

## Properties of Semicrystalline Polyolefins: Poly-4-methyl-1-pentene

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### Synopsis

A study has been carried out of the thermodynamic properties, physical and mechanical properties, and crystallization behavior of poly-4-methyl-1-pentene (poly-4-MP). Data were obtained for the heat and entropy of fusion. Poly-4-MP is characterized by a comparatively high tensile strength, stiffness, and surface hardness. The impact is low at room temperature. The adverse effect of temperature on tensile strength, creep, and other polymer properties is greater for poly-4-MP than for polypropylene. Poly-4-MP is highly transparent, probably due to limited spherulite growth. Spherulitic growth was promoted through copolymerization with propylene by a technique of sequential monomer addition. The resultant product had an increased crystalline melting point (244 vs. 238°C. for the poly-4-MP homopolymer). The significance of these results and the effect of temperature on the birefringence of poly-4-MP are discussed.

Poly-4-methyl-1-pentene (poly-4-MP) is, in many respects, a unique polyolefin. It has a high melting point of 240°C. It has a low density,<sup>1,2</sup> and, surprisingly, the density of the amorphous polymer exceeds that of the crystalline material below 50°C. Its crystallographic identity period of 13.8 Å. is consistent with a helical structure incorporating seven monomer units per two turns of the helix. Although crystalline, poly-4-MP, unlike polyethylene and polypropylene, readily produces transparent films and molded articles. The polymer was described briefly by Campbell<sup>3</sup> and was studied in greater detail by Griffith and Rånby,<sup>4,5</sup> who reported the glass transition temperature as well as higher order transitions and discussed the abnormal density behavior of poly-4-MP. Little, however, has been reported on the thermodynamic properties, physical and mechanical properties, and crystallization behavior of this interesting polymer. Most recently, Inoue<sup>6</sup> reported that poly-4-MP spherulites formed from the melt have sheaflike fibrous structures. These observations were made by phase contrast microscopy since the spherulites could not be observed with polarized light because of weak birefringence.

It was felt that this polymer should manifest its unusual properties in its behavior under stress and at elevated temperatures. Data were obtained for the heat and entropy of fusion. Mechanical properties and

creep were studied as a function of temperature. The effects of crystallization and crystal habit upon the properties of poly-4-MP were also investigated.

## EXPERIMENTAL

Poly 4-methyl-1-pentene polymers were prepared with aluminum alkyl-transition metal catalyst systems in the manner described previously.<sup>3,7,8</sup> Escon polypropylene was supplied by the Enjay Chemical Company, New York City.

### Tensile Measurements

Tensile properties were obtained with an Instron testing machine (Instron Engineering Co., Canton, Mass.) at a crosshead speed of 2 in./min. Effective sample length was 2 in. for dumbbell-shaped test specimens. Fiber properties were measured on 18 strand multifilament with an effective specimen length of 5 in. Load/crosshead records were obtained autographically, and from these tensile values were obtained. For those specimens which yielded, the strength was calculated as the maximum yield load divided by the original cross-sectional area of the specimen. The strength of specimens which broke without yielding was calculated from the breaking load divided by the original cross-sectional area. Elongation is reported as the distance moved by the crosshead in either yielding or breaking the specimen.

### Heat Distortion Measurements

Heat distortion measurements were carried out on a Model 10-201 heat distortion tester sold by the American Instrument Company of Silver Spring, Md. The procedure used was ASTM D-648.<sup>9</sup>

### Melting Point Determination

Melting points were taken as the temperature at which birefringence could no longer be observed from a sample (in the form of a thin film) which was heated on a Kofler hot stage at a rate of 2°C./min.

## RESULTS AND DISCUSSION

### Heat and Entropy of Fusion

An approximate value of  $2850 \pm 450$  calories/mole for the heat of fusion of poly 4-MP was obtained by application of the Flory equation<sup>10</sup> to the melting points of a series of random 4-MP-propylene copolymers. The entropy of fusion is therefore about  $5.6 \pm 0.9$  e.u. Other data in our laboratories have indicated that the entropy of fusion may be closer to 4.8 e.u. and  $\Delta H_u$  about 2500 cal./mole.

### Mechanical and Physical Properties

Poly-4-MP is characterized by a comparatively high tensile strength, stiffness, and surface hardness. As noted previously, it is highly transparent, probably due to limited spherulite growth. The impact is low at room temperature (0.5 ft.-lb./in. of notch compared to 1 ft.-lb./in. for polypropylene). Data are summarized in Table I and are compared with the properties of polypropylene.

TABLE I  
Mechanical and Physical Properties of Poly-4-MP

Polymer properties	Poly-4-MP	Polypropylene
Density, g./cc.	0.83	0.90
Tensile, psi (D-638) <sup>a</sup>	4500	4900
Elongation, %	5	12
Flexural stiffness, psi (D-747) <sup>a</sup>	170,000	140-175,000
Secant modulus (D-638) <sup>a</sup>	$2.24 \times 10^5$	—
Tangent modulus (D-638) <sup>a</sup>	$2.40 \times 10^5$	$1.9 \times 10^5$
Rockwell hardness (D-785) <sup>a</sup>	R80	R90
Shore D hardness (D-1706) <sup>a</sup>	80	75
Izod impact (notched), ft.-lb./in. (D-256) <sup>a</sup>	0.5	1
Clarity	Transparent	Translucent to opaque

<sup>a</sup> ASTM Standards on Plastics.<sup>9</sup>

The poly 4-MP described in Table I had an inherent viscosity of about 2.5 dl./g., as measured in decalin at 135°C. at a concentration of 0.453 g./l.

### Effect of Temperature

Thermoplastics generally lose strength at elevated temperatures. The extent of the loss depends upon the molecular weight, crystallinity, and crystal size. This adverse effect of elevated temperatures on polymer

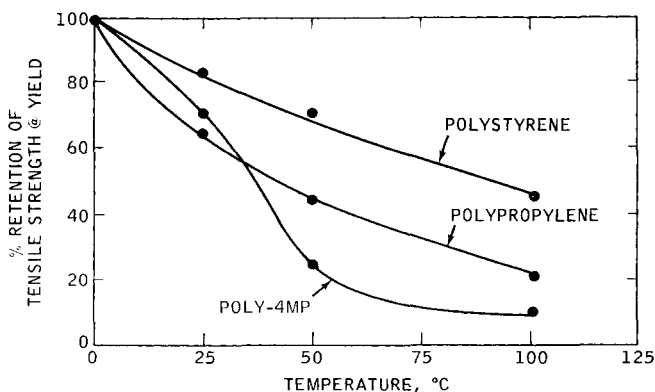


Fig. 1. Adverse effect of temperature on tensile strength.

properties appears to be greater for poly-4-MP than for polypropylene. Strength retention versus temperature data for tensile dumbbells of poly-4-MP and for polypropylene are shown in Figure 1. For comparison, data are also shown for commercial polystyrene. Similar results were obtained with fiber samples. The fibers were chosen for these tests in order to obtain measurements on polymer samples of maximum crystallinity and orientation. Poly-4-MP fibers showed 40% retention of room temperature breaking strength at about 90°C. At the same temperature, polypropylene showed a 60% retention of room temperature strength and nylon 66 over 90% retention.

The comparatively rapid loss in tensile strength with temperature is in line with the observation that poly-4-MP has an abnormally low heat distortion temperature. Comparative data at 66 psi (ASTM-D648) are shown in Table II. It is of interest that the homolog poly-3-methyl-1-butene has a heat distortion temperature closer to that which we would expect from its high melting point.

TABLE II  
Heat Distortion Data For Various Polymers

Polymer	Heat distortion temp., °C.	Melting point, °C.
Poly-4-MP	58	240
Polypropylene	110	170
Nylon 66	185	260
Polycarbonate	143	263
Poly-3-methyl-1-butene	155	310

The definition of heat distortion temperature is arbitrary. In the ASTM test used to obtain the data for poly-4-MP, a  $5 \times \frac{1}{2} \times \frac{1}{8}$  in. beam is supported at two points while a 66 or 264 psi load is applied at the mid-point between them. The load is applied to the  $\frac{1}{8}$  in. edge and the heat distortion temperature is taken as that temperature at which the test specimen has deformed 0.010 in. when the heating rate is 2°C./min. Silicone oil is used as heat transfer medium. Thus, as this test is usually carried out, only a single point on the deflection-temperature curve is recorded. A more significant comparison may be obtained by measurement of the beam deflection over a range of temperatures. Such a comparison is shown in Figure 2 for poly-4-MP and polypropylene under 66 and 264 psi loads at 30–100°C. The data shown confirm that at all temperatures of interest poly-4-MP exhibits lower dimensional stability in a flexure test than does polypropylene.

The creep of poly-4-MP was studied further by obtaining deflection-time curves at 50°C. Data are shown in Figure 3 for poly-4-MP and polypropylene. Again, it is apparent that the initial rate of creep for poly-4-MP is much greater than the rate for polypropylene even at the

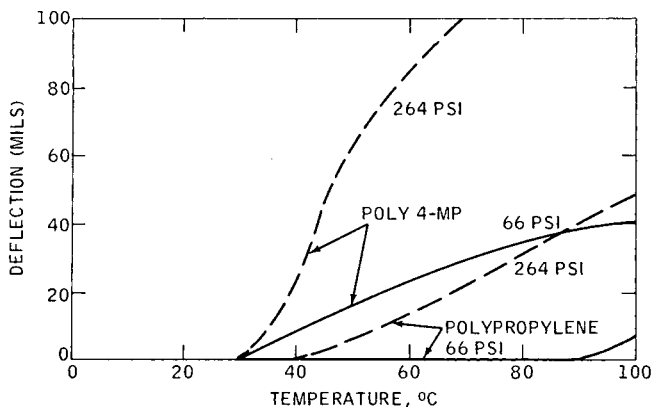


Fig. 2. Heat distortion: deflection vs. temperature.

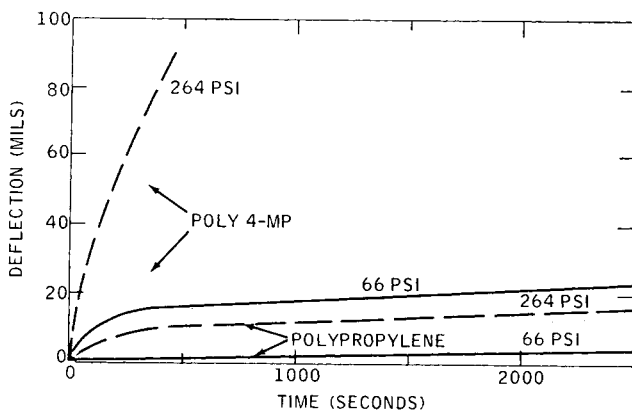


Fig. 3. Heat distortion: deflection vs. time at 50°C.

comparatively low temperature of 50°C. To some extent, the sensitivity to temperature of the strength and creep properties of poly-4-MP may be due to crystalline phase changes and spherulite growth phenomena. Thus, treating a poly-4-MP pad under conditions which can increase crystallinity and spherulite growth, raised the heat distortion temperature by as much as 35–40°C (Table III). As might be expected, decreasing crystallinity results in a sharp reduction in heat distortion temperature. For example, random copolymerization of 4-methyl-1-pentene with propylene has led to a drastic reduction in crystallinity and a marked lowering of the heat distortion temperature even at low propylene incorporation. Introduction of only 3.4% propylene into the polymer leads to a decrease in the crystalline melting point from 238 to 226°C and is accompanied by a reduction in the heat distortion temperature from 58 to 30°C.

In line with the comparatively low heat distortion temperature and comparatively high rate of creep for poly-4-MP, the Vicat softening

TABLE III  
Effect of Treatment on Heat Distortion Temperature (66 psi)

Treatment of test pad	Heat distortion temp., °C. <sup>a</sup>
None (control, 6 min. cooling)	57, 58
Annealing of Control Pad	
6 hr. at 155°C.	71
6 hr. at 195°C.	95
Extracted polymer (100% heptane-insoluble, 6 min. cooling)	79

<sup>a</sup> Polypropylene (6 min. cooling) has a heat distortion temperature of about 110°C.

temperature of poly-4-MP is low. The Vicat softening point is the temperature at which a flat-ended needle of 1 mm.<sup>3</sup> circular cross section penetrates the flat side of a  $\frac{3}{4}$  in. wide,  $\frac{1}{2}$  in. thick thermoplastic specimen to a depth of 1 mm. under a 1000–1100 g. total load. In this test, silicone oil is used as a heat transfer medium, and the temperature of the sample is raised uniformly at a rate of 50°C./hr. This test, while particularly suited for polyethylene, can be used for other materials. The Vicat softening temperature of poly-4-MP is about 40°C. lower than that of polypropylene (100 versus 138°C.).

### Morphological Studies

Although poly-4-MP is a comparatively highly crystalline polymer, very little spherulitic growth is observed with this material with the use of normal modes of preparation. Indeed, the high clarity of molded plaques of poly-4-MP is indicative of small crystallites which are not associated into larger spherulitic aggregates. An attempt was, therefore, made to promote spherulitic growth.

The present research showed that it is possible to promote spherulitic growth in poly-4-MP through copolymerization with propylene by a technique of sequential monomer addition. In this technique, 4-MP is polymerized with an ionic coordinate type catalyst system, and a small quantity of propylene (0–7 wt.-%) is introduced into polymerization mixture before the final stage of polymerization. An additional amount of 4-MP is added after the propylene is consumed. This results in an intimate polymer mixture of polypropylene, poly-4-MP, and a copolymer of the two monomers. Typical fractionation data of a polymer containing 7.0% propylene could be rationalized on the basis of 5.0% of the propylene present as polypropylene homopolymer, the remaining 2.0% of the propylene present as a copolymer. The more interesting aspects of these polymers are manifested in their melting behavior and in the morphology of the system. Figure 4 is illustrative of poly-4-MP homopolymer that has been annealed at 200°C. for 12 hr. No spherulitic growth is apparent, although several areas exhibiting weak birefringence may be observed.

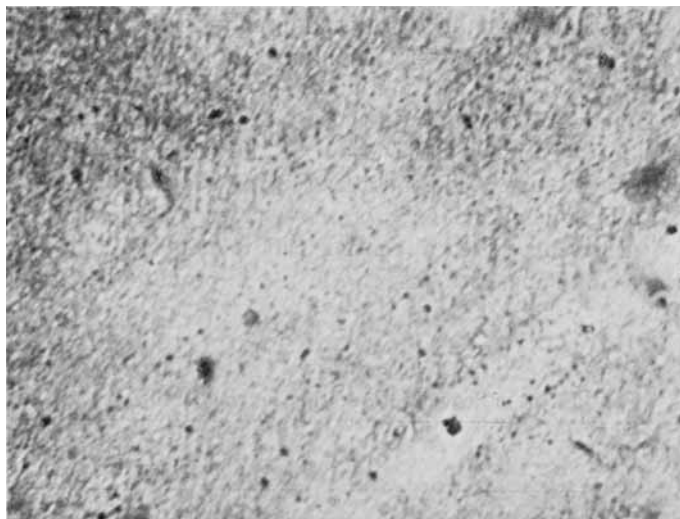


Fig. 4. Photomicrograph of poly-4-MP annealed at 200°C. for 12 hr



Fig. 5. Photomicrograph of high melting poly-4-MP prepared by sequential addition techniques; no annealing.

This is typical of the poly-4-MP samples that have been examined. These samples exhibit crystalline melting points of 238°C. Figure 5 is a sample of poly-4-MP prepared by the sequential addition technique. The large, well-defined spherulitic structures are quite striking. The melting point of this sample was 240°C. In other preparations of this type, it has been possible to raise the melting point of the polymer to 244°C., an increase

of 4–6°C. over that normally observed for poly-4-MP. This increase is observed in spite of the fact that copolymers and polymer mixtures are present.

The development of spherulitic structures in the sequential polymer may be the result of effective plasticization by the propylene homopolymers and copolymers present. The introduction of a comonomer by the sequential addition technique may promote crystallization by increasing the ease with which segmental motion can take place. This increased crystallization and spherulite growth did not improve polymer properties (Table IV).

TABLE IV  
Effect of Sequential Addition Polymerization

	Homopolymer	A...B...A Copolymer*
Propylene, wt.-%	0	6.9
Inherent viscosity, dl./g.	3.6	3.6
Density, g./cc. (annealed)	0.833	0.838
Tensile, psi	4000	3450
Elongation, %	5	3.8
Flexural stiffness $\times 10^3$ psi	155	150
Heat distortion temp., °C.	58	46

\* A = 4-methyl-1-pentene; B = propylene.

TABLE V  
Extraction of the 4-MP-Propylene Polymers  
Prepared by Sequential Addition

Treatment	% Soluble	% Insoluble	$T_m$ , (insolubles), °C.
None	—	—	240
Ether, 35°C., 40 hr.	30.2	69.8	—
<i>n</i> -Pentane, 36°C., 40 hr.	35.2	64.8	217
<i>n</i> -Heptane, 98°C., 40 hr.	44.6	55.4	231
Blend 50% heptane-soluble/ 50% heptane-insoluble	—	—	240

It is of interest to note that extraction of the polymeric mixture with *n*-pentane or *n*-heptane afforded a residue of lower melting point than the total polymer. No spherulites were discernible in either the extracts or the residues. Reblending of the extracted material and the insoluble residue, resulted in a reappearance of the higher melting (240°C.) spherulites (Table V).

The sequential addition polymer studies have also led to some interesting observations concerning the variation of birefringence as a function of temperature for poly-4-MP. Examination of photomicrographs revealed that the spherulites of poly-4-MP are only faintly visible at 27°C. As the



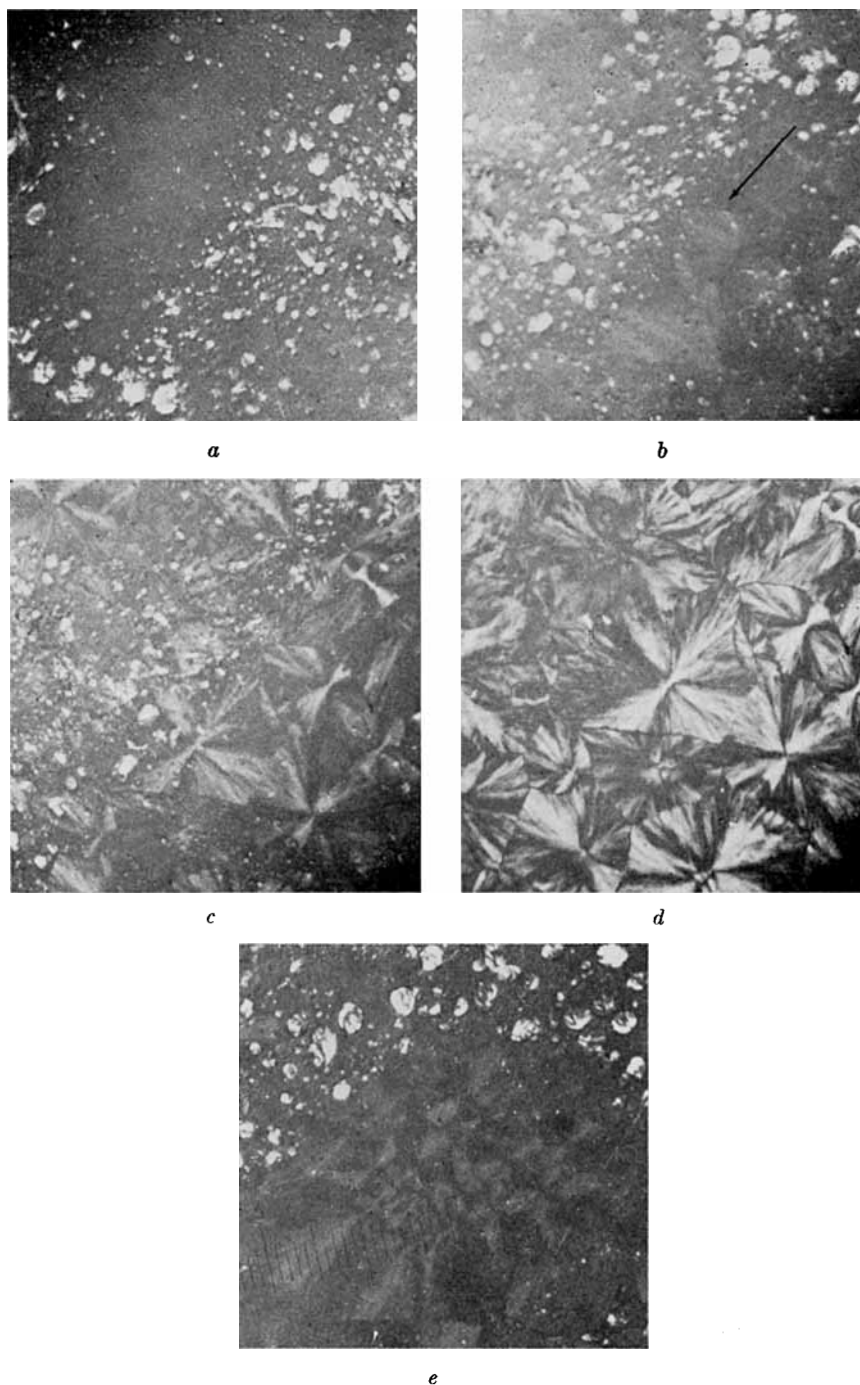


Fig. 6. Photomicrographs of poly-4-MP prepared by sequential addition with propylene: (a) 27°C.; (b) 72°C.; (c) 130°C.; (d) 230°C.; (e) - 30°C.

temperature was increased, the intensity of birefringence diminished so that in the range of about 60–75°C., only the polypropylene present in the mixture was visible under polarized light. Upon further increase in temperature, the poly-4-MP spherulites again become visible, faintly at about 80°C. and more intensely at 130°C. and higher (Fig. 6). At 130°C., the polypropylene (and/or copolymer) began to melt, and at 230°C. the fully grown poly-4-MP spherulites were very well defined with only faint boundaries of the polypropylene melt visible (Fig. 6*d*). This very interesting behavior prompted an examination of photomicrographs taken at low temperature. At –30°C. (Fig. 6*c*) the spherulites of poly-4-MP were once again clearly visible.

There are two principal source of birefringence. One arises from the fact that the polarizability of the polymer molecule parallel to the chain is different from the polarizability perpendicular to the chain. This intrinsic birefringence depends on the crystallinity and degree of orientation of the polymer molecules and is essentially independent of the refractive index of the surrounding medium. However, another aspect of birefringence arises from the anisotropy of the polymer sample as a whole. This form birefringence is exhibited by an ordered array of "particles" (which may be either isotropic or anisotropic) embedded in a medium of different refractive index.<sup>11,12</sup> The intensity of the form birefringence is dependent upon  $(n_c^2 - n_a^2)$ , where  $n_c$  is the index of refraction of the ordered crystallites and  $n_a$  the index of refraction of the amorphous medium. It is an oversimplification to assume that the amorphous region of a polymer such as poly-4-MP is completely random without orientation.<sup>13</sup> More probably, the two phases differ only in degree and not in kind. Accordingly, the specific refraction of the two phases may be essentially the same; in which case the difference in the indices of refraction, or in  $n^2$ , would depend upon the difference in the densities only. The work of Griffith and Rånby<sup>4</sup> has shown that the crystalline and amorphous forms of poly-4-MP have the same density at about 50°C. Accordingly, it is not surprising that the birefringence disappears in this temperature region. At both higher and lower temperature, the density of the two phases differ, and hence birefringence is clearly evident.

It should also be noted that intrinsic birefringence is a sensitive indicator of molecular orientation. The minimum in the birefringence-temperature curve may be indicative of anisotropic expansion of the polymer crystal. Such an anisotropic expansion of the crystal lattice with increasing temperature has been observed for poly-4-MP by means of x-ray diffraction.<sup>5</sup>

We should like to acknowledge the assistance of Mr. E. W. Mace in carrying out many of the experimental studies described.

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## Résumé

On a étudié les propriétés thermodynamiques physiques et mécaniques et le comportement à la cristallisation du poly-4-méthyl-1-pentène (poly-4-MP). On a obtenu des valeurs de la chaleur et de l'entropie de fusion. Le poly-4-MP se caractérise par une résistance à l'extension, une rigidité et une dureté de surface relativement élevées. La résistance au choc est faible à température de chambre. L'effet défavorable de la température sur la résistance à l'extension, le fluage et sur les autres propriétés des polymères se manifeste davantage pour le poly-4-MP que pour le polypropylène. Le poly-4-MP est fortement transparent, ce qui est probablement dû à une croissance limitée de sphérulites. Cette croissance des sphérulites devient plus importante si on le copolymérise avec le propylène par une technique d'addition séquentielle de monomère. Le produit obtenu possède un point de fusion cristalline supérieur (244 contre 238°C. pour l'homopoly-4-MP). La signification de ces résultats et l'effet de la température sur la biréfringence du poly-4-MP sont discutés ici.

## Zusammenfassung

Eine Untersuchung der thermodynamischen, physikalischen und mechanischen Eigenschaften und des Kristallisationsverhaltens von Poly-4-methyl-1-penten (Poly-4-MP) wurde ausgeführt. Schmelzwärme und -entropie wurden bestimmt. Poly-4-MP wird durch verhältnismässig hohe Zugfestigkeit, Steifheit und Oberflächenhärte charakterisiert. Die Eindringtiefe ist bei Raumtemperatur gering. Der entgegengesetzte Einfluss der Temperatur auf Zugfestigkeit, Kriechen und andere Polymereigenschaften ist bei Poly-4-MP grösser als bei Polypropylen. Poly-4-MP ist besonders transparent, wahrscheinlich wegen des begrenzten Sphärolithwachstums. Das Sphärolithwachstum wurde während der Copolymerisation mit Propylen mit einem Verfahren mit aufeinanderfolgender Monomerzugabe gefördert. Das resultierende Produkt hat einen höheren kristallinen Schmelzpunkt (244 bzw. 238°C für Homopoly-4-MP). Die Bedeutung dieser Ergebnisse und der Temperatureinfluss auf die Doppelbrechung von Poly-4-MP werden diskutiert.

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