Properties of Semicrystalline Polyolefins.
II. Copolymers of 3-Methyl-1-pentene and
4-Methyl-1-pentene

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Synopsis

A study of the copolymerization of 3-methyl-1-pentene (3-MP) and 4-methyl-1-pentene (4-MP) showed that the poly-4-MP crystal lattice is capable of incorporating large quantities of 3-MP without a sharp lowering of melting point or adverse effect on physical and mechanical properties. The reactivity ratio of the two monomers in copolymerization are $r(4\text{-MP}) = 6.2 \pm 0.2$ and $r(3\text{-MP}) = 0.1 \pm 0.1$. As a result, mixed feeds containing up to 80% 3-MP produce copolymers composed primarily of repeating 4-MP units, with a random insertion of 3-MP monomer units. Calculations indicate that in a copolymer containing 37% 3-MP, the probability of finding a sequence of 2 units of 3-MP is only a little better than 5%. This copolymer shows a somewhat increased resistance to deformation under load than homopoly 4-MP. Its crystalline melting point is 248°C.

Random copolymerization offers a convenient method of altering the physical and mechanical properties of a high molecular weight polymer. Generally, it has been found that improvement in one area, for example, impact strength or chemical resistance, is gained only at the expense of other vital properties such as melting point or stiffness. A comparatively few copolymer systems have been reported, however, in which isomorphous substitution occurs.[1-4] In these instances, the crystal lattice of a polymer is capable of incorporating large quantities of a related structure without a detrimental lowering of melting point, strength, and stiffness.

As part of a research investigation into the relationships between structure and properties of crystalline polyolefins, a number of α-olefin homopolymers and copolymers were synthesized. An earlier paper[5] dealt with homopoly 4-methyl-1-pentene and select copolymers. This communication is concerned with our studies on the system 3-methyl-1-pentene–4-methyl-1-pentene. A series of high melting crystalline copolymers was formed by using a modified ionic-coordinate catalyst system. The reactivity of the two monomers in copolymerization has been measured, and the physical properties of the resultant copolymers were investigated.

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EXPERIMENTAL

Batch Polymerizations

Batch polymerizations were performed in a two liter resin flask. All glassware was dried in an oven at 140°C. and assembled while hot in a stream of dry nitrogen. Hydrocarbon diluents were percolated through activated alumina and stored over freshly cut sodium ribbon. The copolymerizations were carried out with a triethyl aluminum–$TiCl_3 \cdot 0.2$ $AlCl_3$ catalyst[6] at 80°C. and atmospheric pressure. The triethyl aluminum was complexed with a Lewis base prior to addition of the titanium component.

Continuous Polymerizations

Continuous polymerizations were carried out in the apparatus shown in Figure 1.

A modified two-liter resin flask was used as a continuous reactor (A). The flask had a nitrogen inlet (a) and an outlet (b) for product discharge. The monomer dissolved in the diluent and was stored in a one-liter addition funnel (B) under a nitrogen atmosphere, and it was pumped continuously
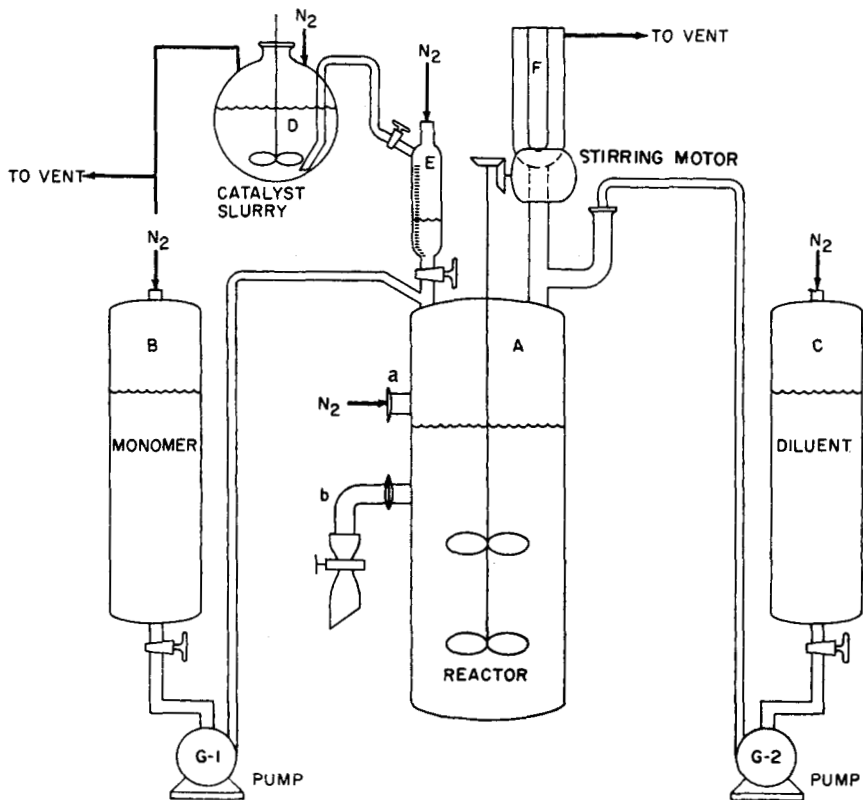

Fig. 1. Laboratory-size continuous polymerization unit.

to the reactor by pump G-1. Additional diluent was stored in a second one-liter funnel (C) from which it could be pumped continuously to the reactor by pump G-2. In several of the polymerizations, the solution of the complexed triethyl aluminum was introduced from funnel C. The transition metal component of the catalyst (as a slurry) was stored in a four-necked round-bottomed flask (D). It was siphoned from D to a graduated 100-ml. addition funnel (E) and intermittently added to the reactor. The reactor was provided with a condenser (F) and an efficient glass stirrer. Residence times up to 2 hr. were studied.

The polymerization was always started batchwise with both monomer and catalyst concentrations close to the steady-state values. After the continuous reaction had been started and steady-state conditions established, samples were withdrawn from the reactor periodically. The liquid phase was analyzed by gas–liquid phase chromatography using a Perkin-Elmer Model 154D Fractometer. Ucon oil LB-550-X was employed as the liquid phase supported on diatomaceous earth. The column was operated at 120°C. and 25 psi pressure. The solid polymer was isolated by precipitation with methanol.

RESULTS AND DISCUSSION

Reactivity Ratios

Reactivity ratios for 3-methyl-1-pentene (3-MP) and 4-methyl-1-pentene (4-MP) were determined by use of data from a series of batch copolymerizations carried out at low conversion (<5%). The graphical procedure of Fineman and Ross[7] was employed to obtain the relative reactivities of the two monomers. The data are plotted in Figure 2. A linear regression analysis gave values of $r(4\text{-MP}) = 6.2 \pm 0.2$ and $r(3\text{-MP}) = 0.1 \pm 0.1$. These values indicate that in the copolymerization studies described below, using mixed feeds containing up to about 80% 3-MP, the resultant copolymer is composed primarily of repeating 4-MP units with a random insertion of a 3-MP monomer unit. This is evident from the data
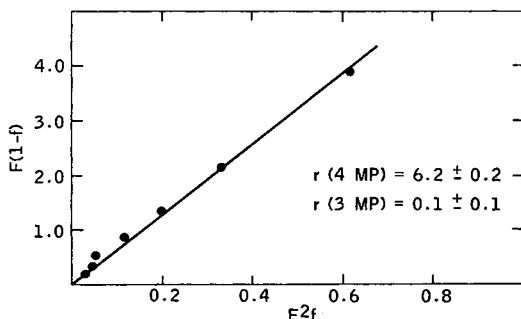

Fig. 2. Graphical solution of the copolymerization equation for 3-methyl-1-pentene and 4-methyl-1-pentene.
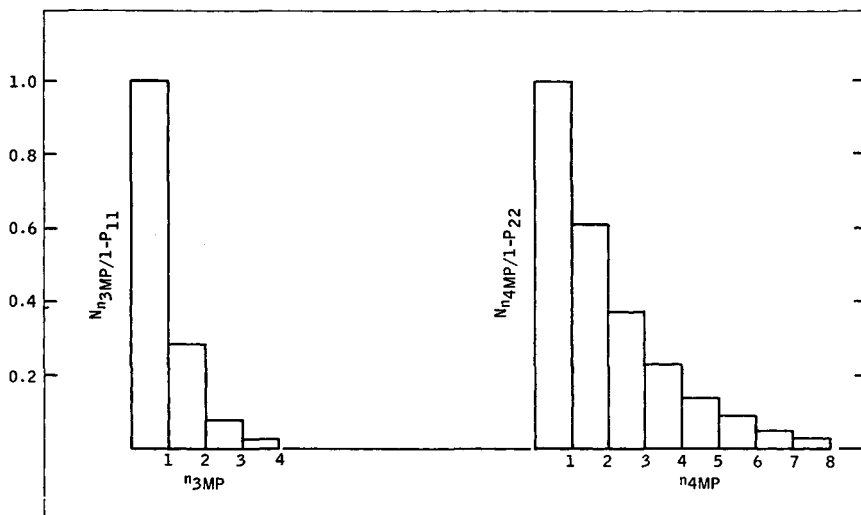
Fig. 3. Sequence length distribution in a 3-methyl-1-pentene–4-methyl-1-pentene copolymer containing 37% 3-methyl-1-pentene.

in Figure 3. Here, the probability that a 3-MP sequence picked at random contains n_1 members is given by:[8]

$$N\ (m_1 n_1)\ =\ P_{11}{}^{(n_1-1)}(1\ -\ P_{11})$$

and similarly the number distribution function for 4-MP sequences is given by:

$$N\ (m_2 n_2)\ =\ P_{22}{}^{(n_2-1)}(1\ -\ P_{22})$$

P_{11} is the probability of a 3-MP monomer unit adding to a chain ending in 3-MP and P_{22} is the probability of a 4-MP monomer unit adding to a chain ending in 4-MP. With a monomer feed of 80% 3-MP, the probability of finding a sequence of 2 units of 3-MP in the copolymer is only slightly more then 5%.

Copolymer Analysis

Infrared spectra of the copolymers and polyblends showed an absorption band at 13.1 μ characteristic of poly-3-MP. This is probably due to a skeletal mode associated with the sec-butyl group. Analyses of the copolymers were based on this absorption. A base line was drawn between 12.85 and 13.80 μ, and maximum absorbance of the 13.1 μ peak was measured. A plot of absorbance/mil of film thickness as a function of 3-methyl-1-pentene content was used to determine the concentration of 3-MP in the 3-MP/4-MP copolymers. Comparison of the spectra of the copolymers with spectra of polyblends prepared from the pure homopolymers showed differences in the 8–9 μ region.

3-MP is a highly insoluble and extremely brittle polymer. The homopolymer is essentially insoluble in hot toluene. The copolymers formed,

however, are completely soluble in toluene.   The 3-MP in a physical blend of 4-MP and 3-MP remained insoluble in this solvent.   Extraction experiments performed for 24 hr. at the boiling point of toluene are given in Table I.   They would tend to indicate that copolymers rather than mixtures of homopolymers were formed in these reactions.

TABLE I
Extraction of 3-MP/4-MP Polymers With Toluene

	Initial wt., g.	Wt. solubles, g.	Wt. insolubles, g.
4-Methyl-1-pentene homopolymer	1.00	1.00	0.00
3-Methyl-1-pentene homopolymer	1.00	0.03	0.97
Copolymer of 3-MP/4-MP(30% 3-MP)	1.00	0.99	0.01
50/50 Blend of 3-MP/4-MP	2.00	0.98	1.02

Differential thermal analysis offers a convenient method for studying phase transitions in crystalline copolymers.   DTA curves of two blends of poly-4-MP and poly-3-MP revealed a melting point quite close to the melting point of pure poly-4-MP and a second-phase transition between 250 and 270°C.   The thermograms of two copolymers (containing 10% and 30% 3-MP, respectively) showed distinct melting points differing from either that of pure 4-MP or the transitions shown by the blends.

Poly-3-MP[9] differs from poly-4-MP in that the former contains an asymmetric carbon atom in the side chain.   The 3-MP used in our studies was a racemic mixture.   This introduced an additional aspect of randomness in the copolymers.

Evaluation of Physical Properties

The copolymers synthesized from a mixed monomer feed should be of a narrow composition range if significant data are to be obtained on the effect of composition on polymer properties.   This was accomplished by the use of the bench-scale continuous tank-flow reactor shown schematically in
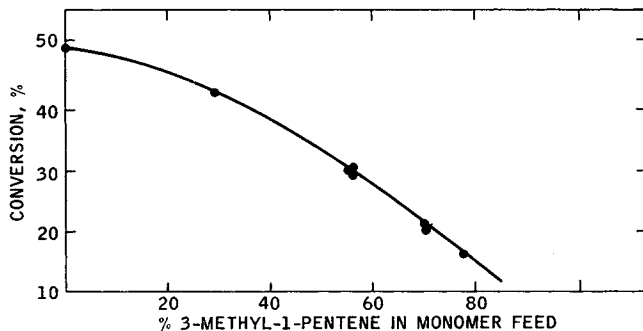

Fig. 4. Effect of feed composition on conversion.

Figure 1. A number of different feed compositions were studied at conversion levels of 20–45 mole-%, based on total feed. Several turnovers of the reactor were necessary before steady-state conditions were established in the reactor. The polymer produced during the steady-state period (with a 2 hr. residence time) was used for evaluation. Figure 4 shows the variation of conversion with changes in total feed composition. A sharp decrease in conversion occurs as the 3-MP concentration is increased. This is due to the low polymerization rate of the 3-MP monomer.

The copolymers formed in these studies were crystalline, as shown by x-ray analysis. Physical and mechanical properties are shown in Table II.

TABLE II

Continuous Polymerization Experiments With 3-Methyl-1-Pentene/4-Methyl-1-Pentene

Feed composition							
4-Methyl-1-pentene, %	43.5	43.5	28.8	43.5	71.7	21.8	28.8
3-Methyl-1-pentene, %	56.5	56.5	71.2	56.5	28.3	78.2	71.2
Polymer Properties							
3-MP in copolymer, %	17.8	—	25.6	13.1	8.6	36.6	29.0
Melting point, °C.	242	—	241	235	241	248	244
Inherent Viscosity, dl./g.[a]	3.0	3.8	2.2	3.5	3.6	1.9	2.3
Density, g./ml.	0.843	0.844	0.852	0.844	0.838	0.856	0.852
Tensile strength (D-638),[b] psi	4290	4203	4100	3819	3330	2990	3750
Elongation, %	4.7	5.3	5.0	4.9	3.9	3.6	4.6
Flexural stiffness (D-747), psi × 10⁻³[b]	173	167	138	146	157	158	150
Vicat softening point (D-1525), °C.[b]	—	—	106	105	105	104	104
Heat distortion temperature 66 psi (D-648), °C.[b]	—	—	71	66	76	72	74

[a] Decalin viscosity at 135°C., 0.0453 g./dl. concentration.
[b] ASTM Standards.[10]

All of the copolymers gave crystalline melting points (i.e., loss of birefringence as observed with polarizing microscope). Moreover, there appeared to be little variation in the creep dependent properties (heat distortion temperature and Vicat softening point) with a wide variation in copolymer composition (8–37% 3-MP in copolymers). However, when compared to the 4-MP homopolymer,[5] the copolymers show a somewhat increased resistance to deformation under load. Unannealed poly-4-MP prepared with the same catalyst has a heat distortion temperature of about 58°C. (66 psi) compared to 66–76°C. for the copolymers. Similarly, poly-4-MP has a Vicat softening point of 100°C. as compared to 105°C. for the copoly-

mers.   The copolymers had lower tensile strengths than 4-MP homopoly-
mer (4500 psi).   Of special interest are the melting point data.   Poly-4-MP
has a crystalline melting point of 238°C.   Copolymers containing about
10–20 mole-% 3-MP melt at 233–235°C., but as the 3-MP content of the
polymer is increased to the 30–36% range, the melting point is increased to
244–248°C.   Poly-3-MP melts at 270–275°C.   Although the copolymers
were all comparatively highly crystalline, as in the case of poly-4-MP, very
little spherulitic growth is observed.   Molded pads exhibited high clarity,
confirming the compatibility of the two monomers and lack of extensive
spherulitic growth.   These data would lend support to the hypothesis that
3-MP and 4-MP are forming a series of cocrystalline copolymers.   Thus,
4-MP can incorporate large quantities of 3-MP in the polymer chain
without disrupting or destroying the crystal lattice.

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Résumé

Une étude de la copolymérisation du 3-méthyl-1-pentène (3-MP) et 4-méthyl-1-pentène (4-MP) a montré que le réseau cristallin du poly-4-MP est à même d'incorporer des quantités importantes de 3-MP sans que l'on observe un abaissement (aigu) du point de fusion ou un effet antagoniste sur les propriétés physiques ou mécaniques.   Les rapports de réactivité des deux monomères au cours de la copolymérisation sont r (4-MP) = 6.2 ± 0.2 et r (3-MP) = 0.1 ± 0.1.   Conséquemment des mélanges monomériques contenant jusqu'à 80% de 3-MP produisent des copolymères composés primodialement d'unités consécutives 4-MP avec une insertion statistique d'unités monomériques 3-MP. Le calcul montre que dans le copolymère à 37% de 3-MP, la probabilité de trouver une diade de 3-MP est à peine supérieure à 5%.   Ce polymère présente une résistance à la déformation sous la charge quelque peu plus élevée que dans l'homopoly-4-MP.   Son point de fusion cristallin est de 248°C.

Zusammenfassung

Eine Untersuchung der Copolymerisation von 3-Methyl-1-penten (3-MP) und
4-Methyl-1-penten (4-MP) zeigte, dass das Poly-4-MP-Kristallgitter grössere Mengen
von 3-MP einlagern kann, ohne eine scharfe Änderung des Schmelzpunktes oder einen

nachteiligen Einfluss auf die physikalischen und mechanischen Eigenschaften. Das Reaktivitätsverhältnis der beiden Monomeren bei der Copolymerisation ist r(4-MP) = 6,2 ± 0,2 und r(3-MP) = 0,1 ± 0,1. Infolge dessen entstehen aus Mischungsansätzen mit bis zu 80% 3-MP Copolymere, die hauptsächlich aus 4-MP-Einheiten aufgebaut sind, mit unregelmässiger Einschiebung von 3-MP-Monomereinheiten. Die Rechnung zeigt, dass in einem Copolymeren mit 37% 3-MP die Wahrscheinlichkeit, eine Sequenz von 2 Einheiten von 3-MP zu finden nur etwas besser als 5% ist. Dieses Copolymere zeigt eine etwas vergrösserte Beständgkeit gegen Deformation unter Belastung als Homopoly-4-MP. Sein kristalliner Schmelzpunkt beträgt 248°C.