

The Relationship Between Structure and Properties of Crystalline, High-Melting Polyhydrocarbons

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In vinyl polymers, it has been a recognized rule of thumb that the substitution of a nonpolar lateral group tends to decrease the melting or softening point. Most of the observations have been made using straight chain substituents, and only very few references to the effect of branching in the side chain may be found. Thus Overberger et al.¹ have reported the T_g (glass transition temperature) of a series of 2-alkyl butadiene polymers. These authors predicted, on the basis of these transition temperatures, that unexpectedly high T_g values would be observed for other polymers with symmetrical, highly branched side chains. Rehberg et al.² measured the brittle points (T_b) of a series of acrylates and methacrylates in which the structure of the esterifying alcohol was varied, while the softening points (T_s) have been reported by Neher³ and others. More recently, Bailey and Naylor⁴ have studied a series of α -alkyl acrylonitriles and the derived methyl α -alkyl acrylates. All of these data are recorded in Table I. In all cases, the higher the degree of branching, the higher the transition temperature of the polymer, although it is never so high as that for the completely unsubstituted polymer. It should be noted that none of the reported transitions are crystalline melting points, hence they may be subject to considerable error in measurement.



Catalysts for the polymerization of olefinic hydrocarbons prepared by the reaction of titanium halides with organometallic reagents have been developed independently.⁵ Similar catalysts for the polymerization of ethylene have been described by Ziegler and co-workers in recent literature.⁶ Natta⁷⁻¹⁰ has reported the application of these catalysts to the polymerization of propylene and styrene to high molecular weight, high melting crystalline polymers.

The high degree of crystallinity and the behavior with regard to melting point* was surprising. Thus, polypropylene has a melting point about 30° higher than that of polyethylene. This is in direct contradiction to the rule stated in the first paragraph regarding lateral substituents, although the effect of subsequent variations in the alkyl group are readily explicable (cf. Table I). It appears that this type of highly crystalline polymers, for which the name "isotactic" has been coined by Natta, is prepared by an asymmetric synthesis, which gives highly ordered chains which pack very well and are stiffened by the favorable arrangement of the alkyl groups. The increase in melting point in going from polyethylene to polypropylene is thus an entropy effect.

In this paper is described a series of polyhydrocarbons prepared by polymerization of monomers of the type R—CH=CH₂, in which the entropy effect is made more pronounced by introducing various degrees of branching into the R group. For comparative purposes, a few polymers based on linear 1-olefins are considered.

POLYMERIZATION

Polymerizations were all carried out at atmospheric pressure and autogenous temperature in open flasks under nitrogen. The polymers, most of which were at least partially soluble in or swollen by the reaction solvent, were isolated by precipitation with alcohol, filtered, and dried. The catalyst used was a product obtained by reduction of titanium tetrachloride with lithium aluminum tetradecyl.

Most of the polymers had good to very high

* It should be remembered that when referring to melting points of polyethylenes, we mean *crystalline* melting points (T_m), which may be determined with considerable reproducibility. With the other classes of polymers, we are dealing with other transitions, which are more difficult to determine accurately, since they depend on numerous factors, for example, molecular weight.

TABLE I
Effect of Substituents on Thermal Properties of Various Polymer Types

Substituent	2-Alkyl butadiene, T_g , °C.	Alkyl acrylates, T_b , °C.	Alkyl methacrylates, T_b , °C.	Alkyl methacrylates, T_g , °C.	Methyl α -alkyl acrylates, T_g , °C.	α -Alkyl acrylonitrile, T_g , °C.
C—	-67	5	90	125	125	115
C—C—	-70	-25	50	60	60	110
C—C—C	—	—	36	38	57	60
C—C—C—C	—	-60	16	33	—	—
C—C—C—C—C	-55	—	-5	—	—	—
C—C—C—C—C—C	-83	-60	—	—	12	15
	-47	0	—	95	—	—
	—	-10	—	62	—	—
	20	> 25	—	—	—	—
	—	-24	54	70	65	55
	—	-32	—	—	—	—
	—	-45	—	—	—	—
	—	> 25	—	—	—	—

crystallinity and could be spun to oriented filaments. No attempts were made to separate the polymers into amorphous and crystalline fractions as has been done for polypropylene.⁸ The polymers were fabricated into oriented fibers or were pressed into film. Crystalline melting points were determined on a Kofler hot stage with the use of a polarizing microscope. The more obvious polymer properties have been collected into Table II.

During this study, no attempts were made to realize the maximum yield of polymer from any one reaction. However, it may be said qualitatively that the rate of polymerization of monomers depends to a great degree on steric hindrance about the vinyl group and the degree of crowding in the polymer chain due to bulkiness of the substituents. Thus, isopropylethylene (3-methyl-1-butene) and styrene polymerize slowly and in poor yield, as do neopentylethylene (4,4-dimethyl-1-pentene), 3-

phenyl-1-butene, and similar monomers. Less drastic branching (e.g., as in 4-methyl-1-pentene) does not seem to change the rate of polymerization over that of the corresponding linear monomer (e.g., 1-hexene).

THE EFFECT OF CHANGES IN STRUCTURE OF THE SIDE CHAIN ON POLYMER PROPERTIES

The two most striking effects of change in the structure of the lateral group, aside from differences in rates of polymerization noted above, are the effect on the melting point and the transition from rubbery, amorphous polymer to hard, crystalline polymer. If one considers the general formula for the monomers studied.

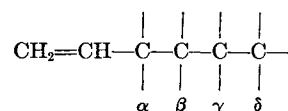


TABLE II
 Polymers From Branched 1-Olefins

Monomer	Crystal- linity	T_m , °C. ^a	PMT, °C. ^b	Remarks
$\text{CH}_2=\text{CH}-\text{CH}_3$	High	165	204	Crystalline.
$\text{CH}_2=\text{CH}-\text{CH}_2\text{CH}_3$	High	125	—	Data of Natta. ⁸ Crystalline.
$\text{CH}_2=\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3$	High	75	—	Ref. 10
$\text{CH}_2=\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	None	None	134	Rubber. Noncrystalline.
$\text{CH}_2=\text{CH}-\text{CH} \begin{array}{l} / \text{CH}_3 \\ \backslash \end{array}$	High	310	262	Very high crystallinity. Capable of high orientation. Hard polymer. (Compare Refs. 10 and 11).
$\text{CH}_2=\text{CH}-\langle \text{S} \rangle$	High	305	28	Hard, crystalline polymer. High yield.
$\text{CH}_2=\text{CHCH}_2\text{CH} \begin{array}{l} / \text{CH}_3 \\ \backslash \text{CH}_3 \end{array}$	High	235	230	Very high crystallinity. Capable of high orientation. Hard polymer. (Compare Refs. 10 and 11.)
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH} \begin{array}{l} / \text{CH}_3 \\ \backslash \text{CH}_3 \end{array}$	Medium	110	138	Somewhat rubbery, but crystalline. (Compare Ref. 10.)
$\text{CH}_2=\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH} \begin{array}{l} / \text{CH}_3 \\ \backslash \text{CH}_3 \end{array}$	None	None	180	Rubber. Noncrystalline.
$\text{CH}_2=\text{CH}-\text{CH}_2\text{CH} \begin{array}{l} / \text{CH}_2\text{CH}_3 \\ \backslash \text{CH}_3 \end{array}$	Medium	157-160	196	Hard polymer, crystalline. (Compare Ref. 10.)
$\text{CH}_2=\text{CH}-\text{CH}_2-\langle \text{C} \rangle$	Medium	225	220	Hard polymer, crystalline.
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{C} \begin{array}{l} / \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{array} - \text{CH}_3$	High	> 350	330	Hard, crystalline. (Compare Ref. 11.)
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{C} \begin{array}{l} / \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{array} - \text{CH}_2\text{CH}_3$	Medium	> 350	314	Hard, crystalline.
$\text{CH}_3(\text{CH}_2)_{15}-\text{CH}=\text{CH}_2$	Medium	100	—	Crystallinity due to crystallization of long lateral groups, not between chains. (Compare Ref. 11.)
$\text{CH}_2=\text{CH}-\text{CH}_2-\langle \text{S} \rangle$	Medium	230	180	Hard and crystalline.
$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	High	250	285	High orientation possible. Hard, crystalline. (Compare Ref. 8.)
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$	Medium	230	276	Orientable. Hard, crystalline.
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	Medium	160	168	Slightly rubbery, but crystalline.
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	None	None	~110	Rubber. Noncrystalline.
$\text{C}_6\text{H}_4(\text{CH}_3)\text{CH}=\text{CH}_2$	None	—	248	Noncrystalline, hard polymer.
$\text{CH}_2=\text{CH}-\text{CH} \begin{array}{l} / \text{CH}_3 \\ \text{C}_6\text{H}_5 \end{array}$	Medium	> 360	338	Very intractable, but crystalline and hard.

^a T_m = crystalline melting point.^b PMT = polymer melt temperature.

for which polymer data are collected in Table I, a number of generalizations on these two features become possible.

1. Completely Linear Monomers

In the series beginning with ethylene, the melting point reaches a maximum with propylene and decreases through 1-pentene. Higher members are amorphous rubbers up to octadecene, which is again crystalline.¹¹

2. Monomers with Branching on the α -Carbon

Single branching on the α -carbon atom as, for example, in 3-methyl-1-butene, styrene, and vinyl cyclohexane, gives the highest crystallinity of any of the classes studied. The melting points were also very high, being in the range of 250–360°C. The polymers were very hard, and films and fibers were very stiff. The effect of unsymmetrical single branching (e.g., 3-methyl-1-pentene was not investigated, but this would probably give a lower-melting polymer (cf. below for β -branching). Simultaneous branching on the α - and β -carbons (3-phenyl-1-butene) gives a hard, very high melting (> 350°) polymer.

3. Monomers with Branching on the β -Carbon

4-Methyl-1-pentene, the simplest example of a monomer with branching on the β -carbon atom, readily gives a hard polymer, melting at about 235°. Other examples of this series with symmetrical branching include 3-cyclohexyl-1-propene, 3-cyclopentyl-1-propene, and allylbenzene. All are hard polymers with remarkably consistent melting points, all being in the same range of 225–240°. Unsymmetrical branching on the β -carbon atom lowers the melting point. Thus, poly-4-methyl-1-hexene melts in the range of 160°. It is still a hard polymer, however. Double branching on the β -carbon atom gives the highest melting polymers observed in this series. Thus, both neopentyl-ethylene and 4,4-dimethyl-1-hexene give hard polymers melting at above 350°C.

4. Branching on the γ -Carbon

Two monomers of this class, 4-phenyl-1-butene and 5-methyl-1-hexene, gave slightly rubbery polymers which were still crystalline, showing melting points of 160° and 110°, respectively. Double branching on the γ -carbon atom (e.g., 5,5-dimethyl-1-hexene) was not investigated, but would probably give a polymer melting in the 250° range.

5. Branching on δ -Carbon Atom

Both 5-phenyl-1-pentene and 6-methyl-1-heptene gave noncrystalline rubbers. Double branching was not investigated.

EXPERIMENTAL PART

General

Titanium Tetrachloride. A commercial product distilled at 136.5° after removal of an appreciable forecut. A stock solution was made up in cyclohexane in 500-ml. batches as needed. A convenient concentration which was usually sought for was about 0.5 *M*. The exact concentration was determined gravimetrically.

Lithium Aluminum Tetradecyl.⁵ A mixture of tetrahydronaphthalene (700 ml.), 1-decene (150 ml.), and lithium aluminum hydride (7.6 g.) was heated with stirring to 135°. A mildly exothermic reaction occurred, and the temperature was allowed to rise to about 180°. The mixture was maintained at this temperature for about 2 hours, then cooled. The originally clear liquid containing lumps of white hydride had become a solution in which was suspended a gray-black flocculent solid. The flask was transferred to a nitrogen-filled dry box and filtered while still warm through a Celite pad. The filtered solution was stored, and the pyrophoric residue on the funnel destroyed at once with isopropanol. For standardization, a 5.0 ml. aliquot of the solution was removed and dissolved in some alcohol. Water (200 ml.) was then added. The resulting mixture was titrated potentiometrically to pH = 7 with standard acid. Under these conditions, only the lithium was titrated, and normality = molarity. A series of preparations had concentrations around 0.2 *M*. It was necessary to prevent contact of oxygen with the lithium aluminum tetradecyl solution. Otherwise, no problems were encountered during storage.

Preparation of Catalyst: General Conditions and Precautions. In general, stoichiometric (1:1 molar ratio) amounts of the catalyst components (titanium tetrachloride and lithium aluminum tetradecyl) were mixed in some inert solvent, usually cyclohexane. Stirring was rapid during mixing and during polymerization. The major cause of trouble in polymerizations was oxygen, which had to be excluded during all phases of the polymerization and preparation of catalysts. Water and other electron-rich substances were also necessarily excluded, since they also inactivate the catalyst.

Preparation of Polymers: General Method. All

of the polymers described below were prepared in essentially the same manner. A three-necked flask or a resin kettle was equipped with a stirrer, a nitrogen inlet, and a simple outlet. A catalyst suspension was prepared in the flask by mixing appropriate amounts of the catalyst components under nitrogen with or without additional solvent. Monomer was then added and the polymerization was allowed to continue for 20-24 hours. The polymer was isolated by addition of alcohol and subsequent filtration and purified by washing in a home mixer with additional quantities of alcohol, being freed of organic solvents in an appropriate manner, usually either with steam or with dry nitrogen at 100-120°.

Determination of Inherent Viscosity. A 25-mg. sample of polymer and 50 mg. of an antioxidant [2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol), Antioxidant 2246, American Cyanamid Co.] were weighed into 25 ml. of decahydronaphthalene and dissolved at 135° in the minimum time with high-speed stirring. The viscosity was then measured at 130°C. [$\eta_{inh} = 2.3 \log (\eta_{rel}/C)$].

Determination of Crystalline Melting Points. Crystalline melting points were determined on highly crystalline polymer samples, either film or fiber. The melting points (Table II) were determined on a Kofler hot stage with a rate of heating approximately 2°/min. Ordinarily, the sample was melted, then allowed to cool slightly until recrystallization occurred, and then remelted in order to check the original value. The heating rate near the melting point was approximately 1° every 2 minutes. The melting point was taken as that temperature at which the last crystalline area disappeared as determined by the complete loss of birefringence. Several of the polyhydrocarbons discussed in this paper have been described previously by Natta, who has reported¹⁰ values for melting points which are consistently lower than our values, the discrepancies being too large to be attributable to individual judgment. We are unable to account for these discrepancies. Polymer melt temperatures (PMT)¹² are recorded also in Table II.

Monomers

The monomers were prepared by conventional methods or obtained commercially. Styrene was freshly distilled before use. Allylbenzene was made from phenylmagnesium bromide and allyl bromide,¹³ b.p. 156-157° (760 mm.). 4-Phenyl-1-butene was prepared from benzylmagnesium chloride and allyl bromide, b.p. 86-87°/35 mm.¹⁴ 5-Phenyl-1-pentene was made from β -phenylethyl-

magnesium bromide and allyl bromide, b.p. 95°/22 mm.¹⁵ 3-Phenyl-1-butene was made by the methylation of sodium allylbenzene.¹⁶

Branched aliphatic hydrocarbons were made generally by the coupling of allyl halide with the appropriate branched Grignard reagent. In this way were prepared 4-methyl-1-hexene, b.p. 86.5°¹⁷ 5-methyl-1-hexene, b.p. 85°,¹⁷ 6-methyl-1-heptene, b.p. 112.5-113°,¹⁸ allylcyclohexane, b.p. 151°,¹⁹ allylcyclopentane, b.p. 125-126°,¹⁹ neopentyl ethylene, b.p. 72-72.5°,^{20,21} and 4,4-dimethyl-1-hexene, b.p. 105.5-106°.²² 4-Methyl-1-pentene (isobutyl-ethylene) and 3-methyl-1-butene, as well as linear 1-olefins, were commercial products (Phillips Petroleum and Humphrey-Wilkinson, Inc.).

Polymers

Poly (1-hexene). A catalyst suspension was prepared from 50 ml. of lithium aluminum tetradecyl (0.18 *M*), 8.2 ml. of titanium tetrachloride (1.08 *M*), and 200 ml. of cyclohexane; to this was added a 100-ml. portion of Phillips 99% 1-hexene. A mildly exothermic polymerization took place, and the mixture rapidly became very thick. After 21 hours, the polymer was isolated as described above. It was obtained in a yield of 41 grams (57%) as colorless, rubbery lumps with an inherent viscosity of 3.86. The polymer was melt-extruded to elastomeric filaments which fused together on handling. They could not be drawn or crystallized.

Poly(3-methyl-1-butene). A catalyst suspension was prepared in a 4-l. resin kettle from 250 ml. of lithium aluminum tetradecyl (0.19 *M*) and 40 ml. of titanium tetrachloride (1.08 *M*) in 1 l. of cyclohexane; a 100-ml. portion (63 g.) of 3-methyl-1-butene, b.p. 20°, was collected in an ice bath from a cylinder and added to the mixture. After 20 hours, the polymer, a fine powder, was isolated by filtration and washed with alcohol. The yield was only 13.8 grams (22%) based on monomer. The inherent viscosity observed (0.94 in decahydronaphthalene) was false, since the polymer was only partly soluble under the usual conditions for determining viscosity. The crystalline melting point of this polymer was difficult to determine on anything but an oriented fiber because of the low birefringence. However, the melting point appeared to be about 280-285°. Poly(3-methyl-1-butene) was extruded at 310°C. to give fibers. These were pulled away from the spinneret rapidly to give fibers with very high crystallinity (about 80%) and orientation *without further drawing*. These showed a $T_m = 310^\circ$. X-ray patterns are given in Figures 2-11.

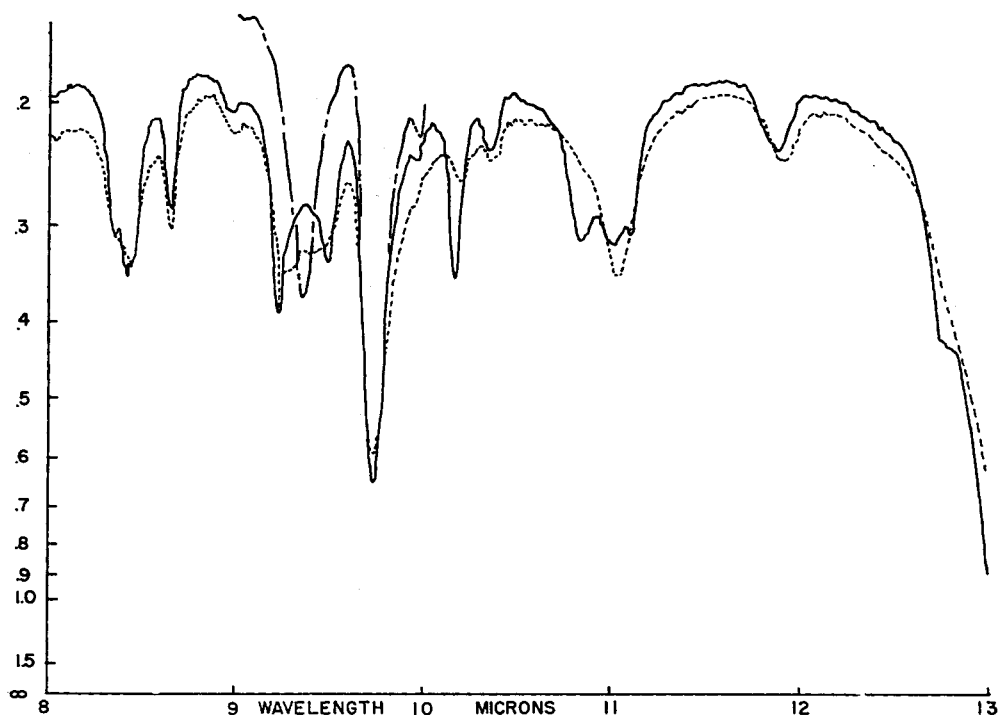


Fig. 1. Infrared spectra of polystyrenes: (—) crystalline polystyrene; (---) amorphous polystyrene; (- -) crystalline polystyrene above crystalline melting point.

Poly(4-methyl-1-pentene). A catalyst suspension was prepared from 200 ml. of lithium aluminum tetradecyl (0.20 *M*) and 31 ml. of titanium tetrachloride (1.08 *M*) in a total volume of 300 ml. of cyclohexane; to this was added a 200-ml. portion of commercial 4-methyl-1-pentene. Polymer began to form rapidly. After 24 hours, the nearly solid mass was isolated in the usual manner to give an excellent yield of white, hard polymer. This polymer was dried and extruded at 250° from a melt-spinning cell. Filaments were wound up which could be drawn at 170° to give fibers with extremely high crystallinity and orientation as observed from their x-ray diagram. The inherent viscosity was 4.25 and the crystalline melting point was 235°.

Poly(4-methyl-1-hexene). A 40-ml. portion of 4-methyl-1-hexene was added to a catalyst suspension prepared from 50 ml. of lithium aluminum tetradecyl (0.18 *M*), 50 ml. of titanium tetrachloride (1.08 *M*), and 200 ml. of cyclohexane. After 20 hours, the polymer, a hard, nontacky, nonrubbery solid, quite similar in appearance to poly(4-methyl-1-pentene) and with an inherent viscosity of 2.72, was obtained in a yield of 11.6 grams. A sample of polymer was extruded through a 0.03-in. spinneret. Rather stiff fibers were wound up with a fairly high spin-stretch factor. They could not be drawn further and showed x-ray orientation.

Samples of film pressed at 200°C. were clear and fairly stiff. Strips of film could be drawn over a hot pin at 140°. The oriented film strips were highly crystalline, as shown by x-ray examination, and exhibited a crystalline melting point of 160°.

Poly(5-methyl-1-hexene). A 25-ml. portion of 5-methyl-1-hexene was added to a catalyst suspension prepared from 25 ml. of lithium aluminum tetradecyl (0.18 *M*) and 3.9 ml. of titanium tetrachloride (1.08 *M*) in 100 ml. of cyclohexane. The mixture was allowed to polymerize for 20 hours, after which the polymer was isolated in the usual way as a slightly rubbery mass with an inherent viscosity of 2.62. The yield was 11.5 grams. Fibers could be drawn and oriented in hot water. X-ray diagrams on the oriented fibers showed them to be moderately crystalline and oriented. The crystalline melting point of an oriented fiber sample was 110°; the drawn fibers relaxed badly at about 50°.

Poly(6-methyl-1-heptene). A catalyst suspension was prepared from 50 ml. of lithium aluminum tetradecyl (0.18 *M*), 5.0 ml. of titanium tetrachloride (1.08 *M*), and 200 ml. of cyclohexane. To this a 40-ml. portion of 6-methyl-1-heptene was added, and the mixture was allowed to polymerize for 20 hours, after which the polymer was isolated and dried. It was a soft, tacky material which could not be crystallized. It was obtained in a

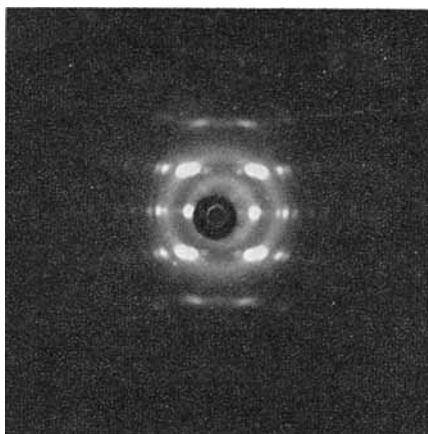


Fig. 2. Poly(3-methyl-1-butene) melt extruded at 310°C. at a high spin-stretch factor.

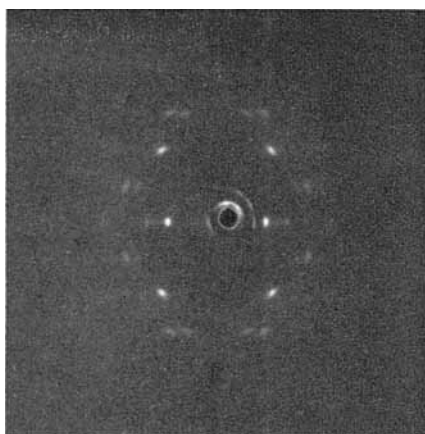


Fig. 4. Poly(4-methyl-1-pentene) fiber drawn 12× at 140°C.

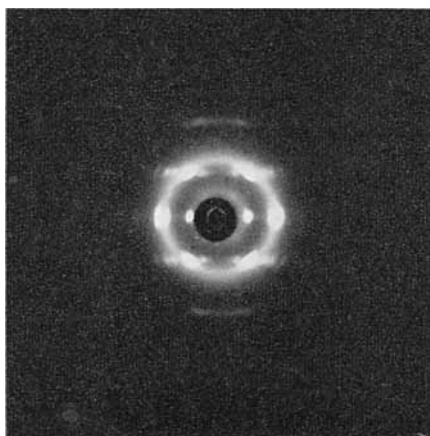


Fig. 3. Poly(5-methyl-1-hexene) fiber drawn 3× at 75°C.

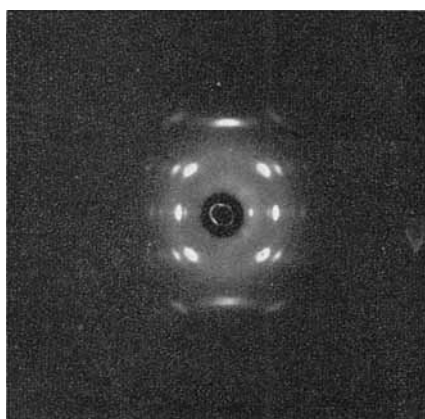


Fig. 5. Crystalline polystyrene fiber drawn 4× at 100°C, heat-set taut.

yield of 17 grams with an inherent viscosity of 2.37.

Poly(4,4-dimethyl-1-pentene). A catalyst suspension was prepared from 50 ml. of lithium aluminum tetradecyl (0.20 *M*) and 9 ml. of titanium tetrachloride solution (1.08 *M*). To this suspension was added 20 ml. of 4,4-dimethyl-1-pentene. After 20 hours, the polymerization was quenched with propanol, and the powdery polymer was filtered. The polymer was obtained in a yield of 2.6 grams as a colorless powder. It could be pressed into an amorphous film at 200°C. This film showed a glass transition temperature near 190° as estimated by disappearance of birefringence due to noncrystalline orientation. Above 190° the film began to crystallize, eventually becoming very highly crystalline. This material did not show a crystalline melting point up to 350°, the limit of the apparatus used.

Poly(4,4-dimethyl-1-hexene). A catalyst suspension was prepared in the usual way from 100 ml. of lithium aluminum tetradecyl (0.19 *M*), 18.5 ml. of titanium tetrachloride (1.08 *M*), and 100 ml.

of cyclohexane. After the addition of 22 ml. of 4,4-dimethyl-1-hexene, the polymerization was allowed to proceed for 20 hours, at which time the polymer was isolated in 1.7-gram yield. The inherent viscosity (1.12) was determined on an ether-extracted sample. The ether removed a fair quantity of sticky, low molecular weight material. The extracted polymer was pressed into a clear, bright film at 200°. This film showed high x-ray crystallinity and no crystalline melting point to 350°.

Poly(3-cyclopentyl-1-propene). After addition of 20 ml. of 3-cyclopentyl-1-propene to a catalyst suspension prepared as in the previous experiment, the polymerization was allowed to proceed for 65 hours. The reaction mixture was then quenched with alcohol, and the polymer was isolated by filtration. It was a hard powder, very similar in appearance to poly(4-methyl-1-pentene). The yield was 13 grams (80%), and the inherent viscosity was 1.75. A sample was melt-spun at 250° with considerable ease, and the fiber was wound up with no

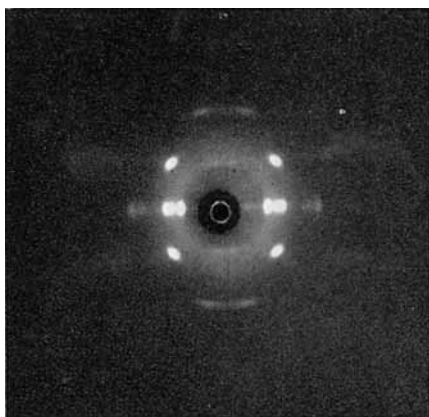
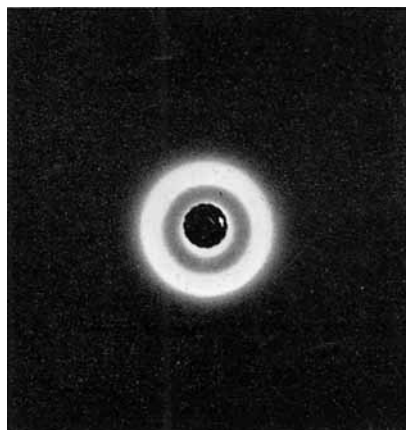
Fig. 6. Polypropylene drawn 8 \times at 150°C.

Fig. 9. Poly(6-methyl-1-heptene).

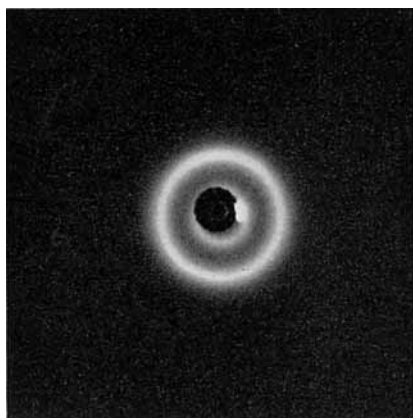
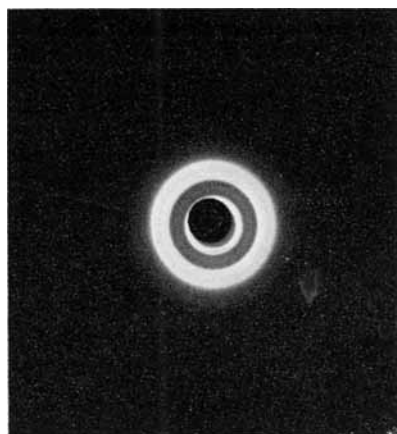
Fig. 7. Poly(vinyl toluene) drawn 3 \times at 120°C., heat-set 1 hr. at 100°C.

Fig. 10. Poly(vinylcyclohexane) film cast from cyclohexane and dried at room temperature.

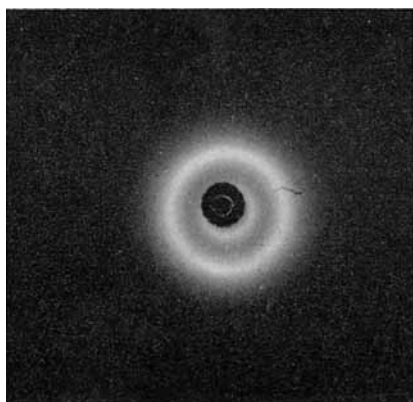


Fig. 8. Poly(1-hexene).

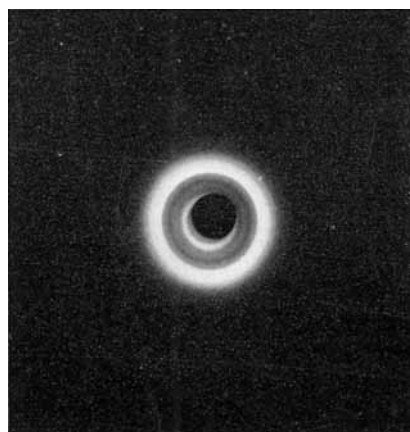


Fig. 11. Poly(4,4-dimethyl-1-pentene) film pressed at 250°C.

difficulty. A fiber sample was elongated 300% at 100°C. to give a sample with a very high x-ray crystallinity and orientation. It exhibited a crystalline melting point of 225°C.

In contrast to most polyhydrocarbons prepared by coordination polymerization, poly(3-cyclopentyl-1-propene) is quite soluble in various organic solvents, e.g., 7.5 grams of the polymer easily dis-

solved in 100 grams of chloroform. This solution could be cast into clear film, dry-spun, or wet-spun. In a typical wet-spinning experiment, the dope described above was extruded into alcohol as a coagulating bath. The spinning was quite satisfactory, and the fine filament yarn was wound up

easily. The as-spun yarn was afterdrawn four times at 100°C. to give a strong product.

Poly (3-cyclohexyl-1-propene). A catalyst suspension was prepared from 100 ml. of lithium aluminum tetradecyl (0.20 *M*), 18 ml. of titanium tetrachloride (1.08 *M*), and 500 ml. of cyclohexane; to this a 100-ml. portion of pure 3-cyclohexyl-1-propene was added. The next day the entire mass was a thick, but not gel-like, solution. The polymer was precipitated with isopropyl alcohol, filtered, washed, redissolved in cyclohexane, pressure filtered, and reprecipitated with isopropyl alcohol. The yield was 33 grams (43%). The inherent viscosity was 1.32. The polymer could be pressed at 225° to clear, stiff film which could be drawn over a hot pin at 150°. Oriented film samples exhibited a crystalline melting point at 225°C. A solution of 10 grams of polyallylcyclohexane in 60 ml. of cyclohexane was quite viscous and dry-spun quite easily.

Polymerization of Styrene. A catalyst preparation was made from 50 ml. of titanium tetrachloride (0.44 *M*) and 175 ml. of lithium aluminum tetradecyl (0.14 *M*) without additional solvent. Styrene (40 g.) was added all at once, and the mixture was stirred for 20 hours. The polymer solution was treated with 200 ml. of 2-propanol and stirred under a stream of air to discharge most of the color due to the lower valent titanium. The polymer was washed several times by decantation, then filtered and dried to give a curdy, white solid, yield 9.3 g.

This polymer was then fractionated by agitation with 200 ml. of anhydrous ether for several hours and collection and drying of the insoluble fraction. The polymer yield was 6.5 g. The ethereal filtrate gave, on evaporation, 2.7 g. of very tacky, low molecular weight polymer which was not investigated. The ether-insoluble fraction was further separated by extraction with boiling toluene. The toluene-soluble fraction (0.5 g.) was pressed to a film of high degree of crystallinity and with a crystalline melting point of about 220°. This fraction had an inherent viscosity of 1.6 in benzene. The toluene-insoluble portion could be pressed into film at above 250°. The film showed a crystalline melting point as high as 250°; it was moderately soluble in tetrachloroethane, in which it had an inherent viscosity of 6.24.

Poly(vinyl toluene). Vinyl toluene (a mixture of the *m*- and *p*- isomers) was distilled rapidly at 75°/30 mm. A catalyst suspension was prepared from 100 ml. of lithium aluminum tetradecyl (0.20 *M*) and 18 ml. of titanium tetrachloride solution (1.08 *M*) in 100 ml. of cyclohexane. To

this suspension was added a 100-ml. portion of freshly distilled vinyl toluene; the mixture became viscous rapidly. After 20 hours, the reaction was quenched with isopropanol, and the polymer was isolated by filtration and dried. It was obtained in a yield of only 2.8 grams and had an inherent viscosity of 3.91 in tetrachloroethane. The polymer was soluble in ether and slightly soluble in acetone. Acetone-insoluble polymer gave a film at 200° which was clear and very stiff. It could be drawn on a hot pin at 110° to give a film strip which exhibited very strong birefringence when examined under a polarizing microscope. However, x-ray patterns showed that the polymer was completely noncrystalline. The birefringence disappeared between 120 and 170°C., indicating a glass transition temperature in this range.

The above experiment was repeated, and the polymerization was allowed to proceed for 65 hours. Under these conditions, the yield of polymer after extraction of low molecular weight material with acetone was 10 grams with an inherent viscosity of 5.16 in tetrachloroethane. Again, films were pressed and strips were drawn over a hot pin at 120°. These films strips showed behavior typical of crystalline polymers; that is, they exhibited a finite draw ratio and showed the phenomenon of necking down. Furthermore, polymer was extruded from a melt-spinning apparatus to give filaments which exhibited similar characteristics. However, none of the stretched samples showed the slightest trace of crystallinity when examined by the x-ray technique.

Poly(allylbenzene). A catalyst suspension was prepared from 100 ml. of lithium aluminum tetradecyl (0.18 *M*) and 16 ml. of titanium tetrachloride solution (1.08 *M*). To this was added a 15-ml. portion of freshly distilled allylbenzene. After 72 hours, the polymer was precipitated with alcohol and filtered. It was a fine, white powder weighing 15.6 grams (36%) after drying. The inherent viscosity could not be determined since it was insoluble in decahydronaphthalene at 130°. The crystalline melting point of a sample of film prepared at 220° was 230–235°.

Poly(4-phenyl-1-butene). A catalyst suspension was prepared from 100 ml. of lithium aluminum tetradecyl (0.18 *M*), 15 ml. of titanium tetrachloride (1.08 *M*), and 180 ml. of cyclohexane. To this suspension was added a 50-ml. portion of 4-phenyl-1-butene. Polymerization appeared to be quite rapid, since after 1 hour the mixture was very thick. On the next day, the polymer was isolated in the usual way. It was a slightly rubbery, white solid, similar in appearance to poly-

propylene. The yield was 24 grams; the inherent viscosity was 3.65. The polymer could be pressed into a clear, rather rubbery film at 200°. Strips of film were drawn four times at 125° over a hot pin. The oriented, crystalline polymer then showed a melting point of 158–160°. Poly(4-phenyl-1-butene) was melt-spun at 225° to give fibers which could not be drawn further. The as-spun fibers (oriented during spinning) showed approximately the same crystalline melting point as the film strips.

Poly (5-phenyl-1-pentene). After addition of 35 ml. of 5-phenyl-1-pentene to a catalyst suspension prepared as in the preceding experiment, the polymerization was allowed to proceed for 20 hours. The polymer, isolated in a yield of 21 grams, had an inherent viscosity of 1.87 and was a soft, tacky, rubbery material with very low if any crystallinity. Melt-spun fibers showed zero strength below 100°C. These fibers showed slight birefringence but no x-ray evidence of crystallinity.

Poly (3-phenyl-1-butene). A 23-g. portion of 3-phenyl-1-butene was added to a catalyst suspension prepared from 100 ml. of lithium aluminum tetradecyl (0.20 *M*), 18.5 ml. of titanium tetrachloride (1.08 *M*), and 100 ml. of cyclohexane. The polymerization was allowed to continue for about 20 hours, after which time the polymer was isolated by precipitation with alcohol followed by filtration. The precipitate was washed with ether and dried. The yield of polymer was 2.3 grams. It was a hard, white powder which was insoluble in decahydronaphthalene at 130°C. It could be pressed to a clear but brittle film at 200°C. This polymer exhibited a polymer melt temperature equal to 330°. The crystalline melting point was over 360°. X-ray examination of the clear, brittle film sample showed high crystallinity.

Infrared Spectrum of Crystalline Polystyrene. In Figure 1 are shown the infrared spectra of isotactic polystyrenes in the solid and in the molten states. These are compared to the spectrum of a sample of ordinary polystyrene. The differences between the isotactic and the random polymer result in the appearance of a doublet at 9.30 and 9.42 μ , in place of the single band normally present at 9.35 μ . This band is present in molten isotactic polystyrene as well as in amorphous but crystallizable polystyrene. The infrared spectrum thus affords a method for detecting crystallizability in uncrystallized polystyrene.

X-Ray Diagrams. X-ray diagrams of various oriented and unoriented samples of polyhydrocarbons are shown in Figures 2–11.

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Synopsis

Twenty-two α -olefin monomers with varying degrees and types of branching in the lateral group have been polymerized and the polymers characterized. In general, the closer the branching in the side chain is to the polyethylene trunk, the higher the degree of crystallinity and the crystalline melting point. The degree of branching and the symmetry of the branches also affects the melting point and crystallinity markedly. Relationships have been drawn between type and position of the branch and melting point.

Résumé

Vingt-deux monomères α -oléfiniques, de caractère divers et de degré de ramification de la chaîne latérale différent, ont

été polymérisé et les polymères ont été caractérisés. En général, d'autant plus que la ramification de la chaîne latérale soit rapproché à la chaîne polyéthylénique principale, le degré de cristallinité et le point de fusion deviennent plus élevés. Le degré de la ramification et la symétrie des chaînes ramifiées influencent sensiblement le point de fusion et la cristallinité. Le rapport entre le type et la position des ramifications et entre le point de fusion a été établi.

Zusammenfassung

Zweiundzwanzig monomere α -Olefine, die Seitenketten

von verschiedenen Verzweigungsgraden und -arten besitzen, wurden polymerisiert, und die Polymere wurden charakterisiert. Im allgemeinen, je näher die Verzweigung in den Seitenketten zum Polyäthylen Stamm ist, umso höher sind der Kristallisationsgrad und der kristallinische Schmelzpunkt. Auch der Verzweigungsgrad und die Symmetrie der Seitenketten haben einen bedeutenden Einfluss auf den Schmelzpunkt und auf die Kristallinität der Polymere. Das Verhältnis zwischen Typus und Stellung der Seitenketten und dem Schmelzpunkt wurde festgelegt.

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