

Heterotactic Polymers of α -Substituted Acrylic Acid Esters

Koichi HATADA, Hikaru SUGINO, Hiroaki ISE,
Tatsuki KITAYAMA, Yoshio OKAMOTO,
and Heimei YUKI

*Department of Chemistry, Faculty of Engineering Science, Osaka University,
Toyonaka, Osaka 560, Japan.*

(Received October 12, 1979)

ABSTRACT: Polymerizations of various methacrylates and α -(*p*-substituted phenyl)acrylates were studied in toluene and tetrahydrofuran by several anionic initiators. The polymerization with octylpotassium in tetrahydrofuran was found to be the most suitable for the formation of the heterotactic polymer, defined as the polymer containing more than 50% heterotactic triads. Methacrylic acid esters of the primary alcohol gave the heterotactic polymers, whose heterotactic contents increased with an increase in the bulkiness of the ester group. Methacrylic esters of secondary alcohol generally gave heterotactic polymers with octylpotassium in tetrahydrofuran. In the polymerizations of methacrylic acid esters of tertiary alcohol, the heterotactic contents decreased with an increase in the bulkiness of the ester group. A perfectly atactic polymer was obtained in the polymerization of methyl α -phenylacrylate with butyllithium in tetrahydrofuran, but it gave the heterotactic polymer when initiated with octylpotassium in tetrahydrofuran. Methyl α -*p*-chlorophenylacrylate produced the heterotactic polymer in tetrahydrofuran with butyllithium as well as with octylpotassium. In the case of methyl α -*p*-bromophenylacrylate, the heterotactic polymer was obtained even in the polymerization in toluene with butyllithium. These results indicate that the acrylic acid ester having the bulkier substituent tends to give the heterotactic polymer more easily by anionic initiator.

KEY WORDS Heterotactic Polymer / Alkyl Methacrylate / α -Substituted Acrylate / Methyl Methacrylate / Methyl α -Phenylacrylate / Cyclohexyl Methacrylate / Octylpotassium / Fluorenylcesium / ^{13}C -NMR Spectrum / Glass Transition Temperature /

Many papers have been published on polymerization in which highly isotactic or syndiotactic polymers were obtained. However, there have been few publications concerning the formation of heterotactic polymers. Heterotactic poly(vinyl alcohol) was reported by Nozakura *et al.*^{1,2} and heterotactic poly(acetaldehyde) by Brame and Vogl,³ and Goodman and Brandrup.⁴ A polymer having more than 50% portion of heterotactic triads should be defined as a heterotactic polymer since the heterotactic contents can attain at most 50% even when the regulation in the polymerization is sterically random. The formation of heterotactic polymer appears to be very interesting since a higher order of stereoregulation would be required for the heterotactic polymerization than for the isotactic or syndiotactic one.

In our previous paper⁵ the formation of heterotactic polymers of methyl α -(*p*-bromophenyl)acrylate and methyl α -(*p*-chlorophenyl)acrylate was briefly reported. In this work, we have studied the anionic polymerizations of various methacrylates and α -phenylacrylates under various conditions, and found that the bulkiness of α -substituent was one of the important factors necessary for the heterotactic growth in the polymerization and that the polymerization in tetrahydrofuran initiated with octylpotassium was suitable for the formation of the heterotactic polymer.

EXPERIMENTAL

Methyl, ethyl, isopropyl, *t*-butyl, benzyl, and 2-*N,N*-dimethylaminoethyl methacrylates were ob-

tained commercially. Diphenylmethyl, α -methylbenzyl, α,α -dimethylbenzyl, phenyl, cyclohexyl, furfuryl, tetrahydrofurfuryl, and 2-methylthioethyl methacrylates were prepared by the reactions of methacryloyl chloride and the corresponding alcohols. Trityl and 1,1-diphenylethyl methacrylates were prepared from silver methacrylate and the corresponding chloride according to the procedure of Adrova.⁶ Methyl α -phenylacrylate was obtained by the reaction of formaldehyde and dimethyl oxalyl phenylacetate, which was prepared from methyl phenylacetate, dimethyl oxalate, and sodium methoxide.⁷ Methyl α -(*p*-bromophenyl)acrylate was prepared by the dehydration of the corresponding hydroxycarboxylic acid⁸ followed by methylation with methanol and concentrated sulfuric acid. bp 95.0~96.0°C(0.1mmHg). *Anal.* Calcd for C₁₀H₉O₂Br: C, 49.82%; H, 3.76%; Br, 33.15%. Found: C, 49.97%; H, 3.67%; Br, 33.17%. The NMR spectrum (10% CCl₄ solution) showed peaks at 3.76 ppm (singlet, 2.9H) assigned to the methoxyl methyl protons, at 5.82 and 6.28 ppm (two doublets, 1.9H) assigned to the β -protons of vinyl group and at 7.18~7.45 ppm (quartet 4.0H) assigned to the phenyl protons. Methyl α -(*p*-chlorophenyl)acrylate was prepared in the same way as that for the preparation of the α -*p*-bromophenylacrylate, bp 85.0~85.5°C(0.1mmHg). *Anal.* Calcd for C₁₀H₉O₂Cl: C, 61.08%; H, 4.61%; Cl, 18.03%. Found: C, 60.71%; H, 4.48%; Cl, 17.74%. The NMR spectrum (neat) showed peaks at 3.66 ppm (singlet, 3.1H) assigned to the methoxyl methyl protons, at 5.76 and 6.25 ppm (two singlets, 1.8H) assigned to the β -protons of vinyl group and at 7.13~7.34 ppm (quartet, 4.0H) assigned to the phenyl protons. Phenyl α -(*p*-chlorophenyl)acrylate was synthesized from α -(*p*-chlorophenyl)propenoyl chloride and phenol in benzene. mp 62.0~63.0°C. *Anal.* Calcd for C₁₅H₁₁O₂Cl: C, 69.64%; H, 4.29%; Cl, 13.70%. Found: C, 69.48%; H, 4.20%; Cl, 13.54%. The NMR spectrum (10% CCl₄ solution) showed peaks at 5.94 and 6.49 ppm (two doublets, 1.9H) assigned to the β -protons of vinyl group and at 7.0~7.5 ppm (multiplet, 9.0H) assigned to the phenyl protons.

Butyllithium and Grignard reagents were prepared in usual manner in hexane and in ether, respectively. Butylpotassium and octylpotassium were prepared by the reaction of potassium 2-methyl-2-butoxide and the corresponding alkyl-lithium in hexane.⁹ Fluorenylcesium was synthesized

by the reaction of fluorene and metallic cesium in 1,2-dimethoxyethane.^{10,11} Diethylaluminum diphenylamide was prepared from triethylaluminum and diphenylamine in toluene.¹²

Polymerization was carried out in a sealed glass ampoule under a nitrogen atmosphere. The polymerization was terminated by adding a small amount of methanol and the reaction mixture was then poured into a large amount of methanol. The precipitated polymer was separated by filtration and washed with methanol several times and dried *in vacuo*.

The triad tacticities of the polymers of methyl, furfuryl, tetrahydrofurfuryl, 2-methylthioethyl, 2-*N,N*-dimethylaminoethyl, benzyl, and diphenylmethyl methacrylates were determined by the intensity measurements of the α -methyl signals in the ¹H-NMR spectra measured in chloroform-*d*₁ at 55°C or in nitrobenzene-*d*₅ at 140°C. The tacticities of poly(ethyl methacrylate) and poly(isopropyl methacrylate) were measured from the peak-eliminated Fourier transform ¹H-NMR spectra taken in toluene-*d*₈ at 110°C.¹³ The polymers of *t*-butyl, α,α -dimethylbenzyl, 1,1-diphenylethyl and trityl methacrylates were hydrolyzed by refluxing them in methanol containing a small amount of hydrogen chloride and water, and the resultant poly(methacrylic acid) was converted into poly(methyl methacrylate) by the methylation with diazomethane in benzene, and subjected to tacticity measurement. The ester group of poly(α -methylbenzyl methacrylate) was eliminated by hydrogen bromide in toluene and the resulting poly(methacrylic acid) was converted into poly(methyl methacrylate) as mentioned above. Poly(phenyl methacrylate) was changed directly into poly(methyl methacrylate) by the reaction with sodium methoxide in dioxane.¹⁴ The triad and pentad tacticities of poly(cyclohexyl methacrylate) were determined from the carbonyl carbon resonances. The tacticity of poly(methyl α -phenylacrylate) was determined from the splittings of the methoxyl methyl proton resonance.¹⁵ Poly(methyl α -*p*-bromophenylacrylate) and poly(methyl α -*p*-chlorophenylacrylate) were converted into poly(2-phenylallyl acetate) and poly(2-*p*-chlorophenylallyl acetate), respectively, by reduction with LiAlH₄ followed by the acetylation of the alcohol with acetic anhydride. The carbonyl carbon resonances of the polyacetates thus obtained split into three peaks which should be assigned to the isotactic, heterotac-

tic, and syndiotactic triads with increasing magnetic field.⁵ In the case of poly(phenyl α -*p*-chlorophenylacrylate), the resonance of the phenyl carbon substituted by chlorine atom split into three peaks at 131.3, 132.2, and 132.8 ppm in chloroform-*d*₁ at 56°C, which was tentatively assigned to isotactic, heterotactic, and syndiotactic triads with decreasing magnetic field.

¹H-NMR spectra were taken on a JNM-MH-100 spectrometer (JEOL) being operated at 100 MHz. The peak-eliminated Fourier transform ¹H NMR spectra were measured using a JNM-FX100 Fourier transform NMR spectrometer (JEOL) at 100 MHz. The ¹³C-NMR spectra were measured in nitrobenzen-*d*₅ at 110–140°C using JNM-PFT-100 and JNM-FX100 spectrometers (JEOL) at 25 MHz. Tetramethylsilane was used as an internal standard for all measurements.

Glass transition temperatures were measured by a Rigaku Denki calorimeter, Model 8001 SL/C, at a heating rate of 10°C/min, using the aluminum sample pans with lids. Aluminum oxide was used as a reference.

RESULTS

The polymerizations of methyl methacrylate were carried out in toluene at –78°C with various initiators and the results are shown in Table I. In the order of the polymers prepared with butyllithium, amylsodium, octylpotassium, and fluorenylcesium,

Table I. Polymerization of methyl methacrylate with various initiators in toluene at –78°C for 24 h^a

Initiator	Yield %	Tacticity/%		
		<i>I</i>	<i>H</i>	<i>S</i>
C ₄ H ₉ Li	72	70	19	11
C ₅ H ₁₁ Na ^b	88	67	25	9
C ₈ H ₁₇ K ^c	90	39	36	25
C ₁₃ H ₉ Cs ^d	87	6	50	44
C ₆ H ₅ MgBr	2	40	18	42
Et ₂ AlNPh ₂	31	2	18	80

^a Monomer 10 mmol; initiator, 0.5 mmol; toluene, 10 ml.

^b Data taken from the literature 16.

^c Initiator, 0.1 mmol.

^d Fluorenylcesium, 0.2 mmol.

the isotactic content decreased with an increase in the fractions of the heterotactic and syndiotactic triads. Octylpotassium and fluorenylcesium gave a polymer containing a fairly large amount of heterotactic triads. The other initiators seem unsuitable to bring about the formation of the heterotactic polymer.

When tetrahydrofuran was used as the solvent instead of toluene, the fractions of heterotactic triads in the polymer obtained were higher than those in the corresponding polymer prepared in toluene as shown in Table II. In the polymer prepared with octylpotassium, the heterotactic contents slightly exceeded 50%, indicating that the polymerization initiated by this initiator in tetrahydrofuran is suitable for bringing about the formation of the heterotactic polymer.

In Table III are shown the results of the polymerization of methacrylic acid ester of primary alcohol with octylpotassium and fluorenylcesium in tetrahydrofuran at –78°C. In the polymerization initiated with octylpotassium, the fractions of the heterotactic triads increased with an increase in the bulkiness of the ester group and the polymer containing 65% heterotactic triads was obtained in the polymerization of benzyl methacrylate. The polymerization initiated with fluorenylcesium gave the polymer having a lower content in heterotactic triads than that for the corresponding polymer prepared with octylpotassium.

In the polymerization of the methacrylic acid ester

Table II. Polymerization of methyl methacrylate with various initiators in tetrahydrofuran at –78°C for 24 h^a

Initiator	Yield %	Tacticity/%		
		<i>I</i>	<i>H</i>	<i>S</i>
C ₄ H ₉ Li	87	7	37	56
C ₅ H ₁₁ Na ^b	32	10	39	51
C ₈ H ₁₇ K ^c	84	11	53	36
C ₁₃ H ₉ Cs ^d	69	5	46	49
C ₆ H ₅ MgBr ^e	4	17	28	55
Et ₂ AlNPh ₂	0	—	—	—

^a Monomer, 10 mmol; initiator, 0.5 mmol; tetrahydrofuran, 10 ml.

^b Data taken from the literature 16.

^c Initiator, 0.1 mmol.

^d Fluorenylcesium, 0.1 mmol.

^e Polymerization temperature, 0°C.

Table III. Polymerization of the methacrylic acid ester of primary alcohol with octylpotassium and fluorenylcesium in tetrahydrofuran at -78°C for 24 h^a

Ester group	Octylpotassium				Fluorenylcesium			
	Yield	Tacticity/%			Yield	Tacticity/%		
	%	<i>I</i>	<i>H</i>	<i>S</i>	%	<i>I</i>	<i>H</i>	<i>S</i>
-CH ₃	84	11	53	36	69	5	46	49
-C ₂ H ₅	74	18	53	29	41	10	46	44
-CH ₂ CH ₂ SCH ₃	96	13	56	31	70	10	51	39
-CH ₂ CH ₂ N(CH ₃) ₂	80	15	59	26	—	—	—	—
Tetrahydrofurfuryl	14	14	55	31	34	9	43	48
Furfuryl	94	10	63	27	35	7	55	38
-CH ₂ C ₆ H ₅	97	13	65	22	100	8	58	34

^a Monomer, 10 mmol; octylpotassium, 0.1 mmol; fluorenylcesium, 0.2 mmol; tetrahydrofuran, 10 ml.

Table IV. Polymerization of the methacrylic acid ester of secondary alcohol with octylpotassium and fluorenylcesium in tetrahydrofuran at -78°C for 24 h^a

Ester group	Octylpotassium				Fluorenylcesium			
	Yield	Tacticity/%			Yield	Tacticity/%		
	%	<i>I</i>	<i>H</i>	<i>S</i>	%	<i>I</i>	<i>H</i>	<i>S</i>
-Iso-C ₃ H ₇	100	18	63	19	—	—	—	—
Cyclohexyl	98	16	64	20	82	11	55	34
-CH(CH ₃)C ₆ H ₅	95	20	64	16	90	19	54	27
-CH(C ₆ H ₅) ₂	92	18	62	20	96	17	44	40

^a Monomer, 10 mmol; octylpotassium, 0.1 mmol; fluorenylcesium, 0.2 mmol; tetrahydrofuran, 10 ml.

of secondary alcohol, the heterotactic triad fraction always exceeded 60%, when initiated with octylpotassium in tetrahydrofuran. When the polymerization was initiated with fluorenylcesium, the polymer rich in heterotactic triads was also obtained but the responding polymer prepared by octylpotassium responding polymer prepared by octylpotassium (Table IV).

The polymerizations of methacrylic acid esters of tertiary alcohols were carried out in tetrahydrofuran at -78°C using octylpotassium as the initiator. The results for this are given in Table V. *t*-Butyl methacrylate gave the heterotactic polymer whose heterotactic content was 60%. With an increase in the bulkiness of the ester group, the heterotactic content decreased with an increase in the isotactic triads and a decrease in the syndiotactic triads. In the poly-

merization of trityl methacrylate, a highly isotactic polymer was obtained, showing the strong tendency of this monomer to form an isotactic polymer. Phenyl methacrylate gave a polymer containing similar amounts of heterotactic and syndiotactic triads with a small amount of isotactic triads.

In order to study the effect of the α -substituent of acrylic acid ester on the formation of the heterotactic polymer, several α -substituted acrylates were polymerized in toluene and tetrahydrofuran with butyllithium and alkylpotassiums. The results are summarized in Table VI, together with the data mentioned in our previous papers.^{5,15} With methyl α -phenylacrylate, the polymerizations initiated with butyllithium in toluene and tetrahydrofuran gave completely atactic polymers but polymerization by octylpotassium in tetrahydrofuran gave a polymer

Heterotactic Polymers of α -Substituted Acrylate

Table V. Polymerization of the methacrylic acid ester of tertiary alcohol with octylpotassium in tetrahydrofuran at -78°C for 24 h^a

Ester group	Yield	Tacticity/%		
	%	<i>I</i>	<i>H</i>	<i>S</i>
$-t\text{-C}_4\text{H}_9$	73	15	60	25
$-\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_5$	94	12	54	34
$-\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_3$	97	39	44	17
$-\text{C}(\text{C}_6\text{H}_5)_3$	99	90	8	2
$-\text{C}_6\text{H}_5$	83	7	51	42


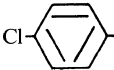
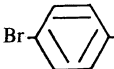
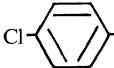

^a Monomer, 10 mmol; octylpotassium, 0.1 mmol; tetrahydrofuran, 10 ml.

containing 66% heterotactic triads. The heterotactic polymer of methyl α -*p*-chlorophenylacrylate was obtained by polymerization in tetrahydrofuran, using butyllithium as well as octylpotassium, but not in toluene with butyllithium. The α -*p*-bromophenylacrylate formed the heterotactic polymer in polymerization by butyllithium not only in

tetrahydrofuran but also in toluene. Phenyl α -*p*-chlorophenylacrylate gave a polymer containing 67% heterotactic triads in polymerization carried out in toluene with butyllithium. From the corresponding methyl ester, the polymer containing only 40% heterotactic triads was obtained under similar conditions. These results indicate that the counter cation at the growing chain end and the bulkiness of the α -substituent and ester group as well are the important factors for the formation of the heterotactic polymer with anionic initiator.

Table VII shows the glass transition temperatures (T_g 's) for various polymethacrylates. With few exceptions, the T_g 's of heterotactic polymers lie between those of isotactic and syndiotactic polymers and rather near to the T_g 's of syndiotactic polymers. The T_g 's for poly(methyl methacrylate)s of various tacticities are shown in Table VIII. T_g increased with an increase in the fraction of the racemic dyads and did not seem to depend on the heterotactic content. The polymer containing 56% heterotactic triads showed the T_g of 122°C , which was near to that of the highly syndiotactic polymer containing only 13% heterotactic triads.

Table VI. Polymerization of α -substituted acrylates

α -Substituent	Ester group	Initiator	Solvent	Polymerization temp	Yield	Tacticity/%		
				$^\circ\text{C}$		%	<i>I</i>	<i>H</i>
	CH_3 - ^a	$\text{C}_4\text{H}_9\text{Li}^c$	Toluene	-30	14	22	52	26
		$\text{C}_4\text{H}_9\text{Li}^e$	THF ^g	-78	57	26	50	24
		$\text{C}_8\text{H}_{17}\text{K}$	THF ^g	-78	34	3	66	31
	CH_3 - ^b	$\text{C}_4\text{H}_9\text{Li}^f$	Toluene	-78	43	25	40	35
		$\text{C}_4\text{H}_9\text{Li}^f$	THF ^g	-78	41	19	61	20
		$\text{C}_8\text{H}_{17}\text{K}$	THF ^g	-78	74	8	64	28
	CH_3 - ^c	$\text{C}_4\text{H}_9\text{Li}^f$	Toluene	-40	66	26	55	19
		$\text{C}_4\text{H}_9\text{Li}^f$	Toluene	-20	20	27	54	18
		$\text{C}_4\text{H}_9\text{Li}^f$	THF ^g	-78	90	21	59	20
		$\text{C}_4\text{H}_9\text{Li}$	Toluene	-40	39	14	67	20
		$\text{C}_4\text{H}_9\text{K}$	THF ^g	-78	90	15	56	29

^a Monomer, 13.6 mmol; initiator, 0.65 mmol; solvent, 7 ml.

^b Monomer, 6.8 mmol; initiator, 0.34 mmol; volume of reaction mixture, 10 ml.

^c Monomer, 5.0 mmol; initiator, 0.25 mmol; volume of reaction mixture, 8.8 ml.

^d Monomer, 7.5 mmol; initiator, 0.375 mmol; solvent, 7.5 ml.

^e Data taken from the literature 15.

^f Data taken from the literature 5.

^g Tetrahydrofuran.

Table VII. Glass transition temperatures of polymethacrylates

Ester group	$T_g/^\circ\text{C}$		
	Isotactic	Heterotactic	Syndiotactic
-CH ₃	58	122	138
-C ₂ H ₅	11	59	68
CH ₂ C ₆ H ₅	55	67	71
-Iso-C ₃ H ₇	31	74	93
Cyclohexyl	84	108	107
-CH(CH ₃)C ₆ H ₅	72	86	108
-CH(C ₆ H ₅) ₂	79	122	131
- <i>t</i> -C ₄ H ₉	73	91	120
-C(CH ₃) ₂ C ₆ H ₅	88	99	78
-C ₆ H ₅	91	117	116

Table VIII. Glass transition temperatures of poly(methyl methacrylate)s of various tacticities

Tacticity/%				T_g °C
<i>I</i>	<i>H</i>	<i>S</i>	<i>r</i> ^a	
96	4	0	2	58
93	5	2	4	65
25	51	24	49	102
12	56	32	60	122
0	13	87	93	138

^a Represents the fractions of racemic dyads.

DISCUSSION

The mechanism of heterotactic growth is of great interest. Many vinyl monomers give a polymer containing a fairly large amount of heterotactic triads in radical polymerization, where the heterotacticity does not exceed 50%, and the mechanism of the propagation can usually be explained in terms of Bernoullian statistics. Most of the methacrylates gave syndiotactic polymers by radical initiators. Large substituents at the α -position of acrylate monomers have been shown to favor the formation of atactic polymers; methyl α -phenylacrylate¹⁵ and alkyl α -(phenoxy)methylacrylates¹⁷ gave almost perfectly atactic polymers but not polymers containing more than 50% heterotactic triads by radical initiation. Thus, the formation of the heterotactic polymer should require the active chain ends having

unusual properties corresponding to the higher degree of stereoregulation. In Figure 1 are shown the carbonyl carbon resonances of poly(cyclohexyl methacrylate)s prepared by radical initiator and octylpotassium. Cyclohexyl methacrylate gave a polymer containing 64% heterotactic triads by octylpotassium in tetrahydrofuran. The peak assignment for the pentad tacticity was done by comparison of the observed peak intensities for the radically initiated polymer with those calculated by assuming Bernoullian statistics (Table IX). The tacticity of the polymer prepared by octylpotassium could be described neither by Bernoullian statistics nor by first-order Markov statistics, as shown in Table IX. This fact indicates that the heterotactic polymer obeys the second-order or higher order Markov statistics in the configurational sequences. This appears reasonable since there should exist at least a penultimate effect in the stereoregulation for the formation of heterotactic sequences.

As mentioned in the foregoing section, the methacrylic acid esters of secondary alcohols are suitable for the formation of heterotactic polymers among several kinds of methacrylates, and the bulky α -substituent also favors heterotactic propagation in the polymerizations of α -phenyl substituted acrylates. These facts clearly indicate that the structure or the bulkiness of the substituent is one of the important factors for the formation of heterotactic polymers.

In the polymerization of methyl α -phenylacrylate initiated by butyllithium, a sterically random polymer was obtained and the fraction of heterotactic triad did not exceed 50% under any polymerization

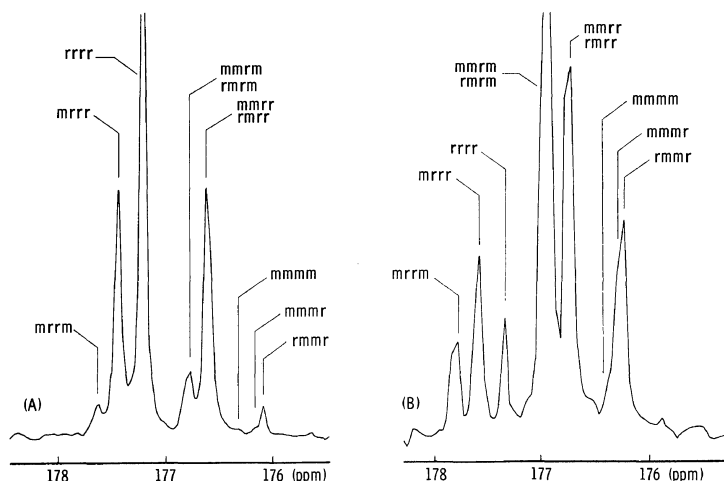
Heterotactic Polymers of α -Substituted Acrylate


Figure 1. Carbonyl carbon resonances of poly(cyclohexyl methacrylate)s prepared with AIBN at 60°C in toluene (A) and with octylpotassium at -78°C in tetrahydrofuran (B).

Table IX. Model fitting for poly(cyclohexyl methacrylate)s

Pentad	Polymer A ^a		Polymer B ^b		
	Observed	Bernoullian $P_m=0.185$ $P_r=0.815$	Observed	Bernoullian $P_m=0.485$ $P_r=0.515$	1st order Markov $P_{m/r}=0.67$ $P_{r/m}=0.63$
mmmm	0.00	0.00	}0.16	}0.24	}0.16
mrrr	0.01	0.01			
rmmm	0.02	0.02			
mrrm	}0.08	}0.06	}0.45	}0.25	}0.41
rrmm					
mmrr	}0.23	}0.25	}0.20	}0.26	}0.24
rrrr					
mrrm	0.04	0.02	0.05	0.06	0.08
mrrr	0.21	0.20	0.09	0.13	0.09
rrrr	0.42	0.44	0.05	0.07	0.03

^a Prepared in toluene with AIBN at 60°C.

^b Prepared in THF with octylpotassium at -78°C.

conditions by using this initiator. However, this monomer gave the heterotactic polymer when the polymerization was initiated with octylpotassium in tetrahydrofuran (Table VI). In the polymerization of methacrylates, both octylpotassium and fluorenylcesium gave polymers rich in heterotactic triads but the polymers prepared by the former initiator were more heterotactic than those prepared by the latter

(Tables III and IV). In the cationic polymerization of vinyl ether, it was mentioned that a bulky substituent was necessary for heterotactic propagation while a counterion was not important.² However, the results mentioned here show that the counter cation of the growing chain end is another important factor for the formation of heterotactic polymers of α -substituted acrylates.

In the literatures, we can find certain data indicating the formation of polymers rich in the heterotactic triads, although most of the authors have not commented on this. These data include poly(methyl methacrylate) and poly(ethyl methacrylate) obtained by octylpotassium,¹⁶ biphenylpotassium¹⁸ fluorenylpotassium¹⁹ or potassium alkoxide²⁰ in polar solvents. Thus the anionic polymerization initiated with potassium compounds in a polar solvent such as tetrahydrofuran appears to be generally suitable for the formation of heterotactic polymers.

It seems very difficult to show the mechanism of heterotactic propagation. The polymerization initiated with octylpotassium in tetrahydrofuran may be favorable to syndiotactic placement rather than to isotactic placement. The syndiotactic addition of the monomer is thus usually favored. However, two successive syndiotactic additions may be hindered owing to the bulkiness of the substituent and/or to the steric effect of the counter-cation and isotactic addition may occur inevitably following the one syndiotactic addition, which will favor the formation of the heterotactic polymer.

Acknowledgement. The authors are grateful to Mrs. F. Yano for her clerical assistance in the preparation of this manuscript.

REFERENCES

1. S. Nozakura, T. Okamoto, K. Toyora, and S. Murahashi, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 1043 (1973).
2. S. Nozakura, S. Ishihara, Y. Inaba, K. Matsumura, and S. Murahashi, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 1053 (1973).
3. E. G. Brame, Jr. and O. Vogl, *J. Macromol. Sci., Chem.* **A1**, 277 (1967).
4. M. Goodman and J. Brandrup, *J. Polym. Sci., A*, **3**, 327 (1965).
5. K. Hatada, Y. Okamoto, H. Ise, S. Yamaguchi, and H. Yuki, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 731 (1975).
6. N. A. Adrova and L. K. Prokhorova, *Vysokomol. Soedin.*, **3**, 1509 (1961).
7. G. R. Ames and W. Davey, *J. Chem. Soc.*, 1794 (1958).
8. E. J. Skerrett and D. Woodcock, *J. Chem. Soc.*, 2804 (1952).
9. A. F. Halasa, private communication.
10. W. Fowells, C. Schuerch, F. A. Bovey, F. P. Hood, *J. Am. Chem. Soc.*, **89**, 1396 (1967).
11. G. W. H. Schere, R. K. Brown, *Can. J. Chem.*, **38**, 2450 (1960).
12. S. Murahashi, T. Niki, T. Obokata, H. Yuki, and K. Hatada, *Kobunshi Kagaku*, **24**, 198 (1967).
13. K. Hatada, K. Ohta, Y. Okamoto, T. Kitayama, Y. Umemura, and H. Yuki, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 531 (1976).
14. H. J. Harwood, *Angew. Makromol. Chem.*, **4/5**, 279 (1968).
15. H. Yuki, K. Hatada, T. Niinomi, M. Hashimoto, and J. Ohshima, *Polym. J.*, **2**, 629 (1971).
16. D. Brau, M. Herner, U. Johnsen, and W. Kern, *Makromol. Chem.*, **51**, 15 (1962).
17. R. W. Lenz, K. Saunders, T. Balakrishnan, and K. Hatada, *Macromolecules*, **12**, 392 (1979).
18. J. Junquera, N. Cardona, and J. E. Figueruelo, *Makromol. Chem.*, **160**, 159 (1972).
19. J. P. Pascault, J. Kawak, J. Golé, and Q. T. Pham, *Eur. Polym. J.*, **10**, 1107 (1974).
20. M. Tomoi, K. Sekiya, H. Kakiuchi, *Polym. J.*, **6**, 438 (1974).