A Study of the Effect of Branching on Certain Physical and Mechanical Properties of Stereoregular Polypropylene

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Synopsis

The properties of stereoregular polypropylene have been modified by the introduction of controlled branching into the polymer chain backbone. Branching is achieved by copolymerizing propylene with certain long-chain 1-olefins by using a standard Ziegler-Natta low pressure catalyst. Physical and mechanical properties of the copolymers are related to the degree and length of branching. It was found that ultimate strength properties of moderate molecular weight polymers could be improved at some expense in short-range deformation properties by adjusting the degree of branching to a suitable level. The copolymers did not show a good combination of low temperature brittleness characteristics along with higher temperature strength properties. It is suggested that the branching technique described will allow the tailoring of polypropylene resins for specific end use applications.

INTRODUCTION

The relationship between molecular structure and physical properties of crystalline polypropylene has been discussed in considerable detail in recent publications.[1-3] These papers deal with work to relate the mechanical properties of various polypropylene samples with the average molecular weight and crystallinity of the resin. Generally, in these experiments, the crystallinity of the polymer has been adjusted by the inclusion of more or less atactic polypropylene in the sample of isotactic material. In the case of polyethylene there are no atactic or isotactic forms since there is no regular sequence of asymmetric carbon atoms along the backbone. For polyethylene studies of structure–property relationships, the technique of chain branching has been used to adjust the crystallinity and determine the effect of variation of this parameter on polymer properties.[4,5] Branching occurs to a considerable extent in the free-radical, high pressure homopolymerization process[6] and results in a resin of relatively low density. The Ziegler-Natta type low pressure catalysts produce a more highly linear, high density product. In order to introduce branching into these more linear materials the technique of copolymerization has been employed. The preferred comonomers, both with respect to price and adaptability to the catalyst system, are the 1-olefins; in particular butene-1[7] and pro-

pylene.[8] Folt has recently published a paper which describes the properties of a series of copolymers of ethylene and various 1-olefins.[9]

In the case of isotactic polypropylene the use of controlled branching to maintain a desired level of crystallinity is to be preferred over inclusion of atactic material for several reasons. Among these are the ease of exact control over density with the use of the 1-olefin copolymerization and the relative insolubility of the resultant copolymers in aliphatic hydrocarbons even at low levels of crystallinity.

Only fragmentary data[2] are available on the preparation and properties of propylene–long-chain 1-olefin copolymers. These branched polypropylenes offer a range of properties not available from the homopolymers alone and hence are of interest from the standpoint of tailoring polymers for specific applications.

This paper will describe the effect of the degree of branching, for two different average branch lengths, on certain physical and mechanical properties of highly isotactic polypropylene.

EXPERIMENTAL

Copolymers of decene-1 and $CH_3(CH_2)_nCH=CH_2$ (where $n = 12-17$, $\bar{n} = 14.3$) with propylene were prepared by using a standard Ziegler-Natta type low pressure catalyst. The ratio of 1-olefin comonomer to propylene in the finished resin was adjusted by control of the feed ratios. Molecular weight of the samples was controlled by the addition of small quantities of hydrogen along with the propylene feed gas. At the conclusion of the polymerization, the polymer slurry was quenched to solubilize catalyst residues and then extracted six times with boiling hexane to assure that no long-chain 1-olefin homopolymer was present in the finished product. Prior experiments had shown that both polydecene and polyoctadecene were soluble in hot hexane. Two of the more highly branched copolymers were further extracted for >16 hr. with boiling hexane in a Soxhlet extraction apparatus. These samples showed essentially no change in composition with the continued extraction. It was concluded that the samples were either true copolymers or blends of copolymer with propylene homopolymer.

Analysis of the copolymers for mole per cent long chain 1-olefin was carried out by infrared spectroscopy with a Perkin-Elmer 221 spectrophotometer. The CH_2 rocking vibration at 719 cm.$^{-1}$ was used as the analytical band. Known blends of polydecene and polyoctadecene with polypropylene were used for calibration. Compression-molded samples of 10–20 mils thickness were prepared from the blends and scanned from 770 to 670 cm.$^{-1}$. The absorbance at 719 cm.$^{-1}$ was obtained, and a plot of absorbance/mil versus mole per cent poly-1-olefin was constructed.[10a] The calibration curves which resulted are shown in Figure 1.

These curves were then used to establish the degree of branching in copolymer samples. This calibration technique makes the tacit assump-
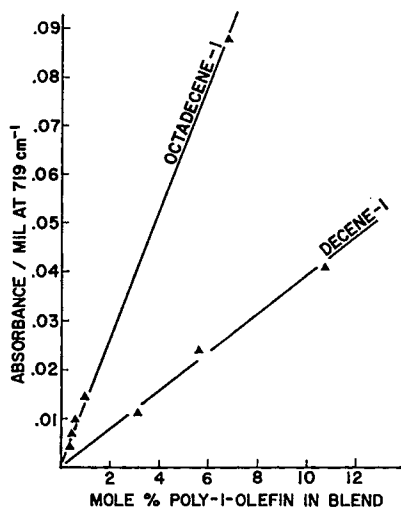
Fig. 1. Mole-% long-chain 1-olefin polymer in the blend vs. absorbance per mil at 719 cm.$^{-1}$.

tion that the absorbance per unit thickness of polyoctadecene is the same as for the polymer of $CH_3(CH_2)_{14.3} CH=CH_2$. The error introduced by this assumption should be small (i.e., compare molar extinction coefficient values for aliphatic hydrocarbons differing by one —CH_2—unit).[10b]

Polymer samples for evaluation of properties were cut from compression molded, annealed slabs of appropriate thickness. Annealing of all samples was carried out at 135°C. for two hours in a forced draft oven. Conditions for the various tests are shown in Table I. All tests were conducted at 23°C. and 50% R.H. unless otherwise stated in the test method.

The stress–strain behavior of the samples was studied on an Instron Model TTB testing machine. Figure 2, curve *A*, shows a typical stress–strain curve for a high molecular weight, highly crystalline polymer.

TABLE I
Testing Procedures for Polymer Evaluation

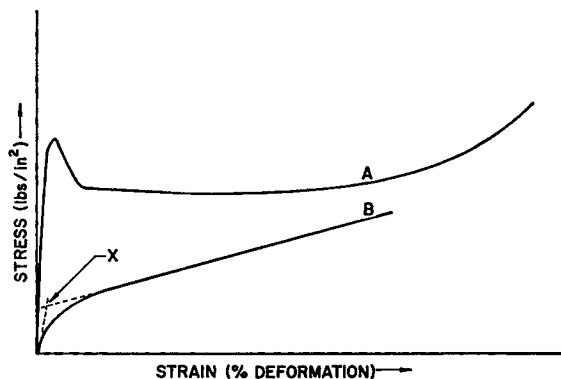| Test for	ASTM testing procedure	Comments
Density	D 792-60T	Method A
5% Secant modulus	D 1530-58T	0.1 in./min. cross-head speed
Tensile, yield	D 638-60T	2 in./min. crosshead speed
Tensile, fail	"	
% Elongation, fail	"	
Izod impact	D 256-56	Method A
Clash-Berg modulus	D 1043-51	Assume Poisson's ratio $\sim 1/2$
Brittleness temp.	D 746-57T	
Melt flow	D 1238-57T	2160 g. wt., 230°C.

Fig. 2. Typical stress–strain curves for (A) a high molecular weight, high density polypropylene and (B) a high molecular weight, low density polypropylene. X denotes the apparent yield strength for the low density sample.

After the initial more or less linear portion of the stress–strain curve, the specimen goes through a yield point which is designated the tensile at yield strength. After this initial yield, the sample begins to cold draw and orientation takes place. This cold drawing continues with little or no increase in stress until the orientation is essentially complete at which time the stress increases rapidly with strain until ultimate failure occurs. The tensile at yield, tensile at fail, and per cent elongation at fail are all obtained from this curve. The fail point may occur anywhere along the curve depending upon the brittleness of the sample. Indeed, certain highly crystalline polymers of low molecular weight break at the yield point before any cold drawing can occur.

Curve B of Figure 2 shows a typical stress–strain curve for a high molecular weight polypropylene of low crystallinity. These materials are quite soft and flow easily at low stress. In these curves there is no well established yield point, and the intercept of the two linear portions of the curve (X) is taken as the "apparent" yield strength. Other values are determined as usual.

RESULTS AND DISCUSSION

A summary of data collected on a series of branched and nonbranched polypropylenes is shown in Table II. Correlations based on these data will be discussed.

A. Degree of Branching versus Density

Folt[9] has pointed out that in the case of branched low pressure polyethylenes, the density of the resin is a function of the number of branches per unit backbone length and is essentially independent of the branch length for C_1 through C_6 branching. In the case of polypropylene with the longer branch lengths, this does not appear to be the case. Figure 3 shows a plot

TABLE II
Summary of Data on Some Branched and Unbranched Polypropylenes

Run no.	Melt flow at 230°C. MF_{230}	Density, g/cc.	1-Olefin in copolymer, mole-%	5% Secant modulus × 10⁻⁴ lb./in.²	Tensile yield, lb./in.²	Tensile fail, lb./in.²	Elongation, fail, %	Notched impact, (ft.-lb./in. notch)	Low temperature brittleness T_b, °C.
HP-1	0.01	0.9082	0.	6.42	4245	5791	570	>10	−6.0
HP-2	0.05	0.9080	0.	6.18	4472	4702	650	>10	−0.6
HP-3	0.21	0.9098	0.	6.82	4681	3642	750	5.5	
HP-4	0.72	0.9105	0.	6.78	4617	3348	480	0.5	+6.2
HP-5	2.61	0.9107	0.	7.43	4935	At yield[a]	<20	0.4	+14.3
HP-6	3.29	0.9113	0.	7.30	4848	At yield[a]	18	0.4	+19.4
C₆-1	1.72	0.9054	0.7	7.61	4968	3204	240	0.7	—
C₆-2	4.00	0.9044	1.1	6.76	4815	2755	190	1.0	+21.0
C₆-3	17.70	0.9022	2.4	6.46	4092	3676	570	1.0	
C₆-4	1.32	0.8994	3.5	4.71	3662	5644	650	3.2	
C₆-5	2.32	0.8996	3.6	4.54	3450	4707	572	2.1	
C₆-6	0.71	0.8960	4.8[b]	3.10	2526	5225	612	>10	
C₁₆-1	≪0.01	0.9057	0.06	5.62	4193	5572	600	>10	
C₁₆-2	1.93	0.9089	0.06	7.31	4792	3100	110	0.4	
C₁₆-3	≪0.01	0.9045	0.10	5.03	4034	5288	600	>10	
C₁₆-4	≪0.01	0.9038	0.20	4.98	3849	5018	500	>10	
C₁₆-5	0.26	0.9075	0.26	6.31	4552	3305	630	1.8	
C₁₆-6	0.14	0.9006	1.4	4.84	3735	5182	570	6.4	
C₁₆-7	4.54	0.8970	2.5	3.46	2370	3129	382	2.9	−2.0
C₁₆-8	1.38	0.8913	4.0	1.81	—	—	—	—	
C₁₅-9	≪0.01	0.8875	4.9[c]	1.53	1552[d]	4508	436	—	
C₁₆-10	≪0.01	0.8739	6.1	0.36	637[d]	1896	288	—	−24.0
C₁₆-11	0.08	0.8778	6.2	0.62	762[d]	1831	346	—	−15.0

[a] Samples show no "neck down" prior to failure.
[b] After >16 hr. extraction with boiling hexane, sample analysis indicates 4.6 mole-% 1-olefin in the copolymer.
[c] After >16 hr. extraction with boiling hexane, sample analysis indicates 5.0 mole-% 1-olefin in the copolymer.
[d] No true yield point for these samples. Value shown is for the first break in the stress–strain curve (see text for explanation).

of density versus mole per cent long-chain 1-olefin in the polymer. The $C_{15\text{-}3}$ branching is clearly more effective in lowering the density at a given molar concentration level than is the C_8 branching.

B. Short-Range Deformation Properties

Certain short-range deformation properties of semicrystalline high polymers have been found to be principally functions of the degree of crystallinity.[11] Among these crystallinity dependent properties are modulus, hardness, tensile at yield strength, and crystalline melting point. Thus, on the basis of data shown in Figure 3, we should expect the modulus and tensile strength at yield of branched polypropylene to decrease in a regular fashion with increasing degree of branching. Figures 4 and 5 show the relationship between the mole per cent long-chain 1-olefin in the copolymer and the modulus and yield strength. In each case the property varies in the expected fashion with the changing degree of branching. It is inter-
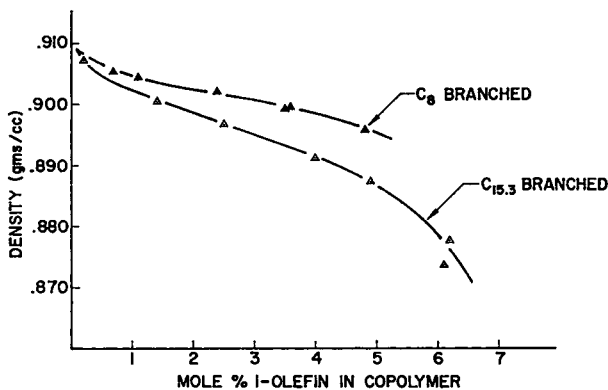
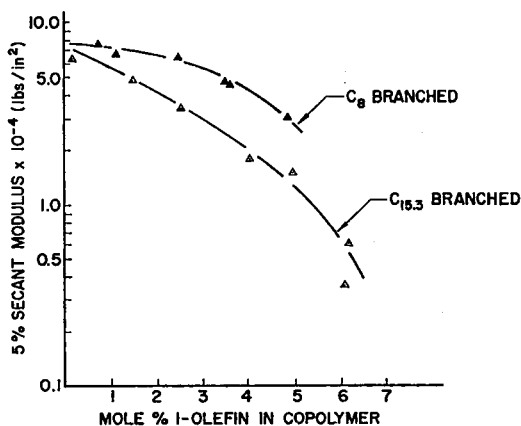Fig. 3. Mole-% long-chain 1-olefin in the copolymer vs. the annealed density.

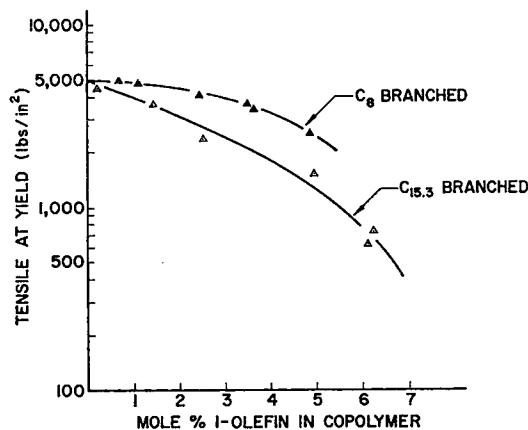Fig. 4. Mole-% long-chain 1-olefin in the copolymer vs. the 5% secant modulus.

Fig. 5. Mole-% long-chain 1-olefin in the copolymer vs. the tensile strength at the yield point.
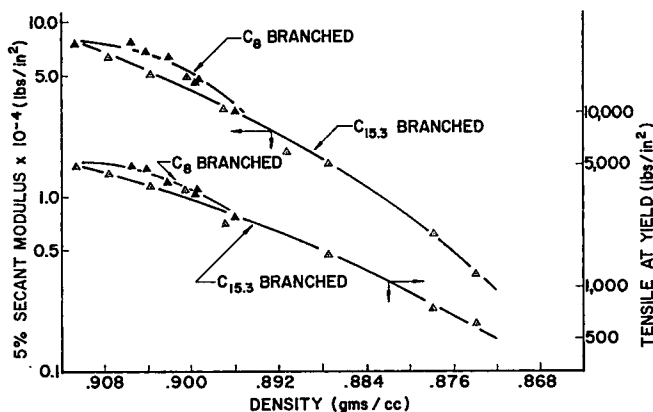

Fig. 6. 5% Secant modulus and tensile at yield vs. density for the two different branch lengths.

esting to note, however, that the same density versus property relationship does not hold for the two different branch lengths. Figure 6 shows that at the lower degrees of branching (i.e., $C_8 < 3$ mole-%) the shorter branch length gives higher modulus and yield strength for a given density than does the longer branch length. The reason for this divergence in the data is not clear but it indicates that one must be cautious in applying density–crystallinity relationships developed for propylene homopolymer to the new copolymer types.

The low temperature modulus of polypropylene is of particular commercial interest in view of the polymer's poor low temperature brittleness characteristics. It should be possible to improve the low temperature impact strength of a resin by reducing the elastic modulus to a suitable level.[12] Figures 7 and 8 show the effect of branching on the modulus of polypropyl-

ene over a wide range of temperatures.   Included in the graphs are data on a commercial rubber–polypropylene blend.   Over the temperature range studied, the rubber blend is superior to either branched polymer in its retention of room temperature modulus for a given lowering of the modulus at low temperature.   As might be expected from the results of Reding, et al.,[13]
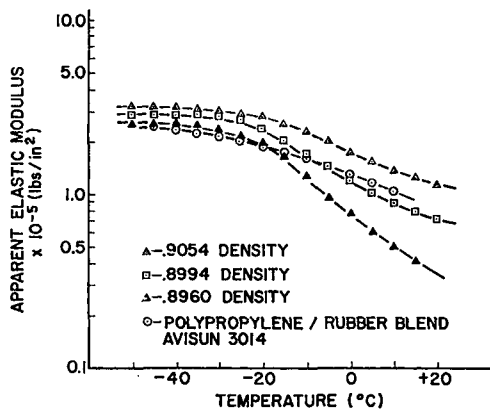

Fig. 7. Apparent modulus vs. temperature for C_3 branched polypropylenes and a rubber–polypropylene blend.
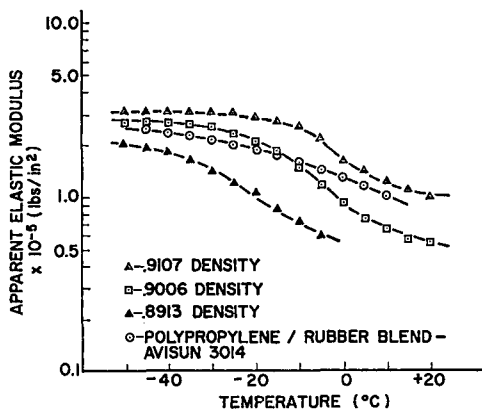

Fig. 8. Apparent modulus vs. temperature for $C_{15.3}$ branched polypropylenes and a rubber–polypropylene blend.

the apparent T_g of the branched polymers (i.e., the break point in the modulus–temperature curve) is not much changed from the T_g of propylene homopolymer.   Since the curves converge rapidly at temperatures below the break point, a small decrease in modulus at low temperature results in a much larger modulus decrease at the higher temperatures.   This is an undesirable characteristic of the copolymer and a weakness from which the blend does not suffer to as great an extent.

C. Long-Range Deformation Properties

The ultimate strength of polypropylene is known to be strongly dependent upon the average molecular weight.[1,2] In the case of polyethylene, it has been shown that the degree of crystallinity has little effect upon the fail strength.[9] In this work the melt flow of the polymer at 230°C. has been used as a measure of average molecular weight. The use of melt viscosity as a measure of molecular weight for branched polymers is a doubtful technique; however, the error involved may not be too large since the branch lengths are short compared to the polymer chain backbone length.[14] At any rate, this melt flow value is important since it is the specified molecular weight parameter in the sale of most resins. Figure 9 shows a plot of density versus tensile at fail for modified polypropylene at two levels of average melt flow. Variation in density for a given average melt flow was achieved by adjusting the degree of branching.

Contrary to the case of polyethylene, relatively low molecular weight polypropylene (i.e., $MF_{230} > 2$) is not soft enough to cold draw to any great extent during the tensile test. Incorporation of branching into the polymer produces a softer material which can flow more easily and, to a point,
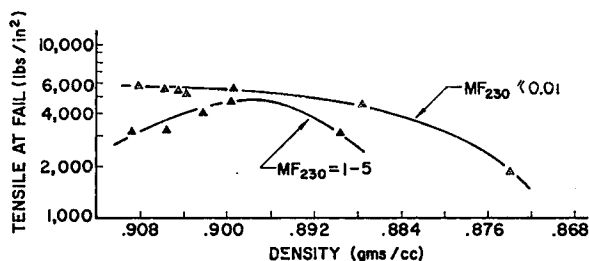

Fig. 9. Density of copolymers vs. the tensile strength at the fail point for two levels of average melt flow.
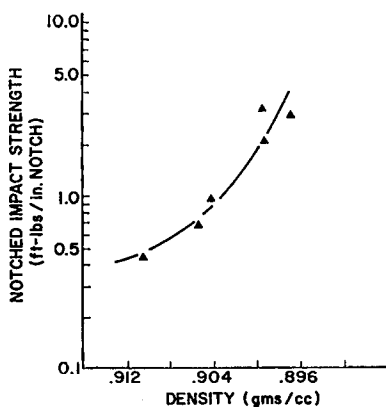

Fig. 10. Density of copolymers vs. the notched impact strength for resins in the 1–5 melt flow range.

will give improvement in the measured fail strength. At very high degrees of branching (i.e., density < 0.896) the tensile at fail value drops off again for these low molecular weight samples. High molecular weight materials ($MF_{230} \leqslant 0.01$), on the other hand show a consistent decrease in fail strength with increasing degree of branching. High molecular weight polypropylene is relatively soft and tough even at high levels of crystallinity (cf. Sample HP-1, Table II). These findings are consistent with Nielsen's suggestion[15] that in brittle polymers crystallites can act as stress concentrators and weaken the sample, whereas, for tough or rubbery polymers, increased crystallinity results in a stronger material.

Izod impact strength is a measure of the energy necessary to cause failure of a polymer sample under shock loading. It is directly related to the ultimate strength and is an inverse function of the elastic modulus.[12] It should be expected, then, that in the case of the lower molecular weight polypropylenes, moderate degrees of branching would result in improvement in impact strength for samples of equivalent molecular weight. Figure 10 shows a plot of Izod impact strength versus density for a series of branched polymers of $MF_{230} = 1$–5. Again the density was adjusted by control of the degree of branching. It is clear that in this melt flow range an increase in branching does result in an improvement in impact strength.

TABLE III
Dependence of the Brittleness Temperature (T_b) on Elastic Modulus and Ultimate Strength

Run no.	T_b, °C.	Elastic modulus $\times 10^{-5}$ at T_b, lb./in.^{2}	Tensile, fail at 23°C., lb./in.^{2}
C_{15}-11	-15.0	0.36	1831
C_{15}-10	-24.0	0.49	1896
C_8-2	21.0	0.98	2755
C_{15}-7	-2.0	1.00	3129
HP-2	-0.6	1.80	4702
HP-1	-6.0	2.10	5791

The low temperature brittleness characteristics of certain branched polypropylenes were compared to similar measurements on propylene homopolymer (cf. Table II). Once again one should expect that the property will be a function of both elastic modulus and ultimate strength since this test is basically a fail or no fail impact test over a range of temperatures. Ultimate strength data as a function of temperature are not available. Table III shows data on the elastic modulus at the brittle temperature plus room temperature ultimate strength data on the samples tested. In a qualitative sense, the dependence of the brittleness temperature on these two parameters is apparent. A high modulus polymer having a high ultimate strength can show an impact strength equivalent to that of a low modulus sample of low ultimate strength.

TABLE IV

Properties of C_8 Branched Polypropylene as a Function of the Degree of Branching for Melt Flow 230 ≃ 3

Property	Decene-1 content					
	0	1 mole-%	2 mole-%	3 mole-%	4 mole-%	5 mole-%
Density, g./cc.	0.910	0.905	0.902	0.900	0.898	0.895
5% Secant modulus × 10⁻⁴, lb./in.²	7.4	7.2	6.6	5.6	4.3	2.8
Tensile, yield, lb./in.²	4950.0	4800.0	4400.0	3900.0	3300.0	2400.0
Tensile, fail, lb./in.²	<3000.0	3800.0	4300.0	4500.0	4500.0	4200.0
Elongation, fail, %	<20.0	200.0	500.0	600.0	550.0	500.0
Notched impact strength, ft.-lb./in. notch	0.5	0.8	1.2	2.0	3.2	~10.0

The rheological properties of the branched polypropylenes have not been studied in detail as yet but it is well known[14,16-17] that branching can have a profound effect on the flow behavior of polymers. Such studies will be required in order to predict the behavior of the new polymer types during commercial molding operations.

SUMMARY AND CONCLUSIONS

This work has shown one way in which polypropylene can be modified in order to improve certain of its mechanical properties. The technique allows improvement in the ultimate and impact strengths at some cost in short range deformation properties. By adjusting the length and degree of branching, the properties of the polymer can be varied over a wide range such that a specific set of properties can be built into a resin designed for a specific end use. As an example of the range of properties available in a particular case, a composite of information on C_8 branched polypropylene of moderate molecular weight is shown in Table IV.

The copolymers described do not show desirable low temperature properties. In order to improve low temperature brittleness characteristics by copolymerization while maintaining good room temperature properties, it would be desirable to find a comonomer which lowers the T_g of the copolymer to an acceptable level with a minimum loss of high temperature modulus and ultimate strength.

References

1. van Schooten, S., H. van Hoorn, and J. Boerma, *Polymer*, **2**, No. 2, 161 (1961).

2. Shearer, N. H., Jr., J. E. Guillet, and H. W. Coover, Jr., *SPE Journal*, **17**, 83 (1961); *ibid.*, p. 88, Table I.

3. Crespi, G., and F. Ranalli, *Trans. Plastic Inst. (London)*, **27**, No. 68, 55 (1959).

4. Nielsen, L. E., *J. Appl. Phys.*, **25**, 1209 (1954).

5. Nielsen, L. E., *J. Appl. Polymer Sci.*, **2**, 351 (1959).

6. Sperati, C. A., W. A. Franta, and H. W. Starkweather, Jr., *J. Am. Chem. Soc.*, **75**, 6127 (1953).

7. Pritchard, J. E., R. M. McGlamery, and P. S. Boeke, *Modern Plastics*, **37**, 132 (1959).

8. Natta, G., G. Mazzanti, A. Valvassori, and G. Pajaro, *Chim. Ind. (Milan)*, **39**, 733 (1957).

9. Folt, V. L., *SPE Trans.*, **2**, No. 4, 285 (1962).

10. West, W., *Chemical Applications of Spectroscopy*, Interscience Publishers, New York, 1956, (a) p. 344; (b) *ibid.*, p. 347.

11. Renfrew, A., and P. Morgan, *Polythene*, Interscience Publishers, New York, 2nd Ed., 1960, p. 169.

12. Alfrey, T., Jr., *Mechanical Behavior of High Polymers*, Interscience Publishers, New York, 1948, p. 493.

13. Reding, F. P., J. A. Faucher, and R. D. Whitman, *J. Polymer Sci.*, **57**, 483 (1962).

14. Peticolas, W. L., *J. Polymer Sci.*, **58**, 1405 (1962).

15. Nielsen, L. E., *Mechanical Properties of Polymers*, Reinhold, New York, 1962, p. 116.

16. Ferry, J. D., *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, p. 173.
17. Schreiber, A. P., and E. B. Bagley, *J. Polymer Sci.*, **58**, 29 (1962).

Résumé

On a modifié les propriétés de polypropylènes stéréoréguliers par l'introduction contrôlée de ramifications dans l'épine dorsale du polymère. La ramification est obtenue en copolymérisant le propylène avec des oléfines-1 à longue chaîne en présence d'un catalyseur standard Ziegler-Natta à basse pression. Les propriétés physiques et mécaniques des copolymères sont reliées au degré de ramification et à sa longueur. Il a été trouvé que les propriétés extrèmes de tension de polymères de poids moléculaires modérés peuvent être améliorées en propriétés de déformation à courte distance par ajustage à un niveau ad hoc du degré de ramification. Les copolymères n'ont pas montré une bonne combinaison entre les caractéristiques de fragilité à basse température et les propriétés de tension aux températures plus élevées. On suggère que la technique de branchement décrite permettra l'élaboration de résines de polypropylène pour des applications à dez fins spécifiques.

Zusammenfassung

Die Eigenschaften von stereoregulärem Polypropylen wurden durch Einführung einer kontrollierten Verzweigung in die Polymerkette modifiziert. Die Verzweigung wird durch Copolymerisation von Propylen mit bestimmten langkettigen 1-Olefinen mit einem Standard-Ziegler-Natta-Niederdruckkatalysator erreicht. Physikalische und mechanische Eigenschaften der Copolymeren werden zu Grad und Länge der Verzweigung in Beziehung gebracht. Die Reissfestigkeit von mässig hochmolekularen Polymeren konnte auf Kosten der Deformationseigenschaften bei kleiner Verformung durch Adjustierung des Verzweigungsgrades auf ein geeignetes Ausmass verbessert werden. Die Copolymeren zeigten keine gute Kombination von Niedertemperatur-Sprödigkeit mit den Festigkeitseigenschaften bei höherer Temperatur. Das beschriebene Verzweigungsverfahren könnte die Anfertigung von Polypropylenharzen nach Mass für spezifische Verwendungszwecke erlauben.