Alternating Copolymerization of Methyl α -Phenylacrylate and Methyl Methacrylate by *n*-BuLi

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In a previous paper we reported the anionic polymerization of methyl α -phenylacrylate (MPhA).¹ This monomer could polymerize at low temperature, giving a stereochemically random polymer under certain polymerization conditions. However, MPhA gave no polymer above 0°C, suggesting that the ceiling temperature of this monomer lay close to 0°C.

In this work the copolymerizations of MPhA and methyl methacrylate (MMA) were carried out in toluene by *n*-BuLi at various temperatures. It was found that the alternate copolymer of these two monomers was produced above 0°C. The alternating tendency of MPhA and MMA had been observed in the radical copolymerization of these monomers by Tsuruta, *et al.*^{2,3}

The results of the copolymerizations are shown in Table I. The initial molar ratio of MMA and MPhA was 1:1. The NMR spectra of three polymer samples are shown in Figure 1.

The polymer obtained at -78°C was found to be a homopolymer of MPhA from its NMR spectrum as reported by Tsuruta, *et al.*^{2,3} The NMR spectrum of the polymer prepared at -40°C was close to the superposition of those of poly(methyl methacrylate) (PMMA) and of poly(methyl α -phenylacrylate) (PMPhA), indicating that the polymer consisted of long sequences of MMA and MPhA or of a mixture of PMMA and PMPhA. This result is very interesting, and the mechanism should be clarified by further investigations. At 0°C and above, the produced polymer contained MMA and MPhA units in a molar ratio of about 1:1 regardless of the polymerization temperature. The spectrum of this copolymer was clearly distinguished from that of the polymer obtained at -40°C by the following features.

(a) α -Methyl proton resonance of the MMA unit appears at 0.90~0.63 splitting into three

Table I. Copolymerization of MPhA and MMA by *n*-BuLi in toluene at various temperatures^a

No.	Temp, °C	Time, hr	Polymer		
			Yield, %	MPhA content, ^b %	η_{sp}/c , ^c dl/g
1	-78	24	15	97	0.086
2	-40	72	68	44	0.142
3	0	72	80	47	0.052
4	30	96	59	47	0.053
5	40	48	33	49	0.059
6	50	48	10	48	0.053

^a MPhA, 6.8 mmol; MMA, 6.8 mmol; *n*-BuLi, 0.68 mmol; toluene, 6.3 ml.

^b Determined by the intensity measurement of the phenyl proton signal in the NMR spectrum of copolymer.

^c Measured in toluene at 30.0±0.03°C (*c*=0.5 g/dl).

Figure 1. NMR spectra of the copolymers of MPhA and MMA prepared at -78°C (A), -40°C (B), and 30°C (C) in toluene by *n*-BuLi. The spectra were taken at 150°C on 10 w/v% solution in nitrobenzene- d_5 at 100 MHz using a JEOL spectrometer (JNM-4H-100). Hexamethyldisilane was used as an internal standard. The peaks labelled X are due to the phenyl protons of nitrobenzene.

peaks, but does not exist at 1.36–1.14 ppm, the region where the α -methyl proton of PMMA resonates.

(b) The resonance of methoxyl methyl protons is clearly different from those of PMMA and PMPHA and splits into three peaks at 3.63, 3.28, and 2.85 ppm.

These results indicate that MMA and MPhA units are alternately incorporated into the polymer chain. The high-field shift observed in the α -methyl proton resonance of the MMA unit

may be attributed to the shielding effect of the benzene rings of MPhA units on both sides. A similar shift of α -methyl resonance has been observed in the spectrum of the alternating copolymer of MMA and styrene.⁴

The peak separations of α -methyl and methoxyl methyl resonances may be due to the differences among the configurational sequences in the polymer chain. It is reasonably assumed that the diamagnetic shielding effect of the phenyl groups in MPhA units is the smallest on the methoxyl methyl protons in MMA, if the configuration of the central MMA unit is the same as those of the neighboring MPhA units. Then the three peaks in the methoxy resonance region can be tentatively assigned to the methoxyl methyl protons of centered MMA in coisotactic, coheterotactic, and cosyndiotactic triads with increasing magnetic field. The first peak overlaps with the methoxy resonance of MPhA, which is not so sensitive to the stereochemical configurations of the chain as in the spectrum of PMMA. The three peaks of α -methyl protons, the situation of which is contrary to the methoxyl methyl protons, can also be assigned to cosyndiotactic, coheterotactic, and coisotactic triads with increasing magnetic field. Using these assignments triad cotacticities of the central MMA in the copolymers were determined as shown in Table II. The values of tactic fractions calculated from the methoxyl methyl proton resonance were in agreement with those from the α -methyl proton resonance.

The proportions of *I* : *H* : *S* in all the alternate copolymers were close to 1 : 2 : 1, indicating that the stereoregulation in this alternating copolymerization was nearly random. It is noteworthy that the random propagation in the stereoregulation was found in the anionic polymerization of MPhA¹ and in the copolymerization of the

Table II. Cotacticity of alternating copolymer of MMA and MPhA

Polymerization temp, $^{\circ}\text{C}$	from $\alpha\text{-CH}_3$ of MMA			from -OCH_3 of MMA		
	<i>I</i>	<i>H</i>	<i>S</i>	<i>I</i>	<i>H</i>	<i>S</i>
0	20.4	47.5	32.1	14.2	53.4	32.4
30	24.8	50.4	24.8	25.6	52.1	22.3
40	24.2	50.7	25.1	18.7	55.6	25.7
50	22.7	49.8	27.5	21.7	55.6	22.7

MMA—Lewis acid complex and styrene.⁴

At 30°C the 1:1 copolymers were obtained over a wide range of monomer feed ratios. This is an additional evidence for the formation of alternating copolymer.

In the anionic copolymerization of MMA and MPhA the growing chain ending in the MPhA unit cannot add MPhA above the ceiling temperature of this monomer. On the other hand, the MMA anion at the chain end may add predominantly MPhA owing to the higher reactivity of the latter. The higher reactivity of MPhA towards the anion is presumed by the lower charge density at the β -carbon of this monomer¹ and the resonance stabilization of its anion due to the phenyl group. Thus the formation of the alternating copolymer of MMA and MPhA at 0°C and above must be attributed to the cross-over propagation occurring predominantly over the homopolymerization of MMA.⁵ The results of further investigations on the effect of the

polymerization conditions will be reported later.

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