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Synthesis of Highly Coheterotactic Poly(Methyl Methacrylate-*alt*-Styrene)

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Highly coheterotactic poly(methyl methacrylate-*alt*-styrene)s have been synthesized by using boron trichloride excess to methyl methacrylate at low temperature below -60 ℃. The highest value of their coheterotacticities in triad sequence was about 90 mol%, which is the highest in heterotacticity among the polymers ever reported.

In the presence of metal halide methyl methacrylate (MMA) radically copolymerizes with styrene (St) to give the alternating copolymer.¹⁾ Stereoregulation in radical polymerization is generally difficult. However, it was reported that the cotacticties of poly(MMA-*alt*-St)s thus prepared depend on the metal halide used.¹,²⁾ Concerning on alternating regulation boron trichloride (BCl_3) is effective even in a catalytic amount.³⁾ Based on these backgrounds we have examined the dependence of cotacticities of the poly(MMA-*alt*-St) on the concentration of BCl_3 at lower copolymerization temperature than -60 ℃.

BCl_3 was prepared according to the method described in the literature.⁴⁾ MMA, St and toluene were dried and purified by a usual method, and were distilled in vacuo over calcium hydride immediately before use. Under dry nitrogen a toluene solvent and MMA were introduced in a Pyrex glass ampoule at first. By freezed-thaw cycle the solution was degassed, and then BCl_3 was introduced into the ampoule by vacuum distillation. At last St was introduced and the ampoule was sealed off in vacuo. Copolymerizations were carried out at desired temperature on photoirradiation with a 500 W high-pressure mercury lamp (Eikosha model PIH-500S). MMA-centered triad cotacticities (f_{SM}, f_{HM}, and f_{IM}) were determined from ^1H NMR spectra measured at 399.8 MHz and St-centered ones

(f_{SS}, f_{HS}, and f_{IS}), from ^{13}C NMR spectra measured at 22.5 MHz as previously reported.[5)]

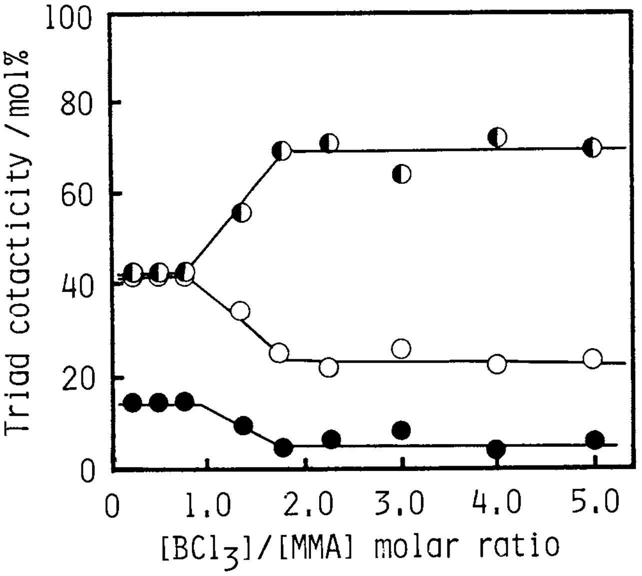


Fig. 1. Plots of the MMA-centered triads cotacticities of p(MMA-*alt*-St)s prepared at -60 °C under photoirradiation vs. the molar ratio of BCl_3 to MMA.

f_{SM} (○), f_{HM} (◐), f_{IM} (●)

Table 1. Highly Coheterotacic Poly(MMA-*alt*-St)s Obtained on Photoirradiation

$[BCl_3]$/[MMA]	Polym. Temp/°C	MMA-centered			St-centered		
		f_{SM}	f_{HM}	f_{IM}	f_{SS}	f_{HS}	f_{IS}
1.8	-60	25	70	5	—	—	—
2.2		22	70	8	24	70	6
3.0		27	64	9	25	65	10
4.0		24	72	4	23	70	7
5.0		24	70	6	25	67	8
1.4	-76	19	76	5	17	76	7
1.8		19	75	6	18	75	7
2.2		19	74	7	17	74	9
1.0	-95[a)]	13	82	5	16	79	5
1.2		15	83	2	15	80	5
1.4		11	86	3	10	87	3
2.0		10	89	1	11	85	4

a) -90 — -100 °C.

Highly coheterotactic alternating copolymer of MMA and St was synthesized at -60 °C using BCl_3 in excess to MMA under the conditions where total monomer concentration = 0.25 mol/l (= mol dm^{-3}) in toluene, MMA content in monomer feed (F_M) = 0.5, BCl_3 molar ratio to MMA = 0.2 — 5.0 and polymerization time = 4.5 min for larger BCl_3 molar ratio to MMA than 1.4. Even on this short irradiation, the conversion was 15% at 2.2 of BCl_3 molar ratio to MMA. As shown in Fig. 1, a clear dependence of triad cotacticity on BCl_3 concentration (BCl_3 molar ratio to MMA) was observed. Triad cotacticities of copolymers synthesized at higher BCl_3 concentration than 1.8 to MMA are completely different from those obtained at lower BCl_3 concentration than equimolar to MMA. Figure 1 also exhibits that the presence of more than 2 moles of BCl_3 to MMA has no additional effect on the cotacticity. In this region the MMA-centered triad cotacticity $f_{SM}:f_{HM}:f_{IM}$ equals 24:70:6. The enhancement of coheterotacticity from 70 to 75 mol% are achieved by lowering the copolymerization temperature from -60 to -76 °C. These results indicate the contribution of the monomer complex composed of one MMA, one styrene and two BCl_3. Therefore, in order to get higher coheterotacticity a copolymerization at much lower polymerization temperature than -76 °C was examined.

When lowering the polymerization temperature to about -95 °C using the ethanol cooled by liquid nitrogen, the poly(MMA-*alt*-St) with the higher coheterotacticity than that prepared at higher temperature has been obtained on photoirradiation. In this case 10 min was enough for the polymerization. The cotacticities of poly(MMA-*alt*-St)s obtained at -95 ℃ are listed in Table 1 together with those obtained at -60 and -76 ℃. Any highly coheterotactic alternating copolymer in Table 1 has the same pattern in both MMA- and St-centered triad cotacticities. The coheterotactic content goes up to more than 80 mol%, e.g., 89 mol% by using BCl_3 with the higher concentration than unity in molar ratio to MMA. This coheterotactic content is the highest among the homo- and co-polymers ever reported.6)

The highly coheterotactic poly(MMA-*alt*-St), whose content in coheterotacticity was 86 mol%, gave a ^1H NMR spectrum as shown in Fig. 2. Just a trace amount of the isotactic content is observed in the highly coheterotactic poly(MMA-*alt*-St)s. Thus, at 399.8 MHz, the peaks (marked with arrow) due to isotactic methyl and methoxyl protons appear very weak and a broad methyne proton peak is observed with seperation from the isotactic methoxyl protons. In methylene proton region, four groups of the clearly splitted 2 × 2 peaks due to the mrm and rmr tetrad are exclusively observed, although appearance of the splitting are different each other.

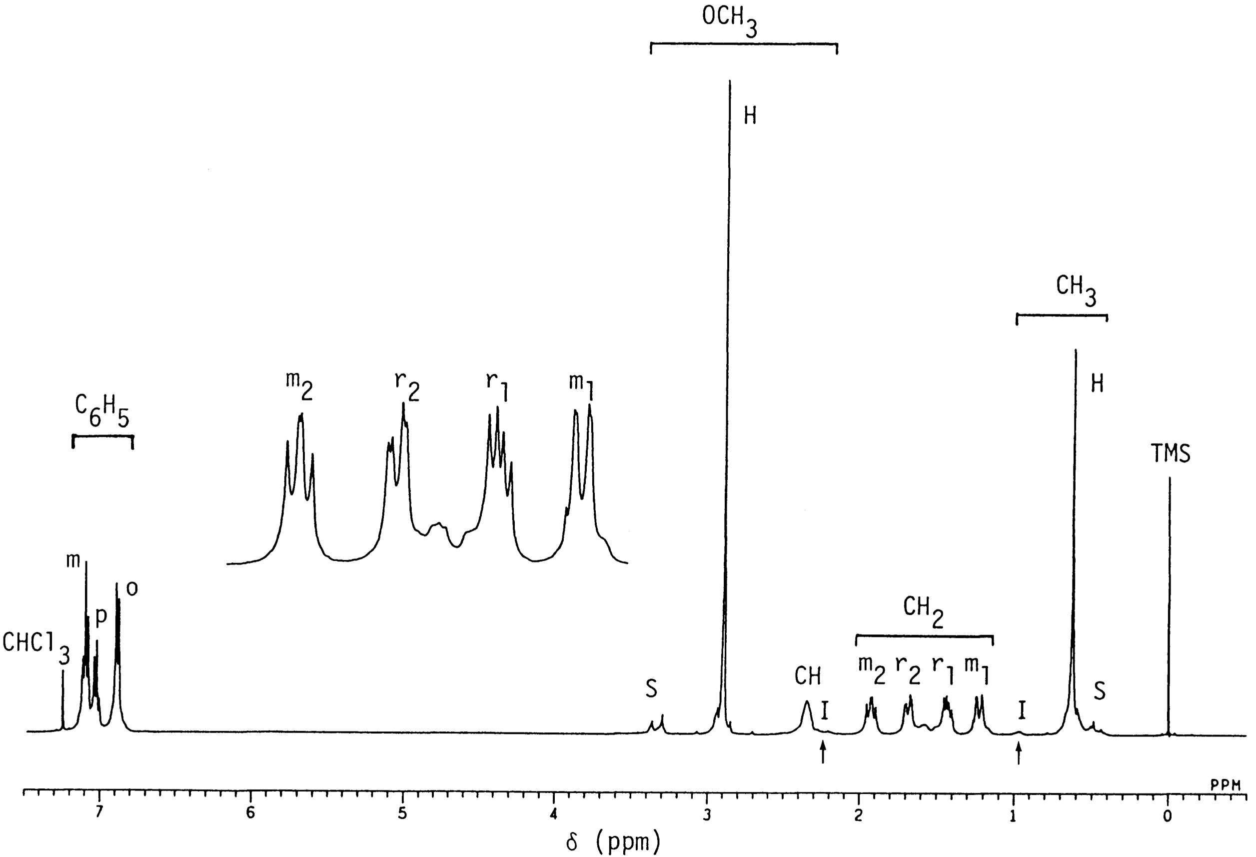
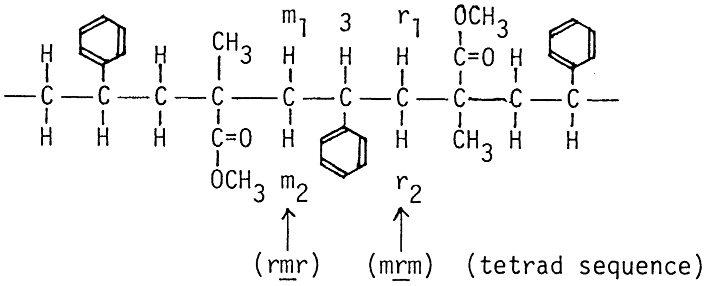


Fig. 2. ^1H NMR spectrum of highly coheterotactic poly(MMA-*alt*-St) prepared by using BCl_3 at -95 °C and $[BCl_3]/[MMA]$ = 1.4 (at 399.8 MHz and 55 °C in $CDCl_3$).
(m_1 and m_2 in the rmr tetrad sequence; r_1 and r_2 in the mrm tetrad sequence).

Assignment of methylene peaks is also shown in Fig. 2. From this spectrum, geminal and vicinal spin-spin coupling constants (^2J and ^3J) and chemical shifts (δ) can be determined. Any methylene proton can couple with the other methylene proton (^2J) and with methyne proton (^3J). $^2J_{12}$ of all methylene protons are -14.0 Hz. The magnitude of $^3J_{13}$ and $^3J_{23}$ of two protons of m_1 and m_2 in rmr tetrad sequence in formula (1) are 2.2 and 10.7 Hz, respectively. These values are coindident with those obtained by simulation based on the spectrum measured at 89.6 MHz and dyad sequence, which were 2.1 and 11.2 Hz, respectively.[5)] The magnitude of $^3J_{13}$ and $^3J_{23}$ of two protons of r_1 and r_2 in the mrm tetrad sequences are 7.6 and 3.7 Hz, respectively. The δ's for m_2, r_2, r_1, and m_1 were determined to be 1.921, 1.682, 1.426, and 1.223, respectively.



(1)

The present synthesis of almost (90 mol%) pure coheterotactic poly(MMA-*alt*-St) clearly makes the splittings due to J-couplings observable for the first time. The polymerization mechanism as well as the physical properties of the highly coheterotactic poly(MMA-*alt* -St) will be quite interest and will be discussed elsewhere.

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