

Stereoregular Polymerizations of Acrylic Ester and its Related Monomers

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Stereoregular polymerizations of acrylic ester and its related monomers were studied with use of some organometallic compounds as catalyst. In a series of alkyl acrylate, ester of the more sterically hindered alcohol gave a polymer of the better crystallizability. The situation was also true of the thiolacrylate polymerization.

Some ate complexes such as strontium (or calcium) zinc tetraalkyl exhibited an excellent stereoregulating ability in the polymerization of alkyl acrylate. Even methyl acrylate also was found to produce a stereoregular polymer under the action of these ate complexes. In polymerizations of alkyl methacrylates other than methyl methacrylate, no crystalline polymers have not yet been obtained, though we have had an evidence for the possibility of stereoregulation in some special methacrylic ester such as trimethylsilyl or benzyl ester. There were obtained no crystalline polymers in the polymerization of α -chloroacrylic ester, but *sec*-butyl α -chlorothiоlacrylate did form a highly crystalline polymer with use of phenylmagnesium bromide as catalyst. Crystalline polymethyl vinyl ketone prepared by calcium zinc tetraethyl catalyst formed beautiful spherulites in its film which was cast from a formic acid solution. Some discussion was advanced concerning the stereoregular polymerization with respect to the catalyst type and the monomer structure.

INTRODUCTION

In 1958, Fox¹⁾ succeeded in preparing crystalline poly(methyl methacrylate) by using 9-fluorenyllithium as catalyst. Thereafter many catalysts for stereoregular polymerization of methyl methacrylate were proposed from a number of research laboratories all over the world. Especially, extensive work of Rohm and Haas researching group^{2,3,4)} is now famous. Nishioka and Watanabe⁵⁾, Nippon Telegraph and Telephone Public Corporation, developed their intensive work concerned with the stereoregular polymerization of methacrylate by use of Grignard reagent.

We studied methyl methacrylate polymerization using various kinds of ate complexes as catalyst. Polymerizations of *n*- and *sec*-butyl methacrylate were also examined.

The stereoregular polymerizations of alkyl acrylates were also reported by some workers. Miller⁶⁾ described that they prepared crystalline poly-*tert*-butyl acrylate by using lithium dispersion or *n*-butyllithium as catalyst. Garret⁷⁾ succeeded in preparing crystalline polyisopropyl, -*sec*-butyl and -*tert*-butyl acrylate with phenylmagnesium bromide. These polymers have an α -branched ester group in

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each monomer unit. Some relationship between the catalyst type and the monomer structure was pointed out by these workers in the stereoregular polymerization of the acrylates. We studied polymerizations of four isomers of butyl acrylate using some anionic catalysts and found a significant feature with respect to the monomer structure and the catalyst type.

Since the stereoregular polymerizations of alkyl thiolacrylate and thiolmethacrylate have drawn very little attention in the literature, we examined the polymerization in detail, especially in comparison with the corresponding acrylate and methacrylate polymerizations.

In this connection, the polymerizations of α -chloroacrylic and α -chlorothioloacrylic esters were also examined with use of the standard anionic catalysts.

Vinyl ketone is known as the monomer which is readily polymerized by anionic and cationic catalysts as well as radical type initiators, but few works are available concerning the stereoregular polymerization of the unsaturated ketone. We adopted some vinyl ketones as the related monomers to the acrylic ester.

In this paper, we would like to describe results obtained in the above mentioned study. Some discussion will be given with respect to the relation between structure and reactivity of monomer as well as catalyst and stereoregulation in the propagation step of the anionic polymerizations catalyzed by organometallic compounds.

I. ALKYL ACRYLATE AND ALKYL METHACRYLATE

I-1. Alkyl Acrylate^{*8)}

Acrylic esters examined were *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl and methyl acrylates.

1.1. Extent of polymerization. The extent of polymerization of four butyl

Table 1. Extent of polymerization

Catalyst	Catalyst ratio to the monomer (mole %)	Solvent	Temp. (°C)	Reaction time (hrs.)	Polymerization yield (%)					
					<i>n</i> -Butyl acrylate	Iso-butyl acrylate	<i>sec</i> -Butyl acrylate	<i>tert</i> -Butyl acrylate	Methyl acrylate	
I	AIBN	2.0	<i>n</i> -Hexane	60- 65	30	95.3	88.4	ca. 100	90.1	—
	(<i>n</i> -Bu) ₃ B and BPO	2.0	<i>n</i> -Hexane	-70--78	24	86.6	96.2	ca. 100	93.8	—
II	<i>n</i> -BuLi	2.0	Toluene	-70--78	24	23.1	43.0	62.5	81.1	—
	PhMgBr	3.0	Ethyl ether	-70--78	24	11.5	15.2	50.2	24.5	—
III	<i>n</i> -BuLi · Et ₃ Al	ca. 2.0	Toluene	-70--78	70	14.2	20.5	34.9	37.0	—
	<i>n</i> -BuLi · Et ₂ Cd	ca. 3.0	Toluene	-70--78	24	trace	49.0	70.0	92.5	—
IV	Sr-ZnEt ₄	ca. 2.0	Toluene	-70--78	60	23.4	54.8	ca. 100	82.9	23.9
	Ca-ZnEt ₄	ca. 2.0	Toluene	-70--78	24	38.2	36.8	97.8	ca. 100	—

* Experimented by Tsutomu Makimoto.

acrylates and methyl acrylate under the same conditions is shown in Table 1. The polymerization yield seems to suggest that the greater the steric hindrance in the monomer molecule, the greater is the polymerization reactivity.

Table 2 shows the solubility of polyacrylates prepared with strontium zinc tetraethyl complex as catalyst.

Table 2. Solubility of polyalkyl acrylates.

Solvent	Polymethyl acrylate	Poly- <i>n</i> -butyl acrylate	Polyisobutyl acrylate	Poly- <i>sec</i> -butyl acrylate	Poly- <i>tert</i> -butyl acrylate
Chloroform	sol.	sol.	sol.	sol.	
Carbon tetrachloride	sol.	sol.	sol.	sol.	swel.
Toluene	sol.	sol.	sol.	sol.	insol.
3-Heptanone	sol.	sol.	sol.	swel.	swel.
Dimethylformamide	sol.	sol.	sol.	insol.	—
Dioxane	sol.	sol.	sol.	insol.	insol.
Acetone	sol.	sol.	swel.	insol.	insol.

1.2. Properties of polyacrylates. Table 3 shows physical appearance, reduced viscosity and melting point under polarized microscope of polyacrylates.

Table 3. Physical properties of polyalkyl acrylates.

Polyacrylate	Appearance	$\frac{\eta_{sp}}{c}$ ($c = \text{g./100 ml.}$)	Mol. Wt.	M.p. (°C.) ^{a)}
Poly- <i>n</i> -butyl acrylate	Tough rubbery	1.8 (0.412)	—	43– 47
Polyisobutyl acrylate	Tough rubbery	1.8 (0.224)	—	72– 81
Poly- <i>sec</i> -butyl acrylate	Solid	1.9 (0.400)	—	125–130
Poly- <i>tert</i> -butyl acrylate	Solid	1.8 (0.400)	640,000	198–200
Polymethyl acrylate	Tough rubbery	0.92(0.282)	—	—

^{a)} Melting points were measured under polarized microscope. Polymethyl acrylate's value was not measured because it could not be oriented at room temperature (23°C.).

Poly-*n*-butyl, -isobutyl and -methyl acrylates prepared by radical type initiators or homogeneous anionic catalysts such as *n*-butyllithium in toluene were normally very soft semisolids. However, heterogeneous anionic catalysts such as strontium zinc tetraethyl complex resulted in the formation of a tough and rubbery polymer capable of forming a solid film. These polymers were confirmed to be crystalline from the discrete diffraction rings in their X-ray photographs. According to X-ray analysis, these crystalline polymers have been found to be isotactic, whose polymer chains have a three fold screw axis in the crystalline state. Table 4 shows results of X-ray analysis, together with calculated and observed values of polymer density. A considerable disagreement seen in the density of polyisobutyl acrylate probably arose from the incomplete fractionation of the crystalline part from the amorphous part. Poly-*n*-butyl and -methyl acrylates prepared under the same conditions were found to show only diffused rings in their X-ray photographs.

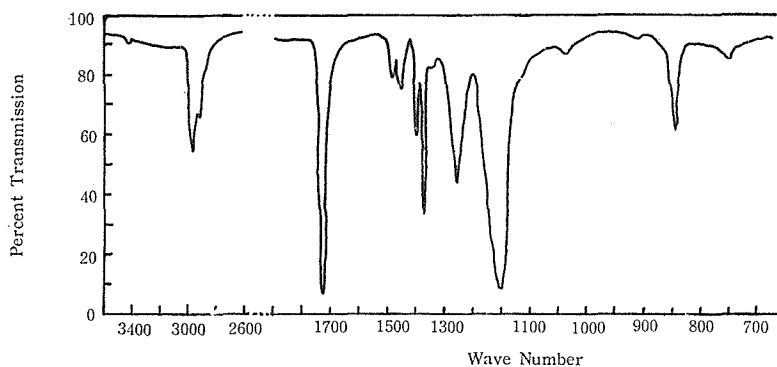
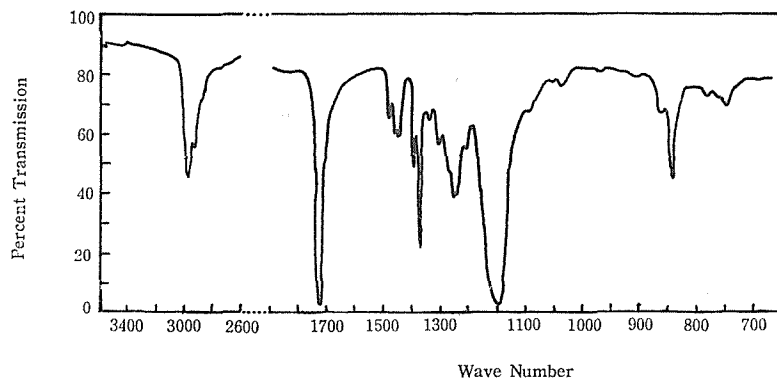
Table 4. Results of X-ray analysts of crystalline polybutyl acrylates.*

Polybutyl acrylate	Helix type	Lattice constants				Density (g./ml.) at 30°C.	
		$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\gamma(\text{\AA})$	$d_{calc.}$	$d_{obs.}$
Polyisobutyl acrylate	3_1 Isotactic	17.92	17.92	6.42	90	1.24	1.05
Poly- <i>sec</i> -butyl acrylate	3_1 Isotactic	10.34	10.34	6.49	90	1.06	1.05
Poly- <i>tert</i> -butyl acrylate	3_1 Isotactic	17.92	10.50	6.48	90	1.04	1.03

* Measured by Go Wasai

Infrared spectra of crystalline polyisobutyl, -*sec*-butyl and -*tert*-butyl acrylates show crystalline sensitive bands, especially in region 1350 to 1150 cm^{-1} , distinct changes of bands ascribed to crystallinity being observed.

For example, infrared spectra of amorphous and crystalline poly-*tert*-butyl acrylates are shown in Figs. 1 and 2.

Fig. 1. Infrared spectrum of amorphous poly(*tert*-butyl acrylate).Fig. 2. Infrared spectrum of crystalline poly(*tert*-butyl acrylate).

The infrared spectrum of amorphous poly-*n*-butyl acrylate prepared by the strontium catalyst differs clearly from that of the ordinary radical polymer, as shown in Figs. 3 and 4.

This suggests that the poly-*n*-butyl acrylate is also stereoregular in the same way as the other polybutyl acrylates, but it is not crystallizable, at least, under

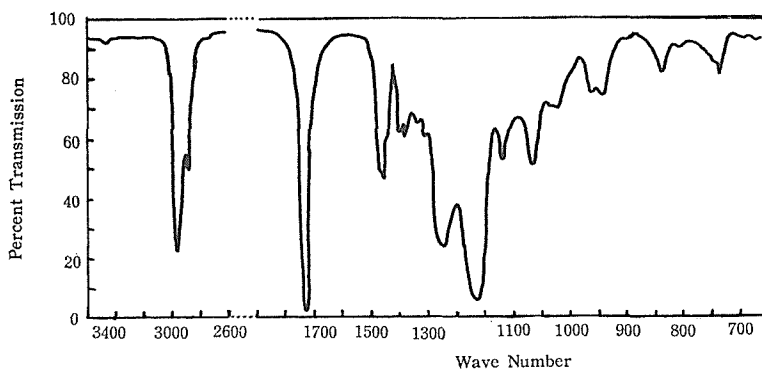


Fig. 3. Infrared spectrum of poly(*n*-butyl acrylate) prepared by AIBN catalyst.

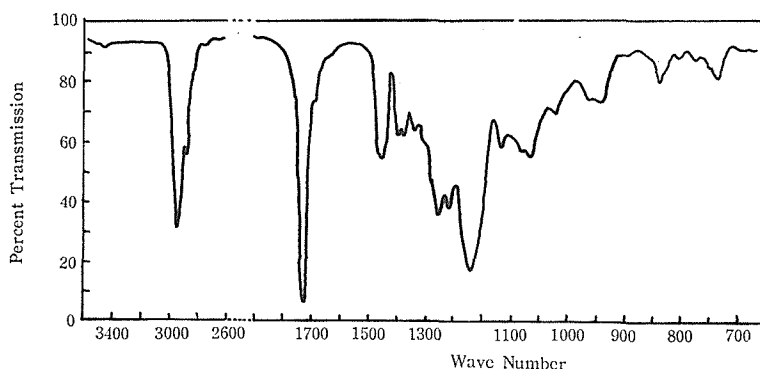


Fig. 4. Infrared spectrum of poly(*n*-butyl acrylate) prepared by strontium zinc tetraethyl catalyst.

the conditions.

Polymethyl acrylate prepared by strontium zinc tetraethyl complex and by the ordinary radical initiator had the same infrared spectra and both showed only dif-fused rings in their X-ray photographs.

In order to determine whether or not the configuration of polyacrylates pre-pared by the heterogeneous anionic catalyst differs from that of the polyacrylates by radical catalysts, the polymers were hydrolyzed to polyacrylic acid and the properties were investigated by X-ray diffraction and infrared spectra.

1.3. Properties of polyacrylic acid obtained from various polyacrylic esters.

Polyacrylic acid obtained from crystalline polyisobutyl acrylate was found to be crystalline, showing discrete Debye-Scherrer's rings in its X-ray photograph. Poly-acrylic acid from poly-*n*-butyl acrylate prepared by the strontium catalyst was crystalline, too. Furthermore, polymethyl acrylate prepared by the above anionic catalyst was hydrolyzed to give rise to a crystalline polyacrylic acid, though the degree of crystallinity seemed somewhat lower. On the contrary, polyacrylic acid obtained from the authentic amorphous polyacrylates prepared by AIBN was found to be amorphous. Results obtained are listed in Table 5.

These results indicate, that poly-*n*-butyl and -methyl acrylates prepared by strontium zinc tetraethyl are stereoregular and isotactic, but it seems very difficult

Table 5. Properties of polyacrylic acid obtained from polyacrylic ester.

Polyacrylate (catalyst)	Before hydrolysis polyacrylate	After hydrolysis polyacrylic acid
Poly- <i>n</i> -butyl acrylate (AIBN)	Amorphous	Amorphous
Poly- <i>tert</i> -butyl acrylate (AIBN)	Amorphous	Amorphous
Poly- <i>n</i> -butyl acrylate (Sr-ZnEt ₄)	Amorphous	Crystalline
Polyisobutyl acrylate (Sr-ZnEt ₄)	Crystalline	Crystalline
Polymethyl acrylate (Sr-ZnEt ₄)	Amorphous	Crystalline
Poly- <i>tert</i> -butyl acrylate (Li)	Crystalline	Crystalline

Table 6. Properties of polyalkyl acrylates.

Catalyst	Polymethyl acrylate	Poly- <i>n</i> -butyl acrylate	Polyisobutyl acrylate	Poly- <i>sec</i> -butyl acrylate	Poly- <i>tert</i> -butyl acrylate
I {	AIBN	Amorph.	Amorph.	Amorph.	Amorph.
	(<i>n</i> -Bu) ₃ B-BPO	—	Amorph.	Amorph.	Amorph.
II {	<i>n</i> -BuLi	—	Amorph.	Amorph.	Crystal.
	PhMgBr	—	Amorph.	—	Crystal.
III {	<i>n</i> -BuLi-Et ₃ Al	—	—	—	Crystal.
	<i>n</i> -BuLi-Et ₂ Cd	—	Amorph. ^{a)}	Crystal.	Crystal.
IV {	Sr-ZnEt ₄	Amorph.	Amorph. ^{a)}	Crystal.	Crystal.
	Ca-ZnEt ₄	Amorph.	Amorph. ^{a)}	Crystal.	Crystal.

^{a)} means that its infrared spectrum clearly differed from that of the authentic amorphous polymer.

Table 7. Anionic polymerization of *tert*-butyl acrylate.

Catalyst	Catalyst ratio to the monomer (mole %)	Solvent	Yield (%)	Crystalline (%)	Mol. wt.
<i>n</i> -BuLi	2.0	Ethyl ether	52.2	39.9	580.000
<i>n</i> -BuLi	2.0	Toluene	81.1	29.2	780.000
Disodium trinaphthyl boron	1.9	T. H. F.	48.2	50.8	360.000
Dipotassium benzophenone	1.4	T. H. F.	46.3	43.0	57.000
<i>n</i> -BuLi-Et ₃ Al	ca. 2.0	Toluene	>37.0	19.5	—
<i>n</i> -BuLi-Et ₂ Cd	ca. 3.0	Toluene	92.5	—	360.000
Li-CdEt ₃	ca. 2.8	Toluene	ca. 100	70.2	970.000
Li-ZnEt ₃	ca. 2.0	Toluene	89.8	29.0	640.000
NaH-ZnEt ₂	ca. 3.0	Toluene	92.3	40.6	190.000
Sr-ZnEt ₄	ca. 2.0	Toluene	82.9	61.3	640.000
Ca-ZnEt ₄	ca. 3.0	Toluene	ca. 100	60.0	670.000

for them to form crystal lattices, at least, at room temperature on account of their intrinsic properties.

Table 6 shows the X-ray properties of polyacrylates arranged according to the monomer structures and catalyst types.

In radical polymerizations, all polyacrylates formed were amorphous even if the polymerizations were conducted at temperatures as low as -78°C to -70°C . In anionic polymerizations, poly-*tert*-butyl acrylate having the bulkiest ester group was always isotactic and crystalline, irrespective of the type of catalyst and solvent used (Table 7). Polyisobutyl and *n*-butyl acrylates were found to be stereoregular only when they were prepared with a heterogeneous anionic catalyst. The situation was true of the polymer of methyl acrylate. These results may lead us to the conclusion that the heterogeneous polymerization system is often superior for formation of a stereoregular polymer.

I-2. Alkyl Methacrylate

2.1. Methyl methacrylate*. There are three types of stereoregular polymethyl methacrylate as seen in Table 8.

Table 8. Stereoregular polymethyl methacrylates.

Catalyst	Polymer type	M.p. ($^{\circ}\text{C}$.)	Specific gravity	<i>J</i> -value
Free radical at low temp. or anionic (e.g., LiAlR_4)	I (syndiotactic)	190-200	1.19	100-115
Anionic (e.g., $\text{C}_6\text{H}_5\text{MgBr}$)	II (isotactic)	160 160	1.22	25-35
Anionic (e.g., CaZnEt_4)	III (iso-syndio-block)	170	1.20-1.22	40-80
Free radical	atactic	—	1.188	95-100

We examined the methacrylate polymerization using various types of ate complex as shown in Table 9. It seems difficult to draw some conclusions on relation between catalyst type and crystallinity of the polymer formed. However, if our discussion is confined to lithium aluminum complexes, LiAlR_mH_n , the most suitable catalyst for the isotactic polymerization is LiAlH_4 , *i.e.*, $m=0$ and $n=4$, whereas LiAlR_4 ($m=4$; $n=0$) gives most readily the syndiotactic polymer. Complexes of

Table 9. Methyl methacrylate polymerization by ate complexes.

Catalyst system	Polymerization temp. ($^{\circ}\text{C}$.)	Solvent	Crystallinity type
BuLi-organometallics			
BuLi- AlEt_3	-70°	Ether or toluene	I
BuLi- ZnEt_2	-70°	Ether	II-III
BuLi- CdEt_2	-70° -r.t.	Ether or toluene	III
BuLi- BBu_3	No catalytic activity		
EtMgBr-AlEt_3	-70° -r.t.	Hexane or toluene	III

* Experimented by Yukio Nakayama.

Metal-organometallics			
Li-ZnEt ₂	-70°	Ether or toluene	II-III
Na-ZnEt ₂	-70°	Toluene	II-III
Li-CdEt ₂	-70°-r.t.	Ether or toluene	III
Na-CdEt ₂	-70°--10°	Toluene	III
Li-AlEt ₃	-70°	Ether or toluene	I
Na-AlEt ₃	r.t.	Ether or toluene	Amorphous
Ba-ZnEt ₂	-70°-r.t.	Toluene	II
Sr-ZnEt ₂	-70°-r.t.	Ether or toluene	II
Na-BBu ₃	No catalytic activity		—
Metal hydride-organometallics			
LiH-ZnEt ₂	r.t.	Toluene	III
NaH-ZnEt ₂	-70°	Ether or toluene	III
NaH-CdEt ₂	r.t.	Toluene	III
LiH-AlEt ₃	r.t.	Toluene	III
Metal hydride-metal hydride			
LiAlH ₄	-70°-r.t.	Ether or toluene	II
LiBH ₄	r.t.	Ether	II
LiAlH ₄ -ZnEt ₂ , -CdEt ₂ , -AlEt ₃ , -BBu ₃ , -HgBu ₂ }	-70°-r.t.	Ether or toluene	II

Table 10. Anionic polymerization of *sec*-butyl methacrylate^{a)}

Catalyst	Mole %	Conversion, %
BPO ^{b)}	0.4	93.8
<i>n</i> -BuLi	4	trace
SrZnEt ₄	4	100
C ₆ H ₅ MgBr	4	93.4

^{a)} Monomer, 4 cc.; reaction temperature, -78°C.; reaction time, 95 hrs. 80°C.; 2 hrs^{b)} 80°C.; 2 hrs.

type LiAlR₃H have intermediate stereoregulative activity as seen in Table 9.

2.2. Other alkyl methacrylates*. Only a few methacrylates other than methyl methacrylate were examined. *n*-Butyl and *sec*-butyl methacrylates were polymerized by some anionic catalysts. For example, Table 10 shows a part of the results obtained. Strontium zinc tetraethyl or phenylmagnesium bromide exhibits an excellent reactivity in the polymerization in contrast to *n*-butyllithium, but the polymers formed were much the same in their crystallinity as the conventional radical polymer as shown in Fig. 5.

The difficulty of crystallization of poly-*sec*-butyl methacrylate forms a sharp contrast to the prominent crystallizability of poly-*sec*-butyl acrylate. As the matter of fact, there have not yet been known any crystalline polymethacrylic esters

* Experimented by Kunio Chikanishi.

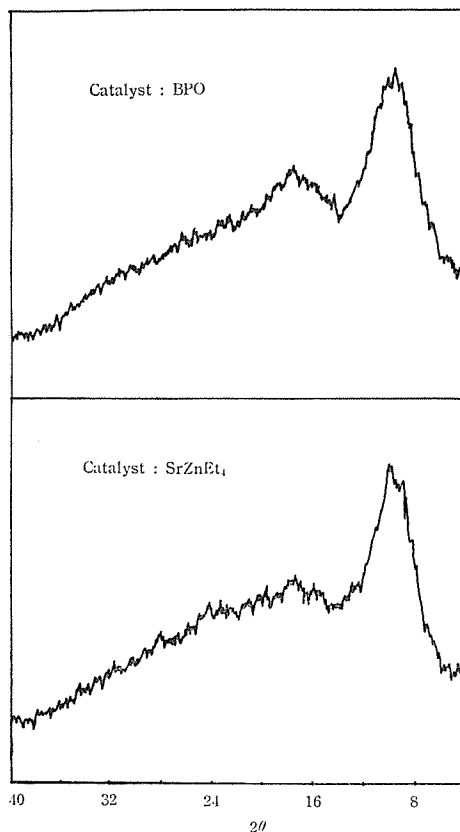


Fig. 5. X-ray spectra of poly-*sec*-butyl methacrylate.

except for methyl ester.

I-3. Tacticity and Crystallizability of Some Acrylic and Methacrylic Esters*

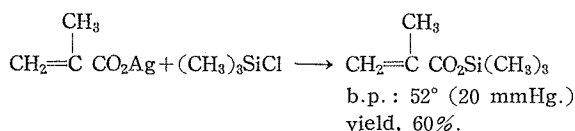
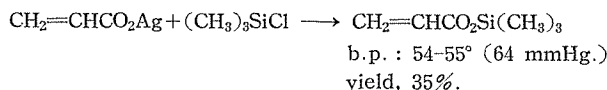
Experimental results stated in the foregoing chapter suggest that acrylic ester can give crystalline polymers more easily than the corresponding methacrylic ester through anionic polymerizations, only one exception being the case of methyl ester. The poorer crystallizability of the methacrylic ester, however, does not necessarily mean the poorer tacticity of the polymer chain, because there may be present unknown steric factors acting unfavorably to the crystallization of the polymer despite of its regular structure.

As we described above, amorphous *n*-butyl acrylate prepared by some anionic catalysts has a stereoregular polymer chain which was confirmed by the crystalline X-ray pattern of the hydrolyzed polymers.

Since polymethacrylic ester, contrary to polyacrylic ester, is generally known to have much greater resistivity to the hydrolysis of ester group, we adopted two kinds of polymethacrylic esters having special alcoholic residues, *e.g.*, polytrimethylsilyl and polybenzyl methacrylates. In comparison, the corresponding acrylic esters were also examined.

* Experimented by Takuma Jinda.

Trimethylsilyl esters of acrylate and methacrylate were prepared as follows :



These silyl esters as well as their polymers were found to be readily hydrolyzed, even by moisture in the air, to give rise to the corresponding free acid. In this sense, the silyl methacrylate is regarded as one of the most appropriate monomers for solving the above problem of stereoregularity. Polymerizations of these acrylate and methacrylate were conducted with use of some anionic catalysts as shown in Tables 11 and 12.

Table 11. Polymerization of trimethylsilyl acrylate^{a)}.

Catalyst	Mole %	Polymer yield, %
<i>n</i> -BuLi	3	9.7
C ₆ H ₅ MgBr	3	—
SrZnEt ₄ (sol.)	—	30.6
SrZnEt ₄ (insol.)	5	41.7
CaZnEt ₄ (sol.)	2	7.4
CaZnEt ₄ (insol.)	5	12.5

^{a)} Monomer, 3.22 ml.; toluene, 3.22 ml.; reaction temp., –78––70°;
reaction time, 72 hrs.

Table 12. Polymerization of trimethylsilyl methacrylate^{a)}.

Catalyst	Mole %	Polymer yield, %
<i>n</i> -BuLi	3	—
C ₆ H ₅ MgBr	3	42.6
SrZnEt ₄ (sol.)	3	7.0
SrZnEt ₄ (insol.)	5	35.4
CaZnEt ₄ (sol.)	3	55.9
CaZnEt ₄ (insol.)	5	21.8

^{a)} Monomer, 3.51 ml.; toluene, 3.51 ml.; reaction temp., –78––70°;
reaction time, 72 hrs.

Polymer formed was precipitated by adding the polymerization mixture into large excess of petroleum ether. The separated polymer was completely hydrolyzed with diluted sodium hydroxide solution. After treating the polymer solution with cation exchange resin, the polymer was precipitated again with concentrated hydrochloric acid. Infrared spectrum of polyacrylic acid derived from polytrimethylsilyl acrylate prepared by SrZnEt₄ catalyst shows distinctly different absorp-

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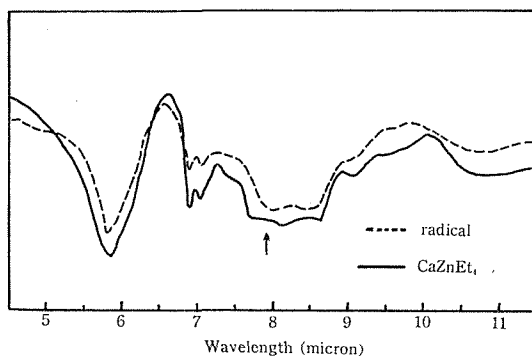


Fig. 6. Infrared spectra of polyacrylic acid derived from polytrimethylsilyl acrylate.

tions from the conventional radical polymer as seen in Fig. 6. The polyacrylic acid exhibited discrete crystalline rings in its X-ray diffraction photograph. On the contrary, polymethacrylic acid derived from the polymethacrylic ester obtained by the strontium catalyst was found to show only amorphous diffused rings. However, the infrared spectrum of the polymer was found to have some different absorptions from that of the conventional radical polymer in the vicinity of 6.5-7 μ and 10.5 μ . Furthermore, we tried to examine the same problem with respect to benzyl esters of acrylic and methacrylic acids. Results of the polymerizations are shown in Tables 13 and 14.

Table 13. Polymerization of benzyl acrylate^{a)}.

Catalyst	Mole %	Polymer yield, %
AIBN ^{b)}	0.5	73.7
<i>n</i> -BuLi	2.0	7.0
C ₆ H ₅ MgBr	2.0	4.1
SrZnEt ₄ (insol.)	3.0	69.8
CaZnEt ₄ (sol.)	2.0	12.4
CaZnEt ₄ (insol.)	3.0	62.5

^{a)} Monomer, 3.83 ml.; toluene, 3.83 ml.; reaction temp., -78°; reaction time, 72 hrs.

^{b)} Reaction temp., 60°; reaction time, 6 hrs.

Table 14. Polymerization of benzyl methacrylate^{a)}.

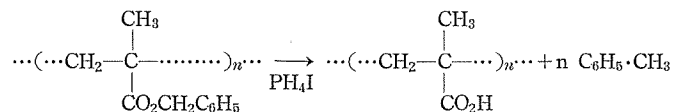
Catalyst	Mole %	Polymer yield, %
AIBN ^{b)}	0.5	100
SrZnEt ₄ (insol.)	3	97.5
CaZnEt ₄ (sol.)	2	8.0
CaZnEt ₄ (insol.)	3	58.2

^{a)} Monomer, 4.20 ml.; toluene, 4.20 ml.; reaction temp., -78°; reaction time, 48 hrs.

^{b)} Reaction temp., 60°; reaction time, 6 hrs.

Polybenzyl acrylate as well as polybenzyl methacrylate gave only amorphous X-ray diffraction photographs, but polyacrylic acid obtained by the hydrolysis of polybenzyl acrylate prepared by the strontium catalyst was confirmed to be crystalline from its infrared and X-ray diagrams.

Polymethacrylic acid was prepared by hydrogenolytic debenzylation of polybenzyl methacrylate with phosphonium iodide:



Polymethacrylic acid derived from polybenzyl methacrylate prepared using strontium zinc tetraethyl complex was found again to give the identical X-ray diagram to the conventional radical polymethacrylic acid.

We prepared the authentic isotactic polymethyl methacrylate using phenylmagnesium bromide as catalyst. The isotactic polymethacrylic ester was then hydrolyzed with concentrated sulfuric acid under drastic conditions. Polymethacrylic acid obtained was dissolved into dimethylformamide and precipitated again by adding hydrochloric acid to the solution. The dried specimen of isotactic polymethacrylic acid exhibited again only diffused ring in its X-ray diffraction diagram. But the different IR absorptions in the vicinity of $6.5\text{--}7.0\mu$ and 10.5μ mentioned above were amplified in the isotactic polymethacrylic acid.

On the other hand, Greber⁹⁾ reported that a syndiotactic polymethacrylic acid could not give crystalline X-ray pattern but had a significantly different IR spectrum compared with the conventional radical polymer.

If we compare the characteristic absorptions of the two doublets at $6.5\text{--}7.0\mu$ and 10.5μ with one another, gradual variation in the relative intensity of two absorptions in every doublet will be noticeable going from syndiotactic polymethacrylic acid to isotactic polymethacrylic acid. These results showed that the polymethacrylic acids derived from the poly-trimethylsilyl and -benzyl methacrylates prepared by the strontium or calcium ate complex catalyst had such a steric structure as to be considerably nearer to isotactic polymer, though these polymethacrylic acid could not form a crystalline structure detectable by the X-ray analysis.

Thus, we obtained the conclusions that, even in the anionic polymerizations of methacrylic ester other than the methyl ester, stereoregulation could occur in some extent.

II. ALKYL THIOLACRYLATE AND ALKYL THIOLMETHACRYLATE

II-1. Alkyl Thiolacrylate^{*10)}

We examined the anionic polymerization of alkyl thiolacrylate, especially in comparison with the acrylate polymers. Monomers chosen were ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*- and *tert*-butyl thiolacrylates. The results of the polymerization are described in Tables 15 and 16. These polyalkyl thiolacrylates

* Experimented by Yukio Nakayama and Akihiro Kawasaki.

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are normally fractionated by acetone into two parts. The less soluble fractions were confirmed to be crystalline or crystallizable. Generally speaking, crystallizability of these polyalkyl thiolacrylates are much larger than that of the corresponding polyalkyl acrylates. For instance, poly-*n*-propyl thiolacrylate prepared by PhMgBr, CaZnEt₄ or SrZnEt₄ were found to be readily crystallizable; and even *n*-butyl thiolacrylate gave rise to a crystallizable polymer when it was polymerized with PhMgBr as catalyst. *n*-Butyllithium as well as LiAlEt₃Bu was revealed again as an inferior catalyst for the stereoregular polymerization of the thiolacrylates.

Table 15 Polymerization of alkyl thiolacrylate (I).

Catalyst	R in alkyl thiolacrylate	Crude yield %	Polymer Fractions (extracted with boiling solvents)		
			Acetone % Nat. ^{e)}	Chloroform % Nat. ^{e)}	Extract. residue % Nat. ^{e)}
BPO ^{a)}	C ₂ H ₅	65.5	100 A	—	—
	<i>n</i> -C ₃ H ₇	63.5	100 A	—	—
	<i>i</i> -C ₃ H ₇	61.0	100 A	—	—
	<i>n</i> -C ₄ H ₉	63.0	100 A	—	—
	<i>i</i> -C ₄ H ₉	41.5	100 A	—	—
	<i>s</i> -C ₄ H ₉	70.0	100 A	—	—
	<i>t</i> -C ₄ H ₉	60.0	100 A	—	—
<i>n</i> -BuLi ^{b)}	C ₂ H ₅	16.7	100 A	—	—
	<i>n</i> -C ₃ H ₇	26.0	100 —	—	—
	<i>i</i> -C ₃ H ₇	15.6	100 A	—	—
	<i>n</i> -C ₄ H ₉	36.0	100 A	—	—
	<i>i</i> -C ₄ H ₉	70.0	100 A	—	—
	<i>s</i> -C ₄ H ₉	83.0	60 A	40 C	—
	<i>t</i> -C ₄ H ₉	44.5	7.5 A	34.5 C	58 C
PhMgBr ^{b)}	C ₂ H ₅	93.5	100 A	—	—
	<i>n</i> -C ₃ H ₇	53.5	30(c) ^{e)} C	—	—
			70(h) C	—	—
	<i>i</i> -C ₃ H ₇	5.8	100 C	—	—
	<i>n</i> -C ₄ H ₉	86.0	100 C	—	—
	<i>i</i> -C ₄ H ₉	84.0	80(c) ^{e)} A	—	—
			20(h) C	—	—
	<i>s</i> -C ₄ H ₉	86.0	33 A	67 C	—
	<i>t</i> -C ₄ H ₉	12.5	35 A	9 C	56 C

^{a)} Experimental conditions: Monomer, 0.025 mole; benzoyl peroxide, 0.015 g.; bulk polymerization at 70°C. in a sealed tube under nitrogen; reaction time, C₂H₅ 4 min., *n*-C₃H₇ 30 min., *i*-C₃H₇ 30 min., *n*-C₄H₉ 10 min., *i*-C₄H₉ 60 min., *s*-C₄H₉ 30 min., *t*-C₄H₉ 20 min.

^{b)} Experimental condition: Monomer, 0.025 mole; catalyst, 0.0005 mole; solvent, toluene 5 ml.; in a sealed tube under nitrogen at -78°C. for 18-24 hrs.

^{c)} Nat., nature; A, amorphous; C, crystalline.

^{d)} Measured in chloroform at 20°C.

^{e)} (c), Soluble in cold acetone, (h), soluble in hot acetone and insoluble in cold acetone.

Table 16. Polymerization of alkyl thiolacrylate (II).

Catalyst	R in alkyl thiolacrylate	Crude yield %	Polymer Fractions (extracted with boiling solvents)			
			Acetone % Nat. ^{a)}	Chloroform % Nat. ^{a)}	Extract. residue % Nat. ^{a)}	
LiAlEt ₃ Bu ^{b)}	C ₂ H ₅	81.0	100 A	—	—	
	<i>i</i> -C ₃ H ₇	86.0	100 A	—	—	
	<i>n</i> -C ₄ H ₉	*	100 —	—	—	
	<i>i</i> -C ₄ H ₉	**	100 —	—	—	
	<i>t</i> -C ₄ H ₉	92.0	52 A	48 C	—	
CaZnEt ₄ ^{c)}	C ₂ H ₅	87.0	100 A	—	—	
	<i>n</i> -C ₃ H ₇	79.0	50(c) ^{f)} —	—	—	
			50(h) C	—	—	
	<i>i</i> -C ₃ H ₇	14.2	70 A	30 C	—	
	<i>n</i> -C ₄ H ₉	83.0	100 A	—	—	
	<i>i</i> -C ₄ H ₉	68.0	78 A	22 C	—	
	<i>s</i> -C ₄ H ₉	81.5	51 A	49 C	—	
SrZnEt ₄ ^{c)}	<i>t</i> -C ₄ H ₉	35.0	27 A	35.5 C	37.5 C	
	C ₂ H ₅	80.0	100 A	—	—	
	<i>n</i> -C ₃ H ₇	86.0	40(c) ^{f)} C	—	—	
			69(h) C	—	—	
	<i>i</i> -C ₄ H ₉	21.5	100 C	—	—	
	<i>n</i> -C ₄ H ₉	73.5	100 A	—	—	
	<i>i</i> -C ₄ H ₉	70.0	81.5 A	18.5 C	—	
	<i>s</i> -C ₄ H	90.0	47 A	53 C	—	
	<i>t</i> -C ₄ H ₉	30.9	34 A	22 C	44 C	

^{a)} Experimental condition: Monomer, 0.025 mole; solvent, toluene 5 ml.; in a sealed tube under nitrogen at -78°C. for 18-24 hrs.

^{b)} LiAlEt₃Bu, 0.0008 mole (*n*-BuLi: AlEt₃, 1:1 (mole ratio)).

^{c)} CaZnEt₄; about 0.0007 mole (based on the weight of calcium or strontium metal added in the syntheses of catalysts).

^{d)} Nat., nature; A, amorphous; C, crystalline.

^{e)} Measured in chloroform at 20°C.

^{f)} (c), soluble in cold acetone; (h), soluble in hot acetone and insoluble in cold acetone.

* Large.

** Mediate.

II-2. Alkyl Thioldmethacrylate*¹¹⁾

Monomers examined were methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, and *sec*-butyl thioldmethacrylates. Among the alkyl esters, only methyl ester was found to produce the crystallizable polymer, contrary to the case of the alkyl thiolacrylates series where *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl and *tert*-butyl thiolacrylates gave crystalline polymers through anionic polymerization. As seen in Table 17, methyl thioldmethacrylate was easily polymerized by some anionic catalysts to give chloroform-soluble polymers in high yields. An insoluble fraction in 3-heptanone was confirmed to be crystalline by X-ray analysis.

* Experimented by Yukio Nakayama.

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Table 17. Polymerization of methyl thiolmethacrylate by some anionic catalysts.

Monomer (mmole)	Catalyst (name)	(mmole)	Toluene (ml.)	Temp. (°C.)	Time (hrs.)	Conversion (%)	η_{sp}/C^a
25	None		0	70	12	8	1.46
50	C ₆ H ₅ MgBr	1.0	50	0-3	2	86	0.025
25	C ₆ H ₅ MgBr	0.6	5	-78	14	100	0.24
25	<i>n</i> -BuLi	0.6	5	-78	14	100	0.50
25	LiAlEt ₃ Bu	0.5	5	-78	14	100	0.38
25	CaZnEt ₄	1.0	5	-78	12	85	1.18
25	SrZnEt ₄	1.0	5	-78	3	88	0.88

^a) Measured in chloroform at 20°C.; C, 0.35-0.37 g./dl.

The infrared spectrum of the crystalline polymer had distinct crystalline bands and was markedly different from those of the amorphous part soluble in 3-heptanone and of the conventional amorphous polymer.

Ethyl, *n*-propyl, *n*-butyl isobutyl, *sec*- and *tert*-butyl thiolmethacrylates are also easily polymerized by various anionic catalysts to give chloroform-soluble polymers in high yields. These polymers are easily soluble in 3-heptanone and could not be crystallized by hot stretching, but had slightly different infrared spectra from those of the conventional amorphous polymers prepared by thermal polymerization.

The lack of crystallizability of these polyalkyl thiolmethacrylates is quite similar to the case of polyalkyl methacrylates stated above.

 III. ALKYL α -CHLOROACRYLATE AND ALKYL α -CHLOROTHIOLACRYLATE*

Polymerizations of methyl and *sec*-butyl α -chloroacrylates were conducted using

 Table 18. Polymerization of methyl α -chloroacrylate^a).

Catalyst	Solvent	Temp. (°C.)	Conversion (%)	η_{sp}/C
BPO ^b)	Dioxane	20	29.6	3.73
<i>n</i> -BuLi ^c)	Dioxane	20	13.1	5.41
<i>n</i> -BuLi	Toluene	-78	3.6	0.239
LiAlEt ₃ Bu	Toluene	20	49.5	0.065
LiAlEt ₃ Bu	Toluene	-78	32.4	0.103
LiCdEt ₂ Bu	Toluene	-78	17.5	0.075
LiZnEt ₂ Bu	Toluene	-78	21.9	—
CaZnEt ₄	Toluene	-78	5.9	0.178
PhMgBr	Toluene	-78	4.9	0.881
AlEt ₃ -VCl ₄ ^c)	Toluene	20	67.6	3.19

^a) Monomer, 25 mmole; catalyst, 0.5 mmole; solvent, 5 ml.; polymerization time, 24 hrs.

^b) 0.12 mmole.

^c) Polymerization time, 48 hrs.

* Experimented by Kunio Chikanishi.

Table 19. Polymerization of *sec*-butyl α -chloroacrylate^{a)}.

Catalyst	(mmole)	Conversion (%)	η_{sp}/C
BPO ^{b)}	0.1	56.1	1.34
<i>n</i> -BuLi	0.5	2.0	0.362
LiAlEt ₃ Bu	0.5	29.0	0.995
SrZnEt ₄	~0.5	36.8	0.289
PhMgBr	0.5	28.2	0.204
AlEt ₃ -VCl ₄ ^{c)}	0.5	43.6	0.326

^{a)} Monomer, 25 mmole; toluene, 3.5 ml.; polymerized at -78°C . for 24 hrs.^{b)} Bulk polymerization at 80°C . for 6 hrs.^{c)} Polymerized at $0-3^{\circ}\text{C}$.

some anionic catalysts. Results obtained are listed in Tables 18 and 19. There were obtained no crystallizable polymers in this series.

We also examined polymerizations of some α -chlorothiolacrylic ester. Results are shown in Tables 20, 21 and 22. The poly-methyl and -ethyl esters exhibited considerably different infrared absorptions from those of the conventional polymers, but had only diffused rings in their X-ray diffraction photographs. On the

Table 20. Polymerization of methyl α -chlorothiolacrylate^{a)}.

Catalyst	(mmole)	Conversion (%)	Boiling chloroform insol. part (%)
BPO ^{b)}	0.1	53.9	0
<i>n</i> -BuLi	0.5	35.0	trace
LiAlEt ₃ Bu	0.5	80.9	trace
SrZnEt ₄	~0.5	93.2	25
CaZnEt ₄ ^{c)}	~0.25	74.5	trace
PhMgBr	0.5	55.5	44

^{a)} Monomer, 25 mmole (2.8 ml.); toluene, 2.8 ml.; polymerized at -78°C . for 24 hrs.^{b)} Bulk polymerization at 80°C . for 10 hrs.^{c)} Polymerized for 96 hrs.Table 21. Polymerization of ethyl α -chlorothiolacrylate^{a)}.

Catalyst	(mmole)	Conversion (%)	Boiling MEK insol. part (%)	Boiling chloroform insol. part (%)
None ^{b)}	—	—	0	0
<i>n</i> -BuLi	0.5	89.5	30	5
LiAlEt ₃ Bu	0.5	81.5	10	0
SrZnEt ₄	~0.5	92.3	7	trace
PhMgBr	0.5	95.0	21	41
AlEt ₃ -VCl ₄ ^{c)}	0.5	73.5	trace	0

^{a)} Monomer, 25 mmole (3.5 ml.); toluene, 3.5 ml.; polymerized at -78°C . for 24 hrs.^{b)} Bulk polymerization at 60°C .^{c)} Polymerized at $0-3^{\circ}\text{C}$.

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Table 22. Polymerization of *sec*-butyl α -chlorothiolacrylate^{a)}.

Catalyst	(mmole)	Conversion (%)	Boiling MEK insol. part (%)
BPO ^{b)}	0.1	69.3	0
<i>n</i> -BuLi ^{c)}	0.5	63.8	46
LiAlEt ₃ Bu	0.5	89.5	0
SrZnEt ₄	0.5	65.5	5
CaZnEt ₄ ^{d)}	0.3	87.5	trace
PhMgBr ^{e)}	0.5	61.2	26
PhMgBr	0.5	63.1	27
EtMgBr	0.5	40.2	trace
Na-naphthalene	0.5	35.6	0
AlEt ₃ -VCl ₄ ^{e)}	0.5	52.5	0

^{a)} Monomer, 25 mmole (3.7 ml.); toluene, 3.7 ml.; polymerized at -78°C . for 24 hrs.

^{b)} Bulk polymerization at 80°C . for 2 hrs.

^{c)} Toluene, 7.5 ml.

^{d)} Polymerized for 96 hrs.

^{e)} Polymerized at $0-3^{\circ}\text{C}$.

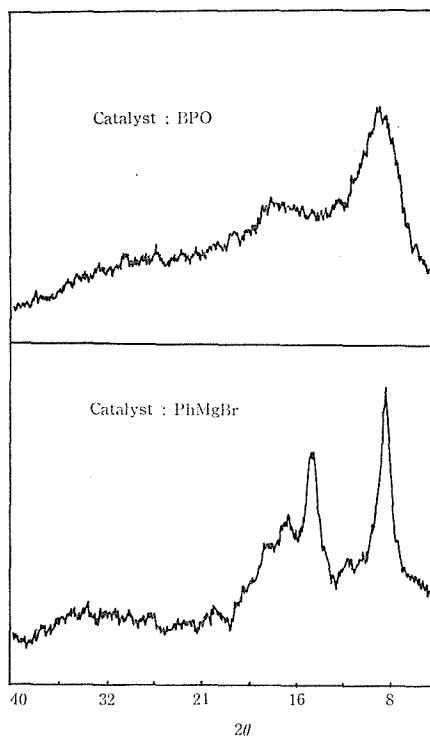


Fig. 7. X-ray diagrams of crystalline and amorphous poly-*sec*-butyl α -chlorothiolacrylates.

other hand, *sec*-butyl α -chlorothiolacrylate was found to give a highly crystalline polymer through anionic polymerization induced by phenylmagnesium bromide. Figure 7 illustrates the X-ray diagram of the crystalline poly(*sec*-butyl- α -chloro-

thiolacrylate) together with that of the corresponding amorphous polymer prepared by benzoyl peroxide as catalyst.

IV. VINYL KETONE^{*12)}

Methyl vinyl ketone has long been known as a monomer which is readily

Table 23. Polymerization of methyl vinyl ketone^{a)}.

Catalyst	(mmole)	Boiling acetone soluble fraction			Boiling acetone insoluble fraction		
		(%)	M.p. (°C.)	X-ray ^{b)} spectrum	(%)	M.p. (°C.)	X-ray ^{b)} spectrum
C ₁₀ H ₈ Na	1	80	140	A	0	—	—
<i>n</i> -BuLi	2	72	130-146	A	0	—	—
LiAlEt ₃ Bu	1	45	70- 80	A	10	160-190	C
PhMgBr	1	61	35- 40	A	4	155-170	C
CaZnEt ₄	1	65	145-160	C	8	162-164	C
AlEt ₃	2	50	65- 70	—	10	145-160	C

^{a)} Monomer, 36 mmole; solvent, toluene 3 cc.; reaction temp., 0°C; time, 3 days.

^{b)} A, amorphous; C, crystalline.

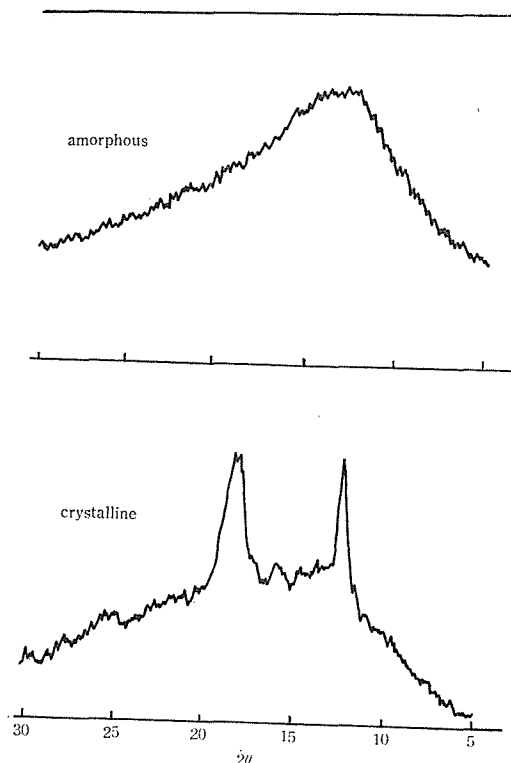


Fig. 8. X-ray diffraction diagram of amorphous and crystalline poly(methyl vinyl ketone).

*) Experimented by Ryota Fujio.

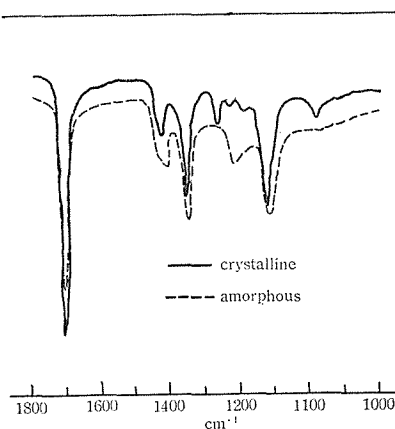


Fig. 9. The infrared absorption spectra of poly (methyl vinyl ketone)

polymerized not only by radical initiator but also by anionic or cationic catalyst. However, stereoregular polymer of methyl vinyl ketone has not yet been known. We examined anionic polymerizations of methyl vinyl ketone and found this unsaturated ketone to be able to give a highly crystalline polymer when appropriate anionic complexes were used as catalyst. Results obtained are shown in Table 23. It is rather surprising that the vinyl ketone can form a crystalline polymer by the single use of triethylaluminum which has so far known to exhibit no catalytic activity in the absence of appropriate co-catalyst.

There have been found beautiful spherulites in a film of the crystalline polymer which was prepared from its formic acid solution. Figures 8 and 9 show X-ray diffraction diagrams and infrared spectra of crystalline and amorphous polymers of methyl vinyl ketone.

CONCLUSION

As seen in the foregoing chapters, the experimental results are so complicated that any conclusions seem to hardly be drawn concerning the stereoregulation in the acrylate polymerizations. However, we would like to try to find some principle from our results.

In a series of alkyl acrylate, ester of the more sterically hindered alcohol gives rise to a polymer of the better crystallizability. In this sense, α -trisubstituted alcohol is the most favorable for formation of the crystalline polymer, β -substituent seemingly having a minor effect in the polymer crystallization. If we assume the crystallizability of polyalkyl acrylates to run parallel with their stereoregularity, β -substituent may also play an only minor role in the steric course of the polymerization. β -Substituted monomers as well as growing polymer ends resulting from the β -substituted monomers have too high degree of freedom in the transition state to effectuate a stereoregular polymerization unless the freedom of the reaction sites was considerably frozen by steric hindrance arising from coordination toward an appropriate complex catalyst such as strontium zinc tetraethyl. Thus, isobutyl acrylate could not produce a crystalline polymer

until the complex catalysts were used as catalyst. Benzyl acrylate gave only an amorphous polymer with the same strontium catalyst, though the polymer was confirmed to be hydrolyzed to a polyacrylic acid which showed some crystallinity.

On the other hand, acrylic ester of α -substituted alcohol produces stereoregular polymer irrespective of the nature of anionic catalyst as stated in Table 7. In this case, the freedom of the reaction sites may be low enough to accomplish the regular propagation on account of the bulkiness of the alcoholic residues, the aid of strong coordination to the complex catalyst being not always required here.

Similar discussions are true of the case of acrylic ester of alkyl thiol. There seems to exist an optimum point in the steric hindrance in monomer as well as growing polymer end.

In polymerizations of alkyl methacrylates other than methyl methacrylate, no crystalline polymers have not yet been obtained, though we have had an evidence for the possibility of stereoregulation in some special methacrylic ester such as trimethylsilyl or benzyl ester. *sec*-Butyl methacrylate failed to form a polymer having improved crystallinity even with the use of the anionic complex catalyst as seen in Fig. 5. Steric hindrance in this monomer may be so large that it will probably oppose to the most favorable isotactic orientation in the transition state.

We cannot account for the lack of crystallizability in poly- α -chloroacrylic ester, but we consider the polar nature of chlorine atom should be taken into consideration to interpret the situation.

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