

Preparation and Properties of Polymers of Secondary Alkyl Crotonates and Related Monomers*

ROGER K. GRAHAM, JAMES E. MOORE,
and JOHN A. POWELL, *Research Division,*
Rohm and Haas Company, Bristol, Pennsylvania 19007

Synopsis

The anionic polymerization of a variety of secondary alkyl crotonates and related monomers initiated by fluorenyllithium (complexed with tetrahydrofuran) in toluene at -78°C . is reported. No crystallinity could be developed in any of the samples, and nuclear magnetic resonance was uninformative about possible tacticity. The polymerization techniques were ineffective when applied to *n*-alkyl esters. Polymer was obtained from isopropyl cinnamate and *N,N*-dimethyl crotonamide, but not from isopropyl thiocrotonate or isopropyl 2-pentenoate. The physical properties of injection-molded specimens of polymers of isopropyl, *s*-butyl and cyclohexyl crotonate were examined in some detail; the polymers exhibited a desirable combination of high service temperatures and good impact resistance for a vinyl homopolymer but were extremely difficult to mold. Poly(isopropyl crotonate) had a heat distortion temperature of 125°C . at 85 psi, a notched Izod impact of 2.4 ft.-lb./in. of notch, and a flexural modulus of 274,000 psi.

Intense interest in the stereoregular anionic polymerization of acrylic and methacrylic esters during the past ten years has led several investigators to examine the polymerization of related α,β -unsaturated esters with substituents other than hydrogen on the β carbon atom of the double bond, the simplest of these systems being esters of crotonic acid. Miller and Skogman¹ have reported studies of the polymerization of *t*-butyl crotonate; they showed that there were limitations on the nature of the anionic initiator that could be employed, both in the ability to initiate polymerization and in the degree of crystallinity of the polymer formed. No physical properties of the polymer were reported other than a glass transition temperature of 86°C . Natta et al.² have disclosed the preparation of crystalline poly(*t*-butyl crotonate) and poly(isopropyl crotonate), the latter softening at 270 – 290°C ., by polymerization in toluene at -78°C . with ether-free phenylmagnesium bromide as initiator.

Since the completion of our experimental program Makimoto, Tanabe, and Tsuruta have reported the polymerization of methyl crotonate with calcium zinc tetraethyl complex in toluene and have stated that this

* Presented before the Polymer Division of the American Chemical Society, Miami Beach, Florida, April, 1967.

initiator is also more effective in polymerizing branched alkyl crotonates than alkyllithium compounds. Their communication also reports a paper in press^{3b} on the polymerization of isopropyl and *sec*-butyl crotonates with LiAlH_4 in diethyl ether. It now appears that calcium zinctetraethyl may be a more general initiator for α,β -disubstituted unsaturated esters than the initiators with which we have worked; this paper will briefly summarize our polymerization results and report on the physical properties of several of the more interesting polymers studied.

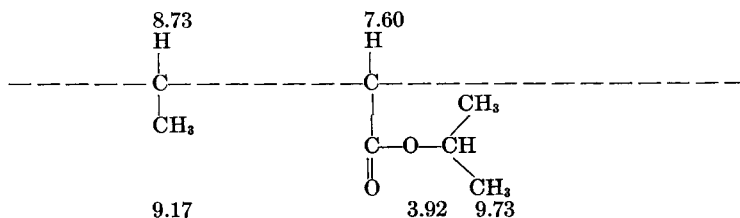
POLYMERIZATION BEHAVIOR

Although we were able to confirm the preparation² of crystalline poly(*t*-butyl crotonate), we were unable to obtain any polymer from isopropyl crotonate. Amorphous polymer from isopropyl crotonate was formed with dibutylmagnesium as initiator in toluene, but the initiator was prepared in, and contained, diethyl ether. Investigation of organolithium compounds showed 9-fluorenyllithium to be the most effective with isopropyl crotonate, and it was the initiator of choice for most of this work. Triphenylsilyllithium was also effective, while lower yields were obtained with triphenylmethylithium and no polymer with *n*-butyllithium or *t*-butyllithium. Neither alkali metal amides in liquid ammonia nor triethylaluminum-titanium tetrachloride would produce polymer.

Polymerizations with fluorenyllithium were successfully carried out in toluene, tetrahydrofuran, and methylene chloride as solvents. Generally, 2-5 mole-% of initiator (based on monomer) was employed; no attempt was made to determine the efficiency of initiation or to determine whether there was one fluorene endgroup per polymer chain, as had been shown previously for methyl methacrylate polymerizations.⁴ In toluene a stiff gel was formed at the end of the polymerization, even at 10% polymer solids. Polymer was isolated by addition of toluene containing a small amount of methanol, followed by precipitation into a large excess of methanol, thorough washing with methanol, and vacuum drying. When polymerizations were carried out in a medium that was a solvent for the monomer but a nonsolvent for the polymer, such as petroleum ether-toluene mixtures, the resulting polymer could not be redissolved. However, these samples were similar to the soluble polymer in that no crystallinity could be developed in any samples. (The initial communication by Makimoto et al.³ does not indicate whether they obtained crystalline or stereoregular polymers with these monomers.)

Intrinsic viscosities were measured in benzene at 30°C. and number-average molecular weights in toluene (Mecrolab Osmometer), but severe experimental difficulties were encountered in the determination of weight-average molecular weights by light scattering, so that no knowledge of the distribution of molecular weights could be obtained. The number-average molecular weights were as high as 675,000 (for an intrinsic viscosity of 2.41 dl./g.).

Nuclear magnetic resonance studies confirmed the polymer structure but gave little information concerning stereoregularity of the polymer, perhaps because of the limited solubility in chloroform or deuteriochloroform and the high viscosities of the soluble samples. Broad peaks with poor resolution were observed as shown (values are in τ relative to tetramethylsilane at 10.0 τ , and were measured on a Varian HR-60);



Only one broad band was found representing the backbone β -methyl group, while a sample of poly(*t*-butyl crotonate) prepared similarly showed two peaks at 9.17 and 9.35; the latter sample, however, was amorphous as prepared.

Our work with crotonate esters is summarized in Table I. Secondary butyl crotonate exhibited polymerization behavior very similar to that of isopropyl crotonate. Cyclohexyl crotonate was polymerized only with fluorenyllithium. Maximum yields of polymer were 90% and 87%, respectively. Amorphous polymer was obtained from all secondary and tertiary esters studied. Under a wide variety of experimental conditions we obtained only oligomers from methyl or ethyl crotonate, confirming the observations of Schuerch and Bockman.⁵ A low yield (4%) of amor-

TABLE I
Anionic Polymerization of Crotonic Esters in Toluene

Ester	Initiator ^a			Crystallinity
	FILi	Li-Nap	Bu ₂ Mg	
Methyl	—	—	—	
Ethyl	—	—	—	
Isopropyl	+	+	+	—
<i>s</i> -Butyl	+	+	+	—
<i>t</i> -Butyl ^b	+	+	+	+ (Mg), — (Li)
Isobutyl	—	—	—	
<i>s</i> -Hexyl	+	+	+	
<i>s</i> -Octyl	+	+	+	
Isobornyl	+			
<i>s</i> -Phenethyl	+			
Phenyl	+			
Neopentyl	+			—
Cyclohexyl	+			—

^a FILi, 9-fluorenyllithium prepared in tetrahydrofuran; Li-Nap, lithium-naphthalene adduct prepared in tetrahydrofuran; Bu₂Mg, dibutylmagnesium prepared in diethyl ether.

^b Data from Miller and Skogman.¹

phous polymer was obtained from the hindered primary ester, neopentyl crotonate.

Thioesters and amides of crotonic acid were also investigated with fluorenyllithium. Here we obtained polymer only with the *t*-butyl thioester, not the isopropyl. The results from the amides were inconsistent; polymer was obtained from dimethyl- and diethylcrotonamides but not dibutyl. Natta et al.² reported low conversions (ca. 1%) of isopropyl cinnamate to crystalline polymer, softening above 290°C. Our best yields of polymer from isopropyl and *t*-butyl cinnamates were 18 and 32%, respectively. Neither polymer was crystalline. Attempts to polymerize isopropyl 2-pentenoate were unsuccessful.

TABLE II
Anionic Polymerization of α,β -Disubstituted Esters, Thioesters, and Amides

R ₁	R ₂	$\begin{array}{c} \text{O} \\ \\ \text{R}_1\text{HC} = \text{CR}_2 - \text{C} - \text{R}_3 \end{array}$	Polymer ^a
CH ₃	H	S—CH(CH ₃) ₂	—
CH ₃	H	S—C(CH ₃) ₃	+
CH ₃	H	N(CH ₃) ₂	+
CH ₃	H	N(C ₂ H ₅) ₂	+
CH ₃	H	N(C ₄ H ₉) ₂	—
CH ₃	H	N(C ₆ H ₅) ₂	—
CH ₃	H	NHC(CH ₃) ₃	—
CH ₃	CH ₃	O—C(CH ₃) ₃	— ^b
C ₂ H ₅	H	O—CH(CH ₃) ₂	—
C ₆ H ₅	H	O—C(CH ₃) ₃	+ ^c
C ₆ H ₅	H	O—CH(CH ₃) ₂	+ ^{c,d,e}

^a Fluorenyllithium initiator.

^b Miller and Skogman.¹

^c Noncrystalline.

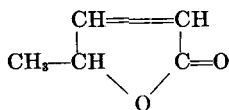
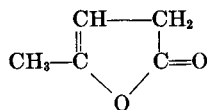
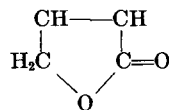
^d Natta et al.² report crystalline polymer in very low yield with ether-free phenylmagnesium bromide.

^e Makimoto et al.³ report polymer from ethyl and *sec*-butyl cinnamates with calcium zinctetraethyl in toluene.

It is of interest to contrast the restrictive effect on polymer formation of substitution at the β position and at the ester function with the earlier work of Chikanishi and Tsuruta,⁶ who showed that methyl α -ethyl, α -*n*-butyl, and α -phenyl acrylates polymerized readily with similar anionic initiators. Indeed, the steric structures required in the ester position will prevent anionic polymerization when present in the α position. The steric structure required for polymerization can be related to the competition that occurs between Michael addition to the double bond and 1,2 addition to the carbonyl group. The latter reaction, which would lead to side products, would include cyclobutane ring formation of the dimers, as described by Schuerch and Bokman,⁴ and initiator addition

to the carbonyl group. An increase in the size of the ester group would increase the steric hindrance at the carbonyl position and favor the Michael reaction, which in turn leads to polymer. Substitution in the β position by groups larger than methyl would have an unfavorable steric effect on the Michael reaction and result in lower yields of polymer. The observation that bulky initiators gave the best results with *sec*-alkyl crotonates and that *t*-butyl crotonate was less selective in initiator requirements is consistent with the steric requirements of the monomer. To date, Makimoto, Tsuruta, and co-workers have offered no explanation other than heterogeneity of the initiator for the pronounced effect of alkaline earth-dialkylzinc reaction products on the polymerization of acrylates,⁷ crotonates,³ and cinnamates.³

In miscellaneous experiments the following were converted to polymer by fluorenyllithium: crotonic anhydride, β -angelicalactone (but not the α isomer), and isopropyl β -nitroacrylate. The apparently anionic polymerization of the lactone of γ -hydroxycrotonic acid with tertiary amines has recently been reported⁸; in all cases it appears that retention of the lactone ring occurred. The polymer from crotonic anhydride was soluble in methanol, suggesting cyclopolymerization.

 β -Angelicalactone α -AngelicalactoneLactone of
 γ -hydroxy
crotonic acid

Physical Properties of Polycrotonates

After drying the polymers were milled at 230°C. for 10 min., chopped, and injection-molded. For all samples with molecular weight high enough to produce good properties the molding was always difficult, with poor flow, dull surfaces, and lamellar structure in broken bars. The curve formed by plotting extrusion pressures at constant load versus temperature for poly(isopropyl crotonate) is much flatter than for engineering plastics such as polycarbonates; this, coupled with thermal degradation at higher temperatures, limited the molding temperature range. Table III shows typical properties of three poly(*s*-alkyl crotonates), which exhibit an interesting combination of high service temperature and toughness not generally encountered in vinyl homopolymers. The polymer of *s*-butyl crotonate was softer and more flexible than poly(isopropyl crotonate), while poly(cyclohexyl crotonate) was the stiffest and hardest of the three. Thermal stability studies (weight loss at 260°C. versus time) indicate the latter is the most thermally stable of the three evaluated in some detail. Examination of poly(isopropyl crotonate) by the thermovolatilimetric technique of Noel⁹ indicates a pyrolysis behavior very similar to that of poly(isopropyl acrylate): i.e., ester decomposition to propylene, water, and poly(crotonic anhydride). The crotonate is more thermally stable

TABLE III
Comparison of Polymer Properties

Polymer	RSV in Benzene ^a	Vicat ^b softening pt., °C.	DTUL, ^c °C. at 85 psi	Rockwell hardness	Flexural values ^d			Izod impact, ^e ft.-lb./in. of notch
					Stress, psi × 10 ⁻³	Deflection, in.	Modulus, psi × 10 ⁻⁴	
Poly(<i>s</i> -butyl crotonate)	1.8	135	106	—	6.5	0.44	2.28	2.5
Poly(isopropyl crotonate)	2.8	169	125	I61	8.7	0.43	2.74	2.4
Poly(cyclohexyl crotonate)	2.6	151	125	—	14.8	0.36	5.08	1.6

^a Reduced specific viscosity (dl./g.); benzene solution, 30°C.

^b ASTM D-1525-58T.

^c ASTM D-648-56; "deflection temperature under load" (term now used by ASTM to replace HDT, "heat distortion temperature").

^d ASTM D-790-49-T.

^e ASTM D-256-56.

than poly(isopropyl methacrylate) because of the concurrent depolymerization, besides side-chain degradation, found with the latter.

EXPERIMENTAL

Monomer Preparations

Most of the materials studied are known compounds, with physical properties comparable to those reported in the literature. Esters of crotonic acid were prepared by direct esterification in most cases. Neopentyl crotonate was prepared from crotonic chloride and neopentanol. Isobornyl, *sec*-hexyl, and *sec*-octyl crotonates were prepared by the addition of the appropriate olefin to crotonic acid with Amberlite XE-230 as catalyst. The cinnamates and thiocrotonates were prepared from the acid chloride and appropriate alcohols or mercaptans with zinc chloride catalyst and triethylamine or dimethylaniline as acid acceptors. Crotonic anhydride was prepared from crotonic acid and acetic anhydride. Isopropyl 2-pentenoate was prepared by direct esterification of the corresponding acid, which in turn was prepared by the condensation of propionaldehyde with malonic acid. Isopropyl β -nitroacrylate was prepared by dehydrochlorination of isopropyl α -chloro- β -nitropropionate with sodium acetate in refluxing ether; the isopropyl α -chloro- β -nitropropionate was formed by the reaction¹⁰ of isopropyl acrylate with nitril chloride. β -Angelicalactone was formed by the isomerization¹¹ of the α isomer with triethylamine in refluxing benzene. The crotonamides were prepared from the corresponding amine (in excess) and crotonyl chloride.

Reagents and Initiators

Toluene was reagent grade and was dried over calcium hydride before use. Tetrahydrofuran was reagent grade, flash-distilled from LiAlH_4 before use. Initiators were prepared by standard techniques or purchased. Fluorenyllithium was prepared by addition at room temperature of fluorene (0.125 mole) in 115 ml. of dry tetrahydrofuran to 0.625 g.-atoms of lithium shot stirred under prepurified nitrogen and wetted with 10 ml. of dry tetrahydrofuran. The mixture was refluxed with stirring for 2-3 hr. after addition was complete. Aliquots were removed with a syringe through a serum cap with nitrogen.

Preparation and Isolation of Polymer

The preparation of poly(cyclohexyl crotonate) is typical of the preparative technique employed. A freshly dried, 3-liter resin kettle was equipped with a stirrer, thermometer, nitrogen inlet and outlet through a mineral-oil bubbler. The apparatus was swept with prepurified nitrogen while 2 liters of CaH_2 -dried toluene and 500 g. (2.975 moles) of cyclohexyl crotonate were added. This solution was cooled to -75°C . and main-

tained for 1 hr. while the solution was degassed with a stream of nitrogen below the liquid surface. Then 95 ml. of a 0.52M solution of 9-fluorenyllithium in tetrahydrofuran (0.05 mole) was added through a serum cap by means of a hypodermic syringe. The temperature rose immediately to -72°C . After 20 min. the solution had become a soft gel, and stirring was stopped. The following day the stiff gel was dissolved in toluene containing a little methanol and precipitated in a Waring Blendor with 10 vol. of methanol. The polymer was washed twice with methanol and dried in a vacuum oven. The conversion was 68.3%, the reduced specific viscosity in benzene was 2.6 dl./g.

We are grateful to many members of the Research Division for preparation of certain monomers and for physical testing. R. L. Kelso and D. L. Ritter performed the milling and molding experiments. The synthesis support of R. L. Rankin and L. W. Cox was most helpful.

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Résumé

On rend compte de la polymérisation anionique de différents crotonates d'alcoyle secondaire et de monomères similaires, par initiation au fluorényllithium (complexé avec le tétrahydrofurane) dans le toluène à -78°C . Aucun échantillon ne présente de cristallinité et la résonance nucléaire magnétique ne donne aucune information en ce qui concerne la tacticité. Les techniques de polymérisation sont inefficaces lorsqu'elles sont appliquées aux esters d'alcoyle-*n*. Un polymère a pu être obtenu au départ de cinnamate d'isopropyle et de *N,N*-diméthyl-crotonamide, mais pas au départ de thiocrotonate d'isopropyle ou de 2-pentoate d'isopropyle. Les propriétés physiques des échantillons, moulés par injection, de polymères de crotonate d'isopropyle, de *s*-butyle ou de cyclohexyle ont été examinées en détails: les polymères présentent à la fois des températures d'utilisation élevées et une bonne résistance au choc pour un homopolymère vinylique, mais sont extrêmement difficiles à mouler. Le polycrotonate d'isopropyle a une température de distortion thermique de 125°C à 85 psi, un impact Izod de 2.4 ft/lbs/in. d'entaille et un module de flexion de 274.000 psi.

Zusammenfassung

Die anionische, mit Fluorenyllithium (mit Tetrahydrofuran komplexiert) in Toluol bei -78°C gestartete Polymerisation einer Vielfalt von sekundären Alkylcrotonaten und verwandten Monomeren wird beschrieben. In keiner der Proben konnte Kristallinität erzeugt werden und die kernmagnetische Resonanz lieferte keine Aufschlüsse über ein mögliche Taktizität. Die Polymerisationsverfahren erwiesen sich bei *n*-Alkylestern als unwirksam. Polymeres wurde aus Isopropylcinnamat und *N,N*-Dimethylcrotonamid, nicht aber aus Isopropylthiocrotonat oder Isopropyl-2-pentoate erhalten. Die physikalischen Eigenschaften von Spritzgussproben der Polymeren aus Isopropyl-, *s*-Butyl- und Cyclohexylcrotonat wurden eingehender untersucht; die Polymeren zeigten eine für ein Vinylhomopolymeres wünschenswerte Kombination von hoher Gebrauchstemperatur und guter Schlagzähigkeit, waren aber äusserst schwer zu bearbeiten. Poly(isopropylcrotonat) besass eine Wärmeformbeständigkeitstemperatur von 125°C bei 85 PSI, eine Izod-Kerbschlagzähigkeit von 2,4 Ft-Lbs/In Kerbe und einen Biegemodul von 274.000 PSI.

Received March 6, 1967

Revised March 29, 1967

Prod. No. 1610