

Poly(4-methyl-1-pentene) and Some Soluble Crystalline Copolymers

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A series of polyhydrocarbons prepared over organometallic titanium-containing catalysts developed within the du Pont Company¹ has been described in a recent article² in which the effect of branching in a 1-olefin was related to the melting point of the corresponding polyhydrocarbon.

One of the most attractive of the higher melting polyhydrocarbons is the polymer from 4-methyl-1-pentene, which has a crystalline melting point of about 240°C. The preparation and characterization of this polymer and some related copolymers will be described in the present article.

HOMOPOLYMERIZATION

4-Methyl-1-pentene polymerized readily with a catalyst made from equimolar parts of titanium tetrachloride and lithium aluminum tetradecyl¹² in an inert hydrocarbon solvent, usually cyclohexane. Polymerization was relatively rapid, and the polymer was isolated in good yield by precipitation from the gel-like reaction mixture with alcohol. The polymer was obtained in the form of a fine white powder which was freed of residual solvent either by steam distillation, by heating at 100°C. in a high vacuum overnight, or by heating in a stream of nitrogen.

The inherent viscosity* of the polymer was invariably too high for melt spinning ($\eta_{inh} = 4.0-6.5$), so it became necessary to devise methods for lowering molecular weight of the polymer. The most obvious approach was to change polymerization conditions, such as the ratio of catalyst components, the temperature of polymerization, the concentration of reactants, the particle size of the catalyst (by altering temperature of preparation), etc. This was done, and it was found that whole polymer of any desired molecular weight could be obtained by use of nearly any of the techniques. However, the polymer was invariably a mixture of

high molecular weight, crystalline polymer and low molecular weight, amorphous product. The observed viscosity was thus an average dependent on the ratio of low molecular weight product to high molecular weight polymer. It would appear that the isotactic type of polymerization to crystalline polymer by means of the particular catalyst system described invariably results in a polymer of high degree of polymerization, and that any alteration in the catalyst designed to cut down molecular weight does so at the expense of crystallinity. Thus, in the case of the experiments with excess $TiCl_4$, the isotactic polymer (crystalline) is probably contaminated with cationic polymer. It should be noted that cationic polymerization alone would not ordinarily give polymer of as high molecular weight as the extractable fractions noted in this work. It is probable that the extractable, noncrystalline fraction is, in effect, a copolymer of cationic and isotactic species.

CRACKING AND FRACTIONATION

Since no catalyst capable of polymerizing 4-methyl-1-pentene directly to a polymer of high crystallinity but molecular weight suitable for laboratory characterization of the polymer in fiber form was available at the time, it was decided to examine the controlled thermal degradation of high molecular weight polymer. Thermal degradation of polymer chains may occur by an "unzipping," in which monomer units are cleaved from the ends of polymer chains, or by a random chain scission. If the former mechanism operated, the thermal cracking of poly(4-methyl-1-pentene) could give lower molecular weight polymer, but with considerable loss of material as monomer. If random chain scission occurred, the various polymer fractions would be lowered proportionately, and no loss of monomer should occur. That random scission actually occurred was shown, since it could be demonstrated that

* $\eta_{inh} = 2.3 \log \eta_{rel}/C$.

thermal cracking in the high vacuum at 270–280° (1) lowered molecular weight gradually and smoothly without loss in weight; (2) did not affect the ratio of crystalline to amorphous polymer; and (3) did not alter in any detectable way the structure of the isotactic polymer chain. Cracking, combined with solvent extraction of the amorphous fraction, was thus employed routinely³ to prepare spinnable polymer.

High molecular weight ($\eta_{inh} > 1.8$) poly(4-methyl-1-pentene) could not be spun satisfactorily unless the temperature was raised high enough to crack the polymer *in situ*. This was not desirable, because of lack of control. Polymer with $\eta_{inh} = 1.3$ –1.8 could be spun, but slowly. For best results, polymer of $\eta_{inh} = 0.9$ –1.2 appeared to be desirable.

It was possible to spin poly(4-methyl-1-pentene) rapidly, but the resulting yarn was highly oriented and crystalline, and could not be afterdrawn. Much better physical properties were obtained by spinning fibers without stretching, and then afterdrawing. Yarn made in this way had tenacities several times greater than that made by the high speed method mentioned above, although the x-ray patterns (Fig. 2) seemed to indicate identical (and very high) crystallinity and orientation.

Considerable variation in fiber properties was noted among various samples. These variations could usually be traced to the character of the polymer. The best properties noted were obtained on fibers made from polymer prepared by first separating low molecular weight noncrystalline fractions by exhaustive extraction, then cracking the polymer. The tensile properties of poly(4-methyl-1-pentene) yarn are generally good at or near room temperature. They drop as the temperature is raised, much as do the properties of polyethylene.

SOLUBLE COPOLYMERS

Since poly(4-methyl-1-pentene) is only slightly soluble in most solvents, it could not be spun from a solution. It was noted previously² that poly-1-olefins in which the lateral group is linear and longer than three carbon atoms in length are readily soluble in hydrocarbons and halogenated hydrocarbons. A study of copolymers of 4-methyl-1-pentene with linear 1-olefins was carried out to see whether a high-melting crystalline copolymer which was also soluble could be prepared.

Copolymers containing 10–25% of linear 1-olefins were prepared and found to be readily soluble.

The crystallinity and melting points of the copolymers were surprisingly high.

The most satisfactory comonomer was 1-hexene, which was used in most of the work. Copolymers containing 10–25% of 1-hexene were easily soluble in cyclohexane, and the solutions could be cast to film. Copolymers of the same composition could also be melt-pressed and afterdrawn.

The copolymers that were prepared during this work were unusual in that when molded into thin films they showed no birefringence when examined with a polarizing microscope, yet exhibited a high degree of crystallinity in x-ray analysis. Ordinarily, birefringence developed as the polymer sample was heated, and it thus became possible to determine a crystalline melting point. No explanation is readily apparent for this unusual behavior.

Mixtures of monomers of composition 80/20 and 90/10 (4-methyl-1-pentene/1-hexene) could be polymerized directly to viscous solutions and cast to tough film without separation of the polymer from the catalyst. The black, viscous reaction mixture was filtered and cast directly to give olive-colored film qualitatively as good as that obtained by melt-pressing purified copolymer. This film rapidly lost its color; after being allowed to stand overnight and being washed with alcohol, it yielded a pure white product.

A soluble, crosslinkable terpolymer was made by copolymerizing 4-methyl-1-pentene, 1-hexene, and divinylbenzene. The polymer was initially soluble; however, a film was rapidly insolubilized at 225° C. by thermal crosslinking of residual vinyl groups.

EXPERIMENTAL PART

Characterization and Testing

Polymer samples were characterized after the fashion described by Beaman and Cramer.⁴ Properties studied were the tenacity T of the fiber in grams per denier, the per cent elongation E of the fiber at the breaking point, the initial modulus M_i in grams per denier, and the fiber sticking temperature, FST .

Homopolymerization

Polymerization of 4-Methyl-1-pentene. A catalyst suspension was prepared from 200 ml. of lithium aluminum tetradecyl² solution (0.19M), 33 ml. of titanium tetrachloride solution (0.87M), and 2 l. of cyclohexane.⁵ Then 450 g. of 4-methyl-

1-pentene monomer were added and the polymerization was allowed to proceed. Polymer was isolated by precipitation with isopropyl alcohol in a high speed mixer. It was washed repeatedly with alcohol until colorless. It was then dried in a vacuum oven at 100° overnight. The yield was 251 g. (58%), and the inherent viscosity was 4.93 in decahydronaphthalene at 130°.²

Polymerization of 4-Methyl-1-pentene. Effect of Temperature of Catalyst Preparation.* A solution of 100 ml. lithium aluminum tetradecyl solution in decahydronaphthalene (0.18M) was placed in a 1-l. polymerization flask and cooled to 0° in an ice bath. To the cold lithium aluminum tetradecyl solution was added all at once 1.5 ml. of undiluted titanium tetrachloride. A 50-ml. portion of 4-methyl-1-pentene monomer was added, and the mixture was allowed to polymerize. Aliquots were removed at regular intervals from the reaction flask and the polymer was isolated from these portions, dried, and weighed, and the inherent viscosity was measured. The data are summarized in Table I.

TABLE I
Polymerization of 4-Methyl-1-pentene

Experiment no.	Time, hr.	Yield, g. ^a	Yield, %	η_{inh}
1	0.5	1.23	41	2.51
2	1	1.45	48	2.99
3	1.5	1.75	58	2.60
4	2	1.70	57	2.62
5	3	1.80	60	2.66
6	4.5	2.00	67	2.51
7	7	2.20	74	2.46
8	22	2.30	77	2.49

^a Yield obtained from 50 ml. aliquot; theoretical yield about 3.0 g.

Polymerization of 4-Methyl-1-pentene in the Presence of Various Catalyst Concentrations. Four polymerizations were carried out in the usual manner as specified in Table II. Catalyst was prepared by mixing the catalyst ingredients at temperatures below 0°. After 1/2 hour the polymer was precipitated, isolated, dried, and analyzed. Data are collected in Table II.

The Effect of the Ratio of Titanium Tetrachloride to Lithium Aluminum Tetradecyl on the Nature of Poly(4-Methyl-1-pentene). A series

* This technique was developed by G. Hoeschele of the Elastomer Chemicals Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

TABLE II
Polymerization of 4-Methyl-1-pentene
(50 ml. of monomer)

Run	LiAlD ₄ (0.17M), ml.	TiCl ₄ (undi- luted), g.	Cyclo- hexane, ml.	Yield, g.	Yield, %	η_{inh}
1	100	2.2	0	22.5	67	2.26
2	50	1.1	50	19.7	55	3.39
3	25	0.5	75	10.1	30	4.19
4	10	0.2	90	3.0	9.0	6.16

of experiments was run in which the ratio of titanium tetrachloride to lithium aluminum tetradecyl was varied widely. The catalyst components were combined in all cases by mixing at temperatures below 0°. This mixture was allowed to stand for about 10 min., then the monomer was added. No further diluent or cooling was used. Polymerization was allowed to proceed for one hour when the polymer was isolated in the usual fashion and analyzed. The data are plotted in Figure 1.

Polymerization of 4-Methyl-1-pentene at Elevated Temperatures. Several experiments were carried out to determine the effect of elevated temperatures on the properties (especially η_{inh}) of poly(4-methyl-1-pentene). These were carried out either in hot decahydronaphthalene or in a sealed tube. High temperature polymerizations invariably gave high proportions of tactic grease.

Spinning and Fractionation of Homopolymer

Drying of Poly(4-Methyl-1-pentene). It was essential to remove all traces of solvents with care, since any solvent remaining in the polymer caused serious bubbling during spinning operations. Three methods were used for drying poly(4-methyl-1-pentene), which retains most solvents tenaciously. In the first method, the polymer to be dried was placed in a three-necked flask and treated with steam for 4 hr. This effectively removed most solvents. The second method employed was to place the polymer to be dried in a three-necked flask equipped with stirrer, a nitrogen inlet, and a long outlet tube. The polymer was then dried by passing a stream of nitrogen into the agitated polymer maintained at 100°C. The third method consisted of heating the polymer for about 20 hr. in a vacuum at 100°C.

High Speed Spinning of Poly(4-Methyl-1-pentene). A sample of polymer with an inherent viscosity of 6.5 was molded into a plug. Preliminary attempts to extrude this polymer at 290° were not

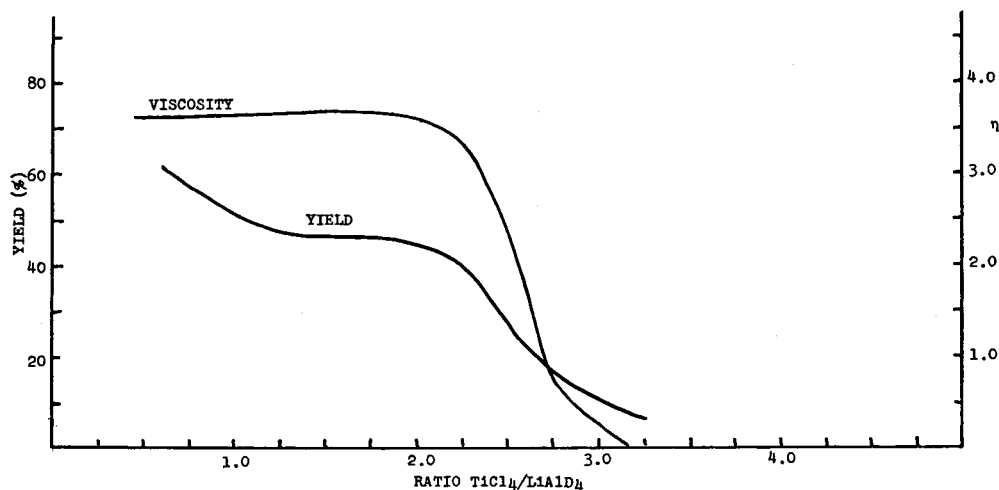


Fig. 1. The effect of the ratio of catalyst components on the nature of the polymer.

successful. However, the spinneret temperature was raised to 315° . At this temperature the polymer spun smoothly at speeds up to 1500 ft./min. Various samples were collected, but these could not be afterdrawn because of high orientation developed during spinning. The viscosity of the fiber was 1.14; the best tensile properties were $T/E/M_t = 0.82/42/11$. Another sample of fiber was collected at a slower speed to avoid orientation during extrusion. This product was afterdrawn $12\times$ at 130° . Tensile properties were $T/E/M_t = 3.3/28/18$ (see Fig. 2 for comparison of x-ray patterns).

Thermal Cracking of Poly(4-Methyl-1-pentene).

A sample of poly(4-methyl-1-pentene) ($\eta = 2.74$) containing 0.3% antioxidant (*N,N'*-di- β -naphthyl-*p*-phenylenediamine) was heated at 280° in a vacuum (1 mm.), and samples were removed after various time intervals. After 75 min. the inherent viscosity was 1.60, and after 150 min. it was 1.2.

Spinning Cracked, Unextracted Polymer. A 25-g. sample of poly(4-methyl-1-pentene) ($\eta_{inh} = 1.4$) which had been prepared by cracking an unextracted polymer ($\eta_{inh} = 2.3$) at 270° was molded to a plug and melt-spun at 255°C . The fiber was wound up slowly to avoid any orientation of the fiber, then afterdrawn $7\times$ (maximum possible) at

TABLE III
Melt-spinning of Cracked,
Extracted Poly(4-Methyl-1-pentene)

Code	Spin temp., $^{\circ}\text{C}$.	η_{inh}	Draw ratio, \times	Draw temp., $^{\circ}\text{C}$.	T	E	M_t
A	ca. 300	2.38	8	175	2.8	23	30
B	275	1.85	12	155	3.7	27	29
C	282	1.35*	13	140	2.4	26	17
D	275	1.9	6.5	155	3.6	26	33
E	250	1.24	12	155	5.1	25	35

* Low molecular weight fraction not extracted.

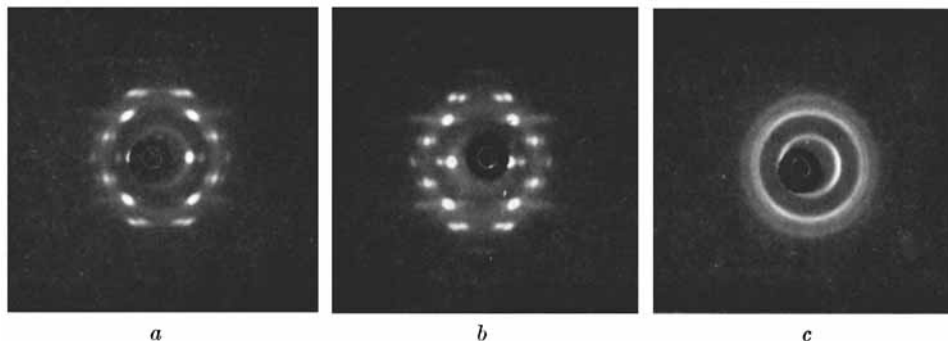


Fig. 2. X-ray diagrams of poly(4-methyl-1-pentene): (a) spun at high speed, no afterdraw; (b) spun at low speed and drawn 12 times at about 130°C .; (c) spun at low speed and not drawn (no orientation).

130°C. The tensile properties were $T/E/M_t = 1.7/30/16$ (cf. Table III).

Fractionation of Cracked and Uncracked Polymer. Two 30-g. samples ($\eta_{inh} = 2.1$) were taken. One sample was cracked at 270° to a polymer $\eta_{inh} = 1.35$. These two samples were extracted in the form of thin flakes in a series of parallel experiments with the following solvents: (1) petroleum ether, (2) cyclohexane, (3) ethyl ether, and (4) acetone. A total of five fractions was obtained from each sample, as follows:

Fraction	Weight, g.		η_{inh}	
	uncracked	cracked	uncracked	cracked
Acetone-soluble	2.0	2.0	oil	oil
Ether-soluble	7.0	—	0.44	—
Petroleum ether-soluble	2.0	5.8	0.82	0.25
Cyclohexane-soluble	6.9	7.7	1.7	1.2
Insoluble	11.5	12.6	3.5	2.0

Spinning of Cracked, Extracted Polymer. A 100-g. sample of poly(4-methyl-1-pentene) powder ($\eta_{inh} = 2.1$) was slurried with 900 g. of ethyl ether and allowed to stand for 4 hr. The mixture was filtered through a stainless steel screen (100 mesh) and the solid was then washed with 250 ml. more of ether. The ether extract was evaporated to give 32 g. of tacky polymer, $\eta_{inh} = 0.99$. This was rejected. The insoluble fraction had $\eta_{inh} = 3.83$. The yield was 66 g. This insoluble fraction was molded into plugs which were cracked by heating in a high vacuum at 265°C. After 10 hr., the inherent viscosity was 2.38. Part of this polymer was remolded and coded A. The rest was cracked further at 288° for 6 hr. in a high vacuum to a polymer with $\eta_{inh} = 1.85$. This was molded into a plug coded B. (In most experiments, it appeared that *extracted* polymer cracked more slowly than *unextracted* material. This may reflect the presence or absence of a catalytic impurity.)

In another experiment, *unextracted* polymer of $\eta_{inh} = 2.1$ was cracked to one with $\eta_{inh} = 1.35$ by heating at 270° for 4 hr. A portion was molded to a plug coded C. An additional 275 g. of this cracked, unextracted polymer was ground up and extracted repeatedly with ethyl ether. In this manner, 82 g. of polymer with $\eta_{inh} = 0.22$ was separated. The insoluble fraction was then extracted exhaustively with cold (i.e., room temperature) cyclohexane to give 46 g. of soluble poly-

mer, $\eta_{inh} = 0.76$. The insoluble polymer weighed 135 g., and had an inherent viscosity of 1.9.

Part of this insoluble sample weighing 135 g. with an inherent viscosity of 1.9 was molded into a plug coded D. Another part was cracked further for 7 hr. at 288°C. to give a polymer with $\eta_{inh} = 1.24$. This was molded into a plug coded E.

The various plugs were then spun by conventional methods. The spinning conditions and fiber properties are listed in Table III.

Properties of Cracked Polymer. Fibers made from cracked polymer and drawn in the usual way have x-ray patterns and infrared spectra identical to those of uncracked material. The crystalline melting point is still at about 235–240°, the *FST* is 215°.

Copolymerization

Copolymerization of 4-Methyl-1-pentene and 1-Pentene. In a 2-l. resin kettle was placed 250 ml. of lithium aluminum tetradecyl solution which was then cooled in an ice-salt bath under nitrogen. Undiluted titanium tetrachloride (5.0 ml.) was added after 10 min., and the mixture was stirred for an additional 5 min. The ice bath was removed and a mixture of 212 ml. of 4-methyl-1-pentene and 38 ml. of pentene-1 was added. After 24 hr., the reaction mixture was precipitated with alcohol, filtered, and washed with additional alcohol. The yield of polymer was good. The inherent viscosity was 2.97 as measured on an 0.1% solution in decahydronaphthalene. This polymer was soluble in hot cyclohexane, hot chloroform, hot carbon tetrachloride, and hot, xylene. The solutions gelled on cooling.

Film samples were prepared by pressing polymer at 235°. Strips could be drawn 6X at 150° over a hot pin. Film samples which showed high x-ray crystallinity and orientation showed no birefringence on a polarizing microscope at room temperature. However, if the sample was heated, birefringence developed, and a crystalline melting point of 170° was observed as the temperature at which this birefringence disappeared.

Copolymers of 4-Methyl-1-pentene and 1-Hexene. A mixture of 40 ml. of 4-methyl-1-pentene and 10 ml. of 1-hexene was polymerized for 3 hr., as in the previous experiment. The polymer was isolated by precipitation with alcohol followed by filtration. The polymer was obtained in a yield of 22 g. with an inherent viscosity of 2.70 in cyclohexane at room temperature. A sample was pressed into a clear, tough film at 220° in a Carver press. Strips

of this film could be drawn 6–8 \times at 125°. These strips, although rather poorly birefringent at room temperature, developed strong birefringence at a temperature over about 100°. The birefringence then disappeared at about 195°, indicating a crystalline melting point of this order.

The copolymer was soluble in cyclohexane up to approximately 20% solids. These were true solutions and did not have the gel-like appearance so characteristic of even very dilute solutions of poly-(4-methyl-1-pentene). Copolymer solutions could be cast to excellent, clear, tough, drawable film which could be stretched and oriented at 80°.

A 60/40 copolymer was prepared in exactly the same manner as the 80/20 copolymer described in the preceding paragraph from 30 ml. of 4-methyl-1-pentene and 20 ml. of 1-hexene. The polymer was obtained in 21.0-g. yield and had an inherent viscosity of 2.14 at 130°; it was rubbery and could not be induced to crystallize. Similarly, a 40/60 4-methyl-1-pentene/1-hexene copolymer was prepared from 20 ml. of 4-methyl-1-pentene and 30 ml. of 1-hexene. The yield was 21.5 g. of polymer with an inherent viscosity of 2.50 at 130°. This copolymer also was rubbery and could not be crystallized.

It appeared that proportions of hexene higher than 25% yielded noncrystalline, rubbery polymers. Therefore, a 90/10 4-methyl-1-pentene/1-hexene copolymer was prepared from 45 ml. of 4-methyl-1-pentene and 5 ml. of 1-hexene. This mixture was allowed to polymerize for 3 hr., after which the polymer was isolated, dried, and then redissolved in 200 ml. of cyclohexane. This solution could be cast to clear, tough film. Film strips could be drawn to give highly oriented products which behaved in a manner similar to that described above for the 80/20 copolymer. A crystalline melting point of approximately 205° was observed.

Polymerization of a Mixture of 4-Methyl-1-pentene and 1-Hexene to a Casting Solution. To a catalyst prepared as above was added a mixture of 40 ml. of 4-methyl-1-pentene, 10 ml. of 1-hexene, and 50 ml. of cyclohexane. Polymerization was rapid, and after 45 min. the mixture was poured into a pressure-filtering apparatus and filtered. The filtrate was cast on a glass plate to a film, with the use of an 0.04-in. doctor knife. After drying for 24 hr., an opaque, tough, low modulus film was obtained. It was virtually colorless and could be stretched 2 \times in both directions simultaneously

at room temperature. Its opacity was well distributed throughout the film and was due to the presence of inorganic matter derived from the catalyst.

Crosslinkable Terpolymer. To standard catalyst prepared as described above was added a 100-ml. portion of cyclohexane diluent, followed by 40 ml. of 4-methyl-1-pentene, 10 ml. of 1-hexene, and 10 ml. of divinylbenzene. After 1 hr. the polymer was isolated in the usual manner and dried. It was obtained in a yield of 18 g. and had a viscosity of 2.69 in decahydronaphthalene at 130°. This terpolymer was completely soluble in cyclohexane and could be cast into film, which was rapidly insolubilized (in less than 15 min.) on heating at 225°.

A Copolymer of 4-Methyl-1-pentene and 1-Octene. A mixture of 212 ml. of 4-methyl-1-pentene and 38 ml. of 1-octene was polymerized as in the two preceding experiments. The polymer, isolated in the usual manner in good yield, had an inherent viscosity of 1.95, and was moderately soluble in cold chloroform and easily soluble in cold cyclohexane, and cold carbon tetrachloride, hot chloroform, hot tetrahydrofuran, and hot xylene.

Film samples were pressed at 235° and strips were drawn at 150°. Again, the film strips showed high x-ray crystallinity but no birefringence at room temperature. Birefringence developed on annealing at 100–120°. The product showed a final crystalline melting point of 188°.

Copolymerization of 4-Methyl-1-pentene and 1-Octadecene. A mixture of 212 ml. of 4-methyl-1-pentene and 38 ml. of 1-octadecene was polymerized in exactly the same fashion as in the preceding experiment. The yield of polymer with an inherent viscosity of 2.08 was good.

This copolymer was moderately soluble at room temperature in cyclohexane, chloroform, and tetrachloride and was easily soluble at the boiling point in cyclohexane, chloroform, carbon tetrachloride, tetrahydrofuran, and xylene.

Film samples were prepared by pressing the polymer at 235°C. Film strips were drawn about 8 \times at 150°C. These film strips showed no birefringence when observed with a polarizing microscope at room temperature. However, birefringence developed on annealing, and a crystalline melting point of 182° was measured. The same drawn film samples which showed no birefringence at room temperature showed high x-ray crystallinity and orientation.

References

1. (a) See, for example, A. W. Anderson and N. G. Merckling, U.S. 2,721,189 (1955); A. W. Anderson, N. G. Merckling, and P. Settlage, U.S. 2,799,668 (1957), British 777,535, 777,538, 776, 326, 778,639, 777,414 and others all assigned to E. I. du Pont de Nemours & Co., Inc. (b) D. B. Ludlum, A. W. Anderson, and C. E. Ashby, *J. Am. Chem. Soc.*, **80**, 1380 (1958).
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Synopsis

Poly(4-methyl-1-pentene) has been prepared by polymerizing the monomer over a catalyst made from titanium tetrachloride and lithium aluminum tetradecyl. The molecular weight of the crystalline polymer was invariably too high for fiber preparation, even when polymerization variables were varied drastically, so a technique for thermal cracking was developed. By heating grease-free, crystalline poly(4-methyl-1-pentene) in a vacuum at about 280°, it was possible to lower smoothly the molecular weight of the polymer to any desired value, without undesirable crosslinking or by-product formation. The polymer was melt-spun by conventional techniques to highly oriented, tough fibers. Copolymerization of 10–25% 1-hexene and other linear 1-olefins with 4-methyl-1-pentene gives products which are still high-melting, but which are readily soluble in such solvents as cyclohexane or chloroform, in contrast to the homopolymer which is only slightly soluble. Polymerization in solvents for the copolymer gave solutions which were converted to fibers and film without intermediate isolation of polymer or removal of the catalyst. An interesting terpolymer in which divinylbenzene was the third component was found to be initially soluble, but was readily crosslinked at elevated temperature.

Résumé

Le poly(4-méthyl-1-pentène) a été préparé par polymérisation du monomère sur un catalyseur à base de tétrachlorure de titane et de lithium aluminium tétradécyle. Le poids moléculaire du polymère cristallin était toujours trop élevé pour la préparation de fibres, même quand les conditions de

polymérisation étaient variées drastiquement de telle sorte qu'une technique de cracking thermique a été mise au point. Par chauffage du poly(4-méthyl-1-pentène) cristallin sous vide à environ 280°, on a pu baisser progressivement le poids moléculaire du polymère jusqu'à n'importe valeur désirable, sans pontage ni formation indésirables de produits secondaires. Le polymère était filé à l'état fondu par les techniques conventionnelles en une fibre hautement orientée et dure. La copolymérisation de 10–25% d'hexène-1 et autres oléfines-1 linéaires avec le 4-méthyl-1-pentène fournit un produit qui fond toujours à température élevée, mais soluble dans des solvants tels le cyclohexane et le chloroforme, contrairement au homopolymère qui n'est que faiblement soluble. La copolymérisation en solution fournissait des solutions qui étaient transformés en fibres et films sans isolement intermédiaire du polymère ni élimination du catalyseur. Un terpolymère intéressant, dans lequel le divinylbenzène était le troisième composant, était au début soluble mais était facilement ponté aux températures élevées.

Zusammenfassung

Poly-(4-methyl-1-penten) wurde durch Polymerisation des Monomeren mit einem aus Titan-tetrachlorid und Lithium-Aluminium-tetradecyl hergestellten Katalysator erhalten. Das Molekulargewicht des Polymeren war auch bei drastischer Variierung der Polymerisationsbedingungen in allen Fällen für die Herstellung von Fasern zu hoch; es wurde daher eine Methode zur thermischen Krackung entwickelt. Durch Erhitzen von fettfreiem, kristallinen Poly-(4-methyl-1-penten) im Vakuum auf etwa 280° war es möglich das Molekulargewicht des Polymeren glatt und ohne unerwünschte Vernetzung oder Bildung von Nebenprodukten auf jeden gewünschten Wert herabzusetzen. Das Polymere wurde nach den konventionellen Methoden im Schmelzspinnverfahren zu hochorientierten, zähen Fasern verarbeitet. Copolymerisation von 10–25 1-Hexen und anderen linearen 1-Olefinen mit 4-Methyl-1-penten ergibt ein Produkt, das zwar noch einen hohen Schmelzpunkt hat, aber, im Gegensatz zu dem nur schwach löslichen Homopolymeren, in Lösungsmitteln wie Cyclohexan und Chloroform leicht löslich ist. Polymerisation in Lösungsmitteln für das Copolymer ergab Lösungen, die ohne vorherige Isolierung des Polymeren oder Entfernung des Katalysators zu Fasern und Filmen verarbeitet wurden. Bei einem interessanten Terpolymeren, dessen dritte Komponente Divinylbenzol war, wurde festgestellt, dass es zunächst löslich war, aber bei höheren Temperaturen leicht vernetzt wurde.

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