore, the stereoregulation giving the highly coheterotactic poly(MMA-*alt*-St) proceeds through the type b) process in Fig. 1. Thus, the step from St unit to MMA unit is highly syndiotactic and that from MMA unit to St unit, highly isotactic.

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Table 1. Cotacticities[a] of alternating copolymers of MMA with styrene-d_2 (or styrene) prepared in the presence of excess BCl_3 to MMA[b]

Comonomers	$[BCl_3]$/[MMA]	Polym. temp °C	MMA-centered triad			St-centered triad			meso dyad
			f_{SM}	f_{HM}	f_{IM}	f_{SS}	f_{HS}	f_{IS}	P_m
MMA, St	1.4	-90	11	86	3	10	87	3	46
MMA, St-d_2[c]	1.4	-100	9	89	2	9	88	3	9

a) mol%. b) MMA ratio in monomer feed = 0.5.
c) Degree of deuteration of poly(MMA-*alt*-St-d_2) is ca. 98 mol%.

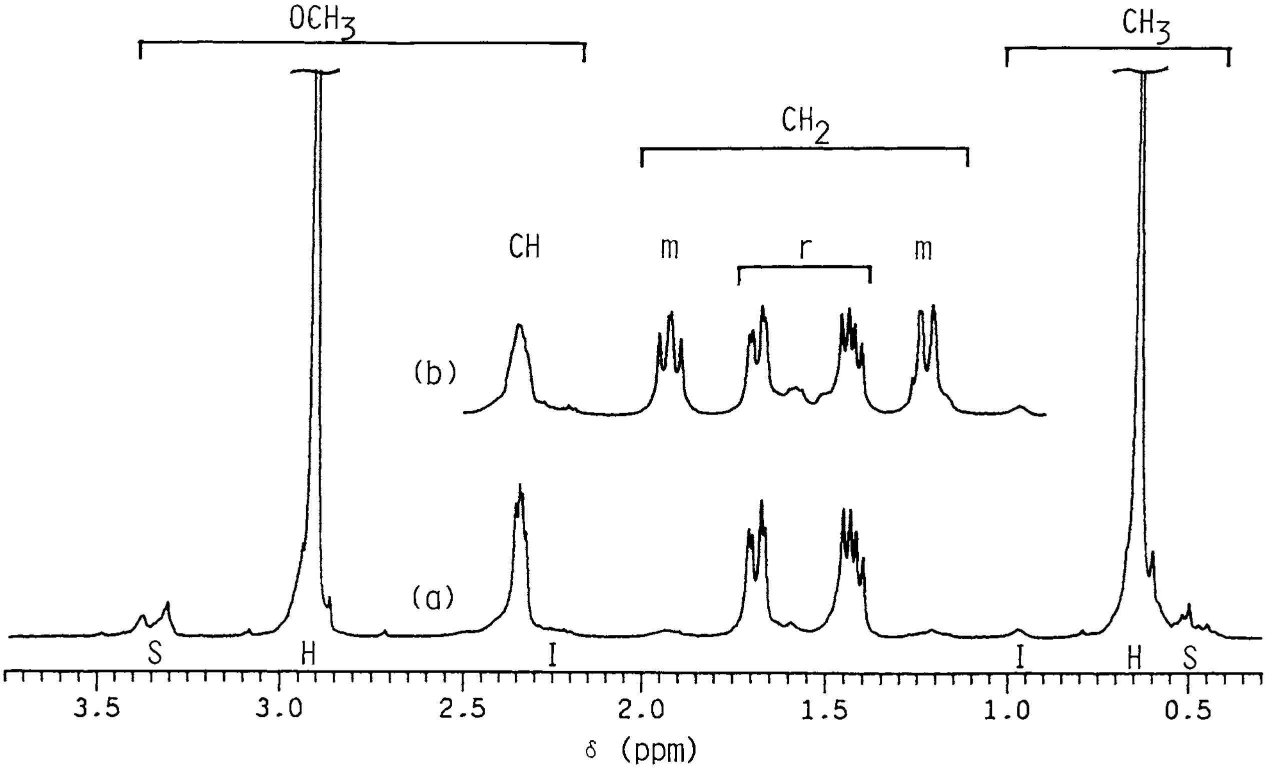

Fig. 2. Methylene proton region of ^{1}H NMR spectra of highly coheterotactic poly(MMA-*alt*-St-d_2) (a) and poly(MMA-*alt*-St) (b) prepared by using BCl_3 at -95 °C and $[BCl_3]/[MMA] = 1.4$ (at 399.8 MHz and 55 °C in $CDCl_3$).

References

1) Y. Gotoh, T. Iihara, N. Kanai, N. Toshima, and H. Hirai, Chem. Lett., 12, 2157 (1990).
2) Propagating terminal radicals are in sp^2 hybrid and rotating. When a styrene terminal radical adds to an MMA, the dyad sequence of the bond between the penultimate MMA and the terminal St is determined. Since the new MMA terminal radical is rotating, the bond between St and MMA is not yet fixed. Therefore, we use the expression shown in the text.
3) L. A. Wall, D. W. Brown, and V. E. Hart, J. Polym. Sci., 15, 157 (1955); A. J. Castro, J. Am. Chem. Soc., 72, 5311 (1950).
4) Y. Gotoh and H. Hirai, "Current Topics in Polym. Sci.," ed by R. M. Ottenbrite, L. A. Utracki, and S. Inoue, Hanser Pub., Munich (1987), Vol. I, pp. 151-167.
5) S. A. Heffner, F. A. Bovey, L. A. Verge, P. A. Miran, and A. E. Tonelli, Macromolecules, 19, 1628 (1986).
6) H. Hirai, T. Tanabe, and H. Koinuma, J. Polym. Sci., Polym. Chem. Ed., 18, 203 (1980).
7) K. Hatada, T. Kitayama, T. Ochi, and H. Yuki, Polym. J., 19, 1105 (1987).
8) By GPC in $CHCl_3$ by using narrow-dispersity polystyrene standards.
9) The $\sigma_1{}^*$ and $\sigma_2{}^*$ values at complete deuteration are calculated to be 0.08 and 0.85, respectively, which are nearly same as the values without the correction.

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