SHORT COMMUNICATION

Anionic Copolymerization of Methyl Methacrylate and Other Methacrylates by *n*-BuLi in Toluene and THF

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A number of studies have been done on the stereospecific polymerizations of methyl[1-4] and other methacrylates[5-11] by anionic initiators, and it has been found that the polymerizations are influenced by many factors, such as the type of solvent, the initiator, etc. However, there have been few reports on the anionic copolymerizations of methacrylates.[12-14] In the present work, the authors investigated the anionic copolymerizations of methyl methacrylate (MMA, M_1) and other methacrylates (M_2), such as benzyl (BMA), *dl*-α-methylbenzyl (MBMA), diphenylmethyl (DPMA), α,α-dimethylbenzyl (DMMA), and trityl methacrylate (TMA) in order to study the effects of the ester group on the reactivity of the monomer and the stereoregularity of the copolymer. The copolymerizations were carried out in toluene and THF using *n*-BuLi as initiator at −78°C. It was found that the monomer reactivity ratios, r_1 and r_2, depended very much on the structure of the ester group and the solvent. The triad tacticity of the copolymers was predominantly isotactic in toluene and syndiotactic in THF.

MBMA, DPMA, and DMMA were prepared from methacryloyl chloride and the corresponding carbinols; TMA was prepared from silver methacrylate and trityl chloride.[7] The reaction was stopped in less than 10-% yield in the copolymerizations for the determination of r_1 and r_2. The copolymers were precipitated in methanol. Copolymer compositions were determined mainly from the pmr spectra of the copolymers. Monomer reactivity ratios were calculated by the least square method according

to the Fineman—Ross equation, and the confidence limits were calculated at 90-% confidence coefficient. The copolymer was converted to poly(methyl methacrylate) (PMMA) by hydrolysis followed by methylation, and the pmr spectrum of the PMMA was measured on a JEOL 100-MHz spectrometer (JNM-MH-100) in deuterochloroform at 60°C by using TMS as an internal standard. The tacticity of the copolymers was obtained from the pmr spectrum of the PMMA.

The pmr spectra of all of the copolymers composed of nearly equimolar M_1 and M_2 showed a rather broad peak due to the methoxy group of MMA unit; the chemical shifts of MMA unit were slightly different from that of PMMA. Furthermore, the methoxy resonance of copoly(MMA—BMA), for instance, shifted upfield linearly from $\delta 3.61$ ppm to 3.45 as the fraction of MMA in the copolymer decreased. These spectral data suggest that the monomer distribution in the copolymer is more or less random.

A summary of the monomer reactivity ratios is shown in Table I. The monomer reactivity ratios were strongly affected by the solvent, and in several cases the reactivity in toluene was reversed in THF. The order of the reactivity $(1/r_1)$ of the monomers towards MMA anion was DPMA≈BMA>MMA>MBMA>TMA>DMMA in toluene and TMA≥BMA>MMA≥DPMA>MBMA>DMMA in THF. The compositions of the oligomers which were isolated in 2—4-% yield in the copolymerizations of MMA—BMA were also examined. They were quite similar to those of the corresponding co-

polymers obtained in toluene and THF, although the pmr spectra of the oligomers showed peaks due to a terminal *n*-butyl group. In toluene, TMA and DMMA, which have a bulky tertiary ester group, were much less reactive than the other monomers. In THF, however, these groups did not seem to play an important role. In this solvent the reactivity of the monomers is roughly explained by the inductive effect, although there exists no good correlation between the reactivity and Taft's σ^*, which is well correlated to the ^{13}C chemical shifts of β carbons

Table I. Monomer reactivity ratios for anionic copolymerizations of MMA(M_1) and methacrylates(M_2) by *n*-BuLi at $-78°C^a$

M_2	In toluene		In THF	
	r_1	r_2	r_1	r_2
BMA	0.59±0.07	1.60±0.42	0.70±0.06	1.46±0.36
MBMA	1.68±0.17	0.78±0.32	2.04±0.16	1.52±0.25
DPMA	0.57±0.15	0.55±0.61	1.11±0.22	1.57±0.61
DMMA	19.1 ±4.0	0.56±0.39	2.59±1.35	2.00±1.10
TMA	6.28±0.30	0.13±0.07	0.62±0.08	0.62±0.32

[a] [Monomers]/[Solvent], 1.0 mol/l; [Monomers]/[*n*-BuLi], *ca.* 50.

of the methacrylates.[15]

It has been shown that in the anionic polymerization of MMA the reactivity of active species in the initial stage will be different from that of the later stage of the reaction.[16] Therefore, the monomer reactivity ratio might vary as the reaction progresses. However, in the present work all the copolymer composition data showed smooth curves, indicating that the r_1 and r_2 values obtained have validity at least for the initial stage of the copolymerization.

The tacticity of the copolymers is shown in Table II together with that of the homopolymers obtained under similar conditions. The copolymers were predominantly isotactic in toluene and syndiotactic in THF. This tendency is the same as that of the homopolymers except for TMA, which formed a highly isotactic polymer even in THF.[7]

The copolymerizations between equimolar amounts of M_2 monomers were also carried out for a long time at $-78°C$. The results are shown in Table III. Since the yields of several copolymerizations in toluene were low, one may discuss the reactivity of the monomers. It is found from the M_2'/M_2 ratio in copolymer that the order of the reactivity was BMA≥MBMA>

Table II. Tacticity of copolymers of MMA(M_1) and methacrylates(M_2) obtained by *n*-BuLi at $-78°C^a$

Solvent	M_2	Yield, wt%	M_2/M_1 in copolymer	$\eta_{sp}/C,^c$ dl/g	Tacticity, %					
					Copolymer			M_2 homopolymer		
					I	H	S	I	H	S
Toluene	BMA	91	0.92	0.32	84	10	6	81	15	4
Toluene	MBMA	75	1.05	0.49	66	27	7	56	35	9
Toluene	DPMA	58	0.50	0.30	80	16	4	99	1	0
Toluene	DMMA	26	0.19	0.56	61	25	14	68	18	13
Toluene	TMA	24[b]	0.16	0.36	74	17	9	96	2	2
Toluene	None	87	—	—	—	—	—	70	17	13
THF	BMA	91	0.85	0.44	8	34	58	6	31	63
THF	MBMA	91	0.98	0.56	7	37	56	8	32	60
THF	DPMA	92	0.84	0.42	6	30	64	2	11	87
THF	DMMA	88	0.87	0.28	7	31	62	8	30	62
THF	TMA	100[b]	1.0	0.12	19	40	41	94	4	2
THF	None	83	—	—	—	—	—	6	40	54

[a] $[M_1]_0=[M_2]_0$, 2.5 mmol; solvent, 10 ml; [*n*-BuLi], 0.25 mmol; time, 24 hr.

[b] Time, 48 hr.

[c] In toluene at 30.0°C; C, 0.5 g/dl.

Table III. Tacticity of copolymers of methacrylates obtained by n-BuLi at $-78°C^a$

M₂	M₂′	Solvent	Yield, wt%	M₂′/M₂ in copolymer	$\eta_{sp}/C,^c$ dl/g	Tacticity, %		
						I	H	S
BMA	MBMA	Toluene	98	0.90	0.67	79	15	6
BMA	DPMA	Toluene	98	1.06	0.46	79	16	5
BMA	DMMA	Toluene^b	40	0.17	—	69	21	10
BMA	TMA	Toluene^b	34	0.11	0.27	81	12	7
TMA	MBMA	Toluene	26	4.17	0.27	59	28	13
TMA	DPMA	Toluene^b	46	—	—	72	20	8
TMA	DMMA	Toluene^b	24	0.70	0.30	41	37	22
BMA	MBMA	THF	84	1.02	0.40	8	27	65
BMA	DPMA	THF	93	1.06	—	6	26	68
BMA	DMMA	THF	98	1.10	—	13	40	47
BMA	TMA	THF	94	0.94	0.11	16	40	44
TMA	MBMA	THF	90	1.08	0.07	22	39	39
TMA	DPMA	THF	97	—	—	26	35	39
TMA	DMMA	THF	94	1.19	0.07	38	41	21

a $[M_2]_0=[M_2']_0$, 2.5 mmol; solvent, 10 ml; n-BuLi, 0.25 mmol; time, 24 hr.

b Time, 48 hr.

c In toluene at 30.0°C; C, 0.5 g/dl.

TMA > DMMA, which is the same as that determined by the r_1 values. The data on the tacticity of these copolymers are given in Table III. The copolymers were also predominantly isotactic in toluene and syndiotactic in THF, except for copoly(TMA—DMMA), which had nearly equal I and H contents regardless of the solvents. However, the stereoregularity of the copolymers, in many cases, was between those of the corresponding homopolymers or less than both, in particular, the copolymers composed of bulky monomers like TMA and DMMA had poor regularity. The structure of the ester groups apparently affects the stereoregularity of the copolymers as well as the homopolymers. However, the details of the effect are not clear at the present time.

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