

SHORT COMMUNICATION

Stereospecific Polymerization of Methyl α -Ethyl- and α -*n*-Propylacrylates

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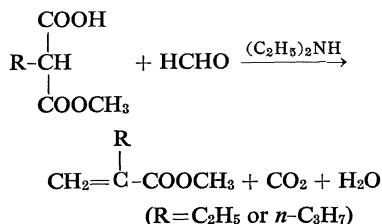
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Stereospecific polymerizations of methyl and other alkyl methacrylates by anionic initiator have been extensively studied. Systematic studies have also been carried out on the effect of ester groups on the tacticity of produced polymers.¹⁻³ However, there have been only a few investigations on the polymerization of α -alkyl acrylates⁴ and little attention has been paid to the effect of α -alkyl group on stereoregulated polymerization. In this work the polymerizations of methyl α -ethylacrylate (MEA) and of methyl α -*n*-propylacrylate (MPA) were carried out by *n*-butyllithium (*n*-BuLi), and it was found that the dependence of the tacticities of these polymers on the polymerization temperature was greatly different from that of methyl methacrylate (MMA).

The monomers were prepared from the corresponding monomethyl alkylmalonates by the Mannich reaction.⁴ The polymerization was



carried out in a sealed tube under nitrogen pressure. The NMR spectra of the polymers were obtained at 70°C with a JNM-4H-100 spectrometer of JEOL at 100 MHz on a 5-10 w/v% polymer solution in benzene. A few per cent of tetramethylsilane was used as an internal standard.

In Table I are shown the results of the polymerizations of MEA by *n*-BuLi. In toluene the yield of the polymer decreased with increasing polymerization temperature. No polymer was obtained at 30°C probably because of the low ceiling temperature of this monomer.

The tacticity of the poly (methyl α -ethylacrylate) (PMEA) obtained at -78°C in toluene was investigated by NMR spectroscopy. The methyl resonance of the ester group of the polymer split into three peaks at 3.53, 3.49 and 3.45 ppm and the peak at 3.53 ppm was most intense. On the other hand, the intensity of the peak at 3.45 ppm was most enhanced in the NMR spectrum of the polymer obtained in tetrahydrofuran by *n*-BuLi at -78°C. A similar spectrum was obtained with a polymer prepared in toluene by (*iso*Bu)₂-AlNPh₂, which gave a highly syndiotactic polymer in the polymerization of MMA.⁵ The methylene protons in the chains of all these PMEAs gave a singlet peak which is rather broadened and obscured by overlapping with the signal due to the methylene proton in α -ethyl group. Thus the three methyl peaks of the ester group are tentatively assigned to isotactic, heterotactic and syndiotactic triads with increasing magnetic fields.

The isotacticity of the PMEA obtained in toluene increased with increasing polymerization temperatures, and a highly isotactic polymer was produced at 0°C. The polymerization in diethyl ether gave a polymer having a predominantly isotactic structure, although the yield was extreme-

Table I. Polymerization of MEA by *n*-BuLi^a

No.	Polymerization			Yield (%)	Polymer		
	Solvent	Temp. (°C)	Time (hr)		Tacticity (%)		
					I	H	S
4	Toluene	-78	143	69	69.5	10.8	19.5
7	"	-40	98	78	86.7	6.7	6.6
8	"	0	98	11	96.8	1.7	1.5
17	"	30	144	0	—	—	—
5	Toluene-THF ^b	-78	143	10	16.3	13.8	69.9
6	THF	-78	696	2	11.7	13.3	75.0
11	Diethyl ether	-40	143	5	82.5	11.6	5.9
70 ^c	Toluene	-40	96	12	88.3	4.9	6.8
71 ^d	"	-40	96	4	—	—	—
18 ^e	Toluene	-40	143	18	13.9	11.7	74.4

^a Monomer 9 mmol, *n*-BuLi 0.25 mmol, Solvent 5 ml

^b Toluene/Tetrahydrofuran = 1/1 vol/vol.

^{c,d} A small amount of methanol was added. Methanol/*n*-BuLi: (b) 0.3, (c) 0.6.

^e Catalyst: (*iso*Bu)₂AlNPh₂ 0.25 mmol.

ly low in a toluene-tetrahydrofuran mixture as well as in tetrahydrofuran. The syndiotactic polymers were formed in lower yields.

The polymerization of MPA was carried out in toluene at various temperatures. The results are shown in Table II. A maximum yield of the polymer was obtained at -40°C and no polymer was produced above 30°C. The tacticity of the polymer was determined from the methyl resonance of the ester group in its NMR spectrum. The resonance split into three peaks at 3.56, 3.49 and 3.41 ppm which were tentatively assigned to isotactic, heterotactic and syndiotactic triads, respectively. The isotacticity of PMPA also increased with increasing polymerization temperatures.

The temperature dependence of the stereoregulation in the polymerization of these two monomers is quite different from that of MMA⁶ as shown in Figure 1. The isotacticity of the polymer produced at -78°C decreased in the order of PMMA > PMEA > PMPA in accordance with the increasing order of the bulkiness of α -substituent. With increasing polymerization temperatures, the isotacticities of PMEA and PMPA were strongly increased while the tacticity of PMMA was only slightly increased.

In the polymerizations of methacrylates by *n*-BuLi in a nonpolar medium it is postulated^{7,8}

Table II. Polymerization of MPA by *n*-BuLi^a

No.	Polymerization			Yield (%)	Polymer		
	Solvent	Temp. (°C)	Time (hr)		Tacticity (%)		
					I	H	S
1	Toluene	-78	24	3	62.5	35.7	1.8
2	"	-40	24	67	74.7	22.0	3.3
3	"	0	182	15	94.7	4.0	1.3
4	"	30	182	0	—	—	—

^a Monomer 9 mmol, *n*-BuLi 0.25 mmol, Solvent 5 ml.

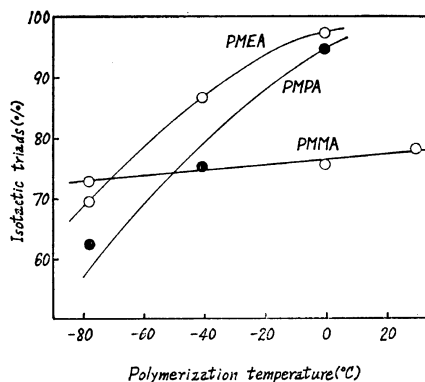


Figure 1. Tacticities of PMMA, PMEA and PMPA prepared in toluene at various temperatures.

that the lithium atom can coordinate with the carbonyl oxygen of the penultimate monomer unit in the growing chain and the resulting cyclic

intermediates dominates the conformation of incoming monomer toward the lithium atom to give an isotactic polymer. In this case the steric interactions between the substituent groups of growing chain and of the incoming monomer are important factors for controlling the addition mode of the incoming monomer. In the polymerization of α -substituted acrylate the steric repulsion between the larger α -alkyl groups may cause a decrease in the rate of isotactic propagation at low temperatures, but at higher temperatures the Li-O interaction will be loosened and the bulkier α -substituent, on the other hand, may favor isotactic propagation.

The possibility that Li methoxide produced during polymerization might have affected the stereoregulated polymerization of MEA and MPA at higher temperatures was considered but rejected because the addition of a small amount of methanol did not affect the tacticity of the polymer obtained (Table I).

Further investigations are now in progress.

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