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Alternating Olefin/Carbon Monoxide Polymers: A New Family of Thermoplastics†

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Significant technological advances by Shell over the past decade have led to the development of a new family of thermoplastics. These new materials are perfectly alternating olefin/carbon monoxide polymers which provide a superior combined balance of performance properties not found in other commercial materials. Shell will market these new polymers under the trade mark CARILON® Polymers.

CARILON® polymers are semicrystalline thermoplastics derived from simple and abundant raw materials of carbon monoxide and ethylene (or other α -olefins.) These new materials have resulted, in part, from a high activity catalyst invention which enables the polymer to be produced with perfectly alternating units of CO and olefin. The excellent physical, chemical, and barrier properties of these aliphatic polyketone polymers places them in the broad class of materials known as “engineering thermoplastics” which are widely used in industrial, automotive, appliance, and electrical applications.

KEY WORDS Olefin/carbon monoxide polymers, alternating ethylene/carbon monoxide copolymers, catalysts, synthesis, thermoplastics, properties, applications.

INTRODUCTION

Polymeric materials which deliver high performance properties are in demand by technology today. Competitive trends and demanding applications continue to push material properties such as strength, stiffness, toughness, wear resistance, chemical resistance, etc., especially at elevated temperatures. These properties and other product needs have provided opportunities for new and improved polymers. Significant technological advances by Shell over the past decade have led to the

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development of a new family of thermoplastics. These new materials are perfectly alternating olefin/carbon monoxide polymers which provide a superior, combined balance of performance properties not found in other commercial materials. This new family of polymers will be marketed world-wide under the trademark CARILON® Polymers.¹

CARILON polymers are semicrystalline thermoplastics derived from the simple and abundant raw materials of carbon monoxide and ethylene (or other α -olefins), Figure 1. These new materials have resulted, in part, from a high activity catalyst invention which enables the polymer to be produced with perfectly alternating repeat units of CO and olefin. This assembly of monomers generates a regular repeating ketone structure, and the polymers are referred to as aliphatic polyketones (PK). The excellent physical, chemical, and barrier properties of aliphatic polyketone polymers position them in the broad class of materials known as "engineering thermoplastics" which are utilized widely in industrial, automotive, appliance, and electrical applications. The excellent properties of polyketone polymers should also make them attractive for fibers, coatings, and food and industrial packaging.

Unlike other engineering materials which many times require expensive and complex monomers (with multistep syntheses, byproducts, heteroatoms), polyketone polymers are prepared by the addition polymerization of very simple monomers such as ethylene and carbon monoxide (C, H, O elements only). The raw materials are abundant, and the excellent properties of polyketone polymers have been envisioned for some time. Aliphatic polyketones have resisted commercialization until now because of limitations associated with polymer synthesis and stability. These problems have been largely overcome by a collaborative effort of Shell researchers, leading to over 300 patents world-wide. Briefly described herein are aliphatic polyketone polymers in general and the research leading to their first commercial production anticipated in 1996.

HISTORY OF ETHYLENE/CO POLYMERS

The incorporation of carbon monoxide into polyolefin polymers has been of considerable interest for many years. Initial reasons for using CO as a polymer building

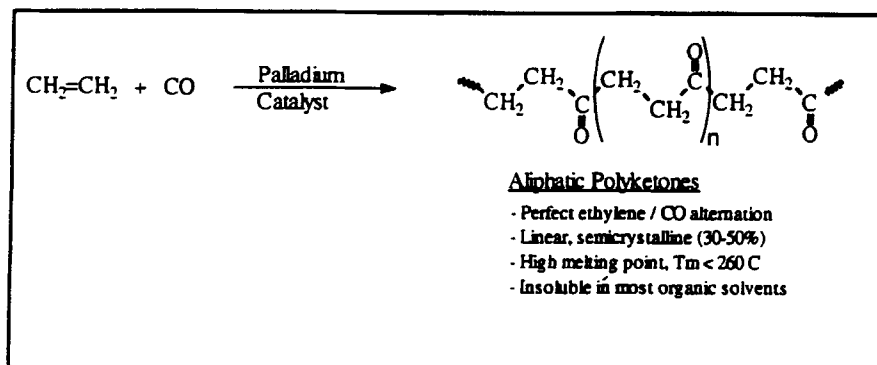


FIGURE 1 Synthesis of ethylene/carbon monoxide copolymers.

block included its low cost, its ability to confer some photodegradability to polyolefins,² and polymers containing CO structural units should be useful as starting materials for preparing other functionalized polymers.³ Carbon monoxide has also been used to modify the compatibility of polymers. For example, limited carbon monoxide incorporation in ethylene-based polymers has been utilized to form flexible polymeric plasticizers for poly(vinyl chloride).^{4,5}

Polyethylene polymers containing small amounts of carbon monoxide have been shown to have properties similar to low density polyethylene; however, copolymers with ethylene/carbon monoxide (E/CO) composition near 1:1 possess much higher melting points and substantially different properties.⁶ Up to now, the potential for perfectly alternating E/CO copolymers has not been explored, but early considerations of economics and structure/property relationships did help develop positive expectations:

With . . .

- Simple, widely available monomers
- High density of polar groups
- Flexible backbone
- Perfect alternating structure

Expect. . .

- Potentially cost effective polymer
- Crystallinity, rapid crystallization
- High melting point
- High strength, stiffness
- High use temperatures
- Solvent resistance
- Good barrier properties

The formation of polyketones through the copolymerization of CO with ethylene has been known since the 1940's.⁷ Brubaker at DuPont showed that CO could be copolymerized with a variety of olefins such as ethylene, propylene, butadiene, etc. using a free-radical initiated process. These polymerizations could produce copolymers with monomer ratios approaching 1.0. However, extreme pressures were required (500-1500 atm, 120-165°C), and the polymers were generally of low molecular weight with irregular CO incorporation. As a result, they had poor physical properties and high solubility in organic solvents. Other radical copolymerization processes have been documented using radical forming sources such as γ -radiation,⁸ but again very high pressures were required (ca. 2000 psi) and perfect alternation of E/CO was not possible.

In contrast, the development of coordination catalysts brought about the ability to produce alternating polymer structures of ethylene and carbon monoxide. The first metal catalyzed copolymerization of E/CO was reported by Reppe and Magin in 1951.⁹ Using a nickel metal catalyst, $K_2Ni(CN)_4$, in water solvent, it was shown that low melting oligomers along with diethylketone and propionic acid could be produced. Later in 1967, Gough at ICI disclosed the ability to prepare aliphatic polyketones with bis(*tert*-phosphine) palladium dichloride complexes.¹⁰ This cat-

alytic process, however, required high pressures and temperatures (2000 psi, 250°C) with low yields of polymer. By the early 70's, palladium based catalysts were improved such that polyketone polymers could be produced under somewhat milder operating conditions. Independently, Fenton at Union Oil and Nozaki at Shell Development Co. demonstrated that $\text{Pd}(\text{CN})_2$,¹¹ $\text{Pd}(\text{PPh}_3)_4$,¹² $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$,¹³ $\text{HPd}(\text{CN})_3$ ¹⁴ were effective catalysts for the copolymerization of α -olefins and carbon monoxide in a variety of solvents at 75–100°C and ca. 800–1000 psi. The palladium catalysts discovered by Nozaki were capable of producing high molecular weight polymers (intrinsic viscosities = 0.1–8 dL/g) with melting points of 250–260°C. While Pd based catalysts dominated polyketone synthesis, further improvements in nickel based catalysts were discovered. Shryne and Holler found that $(\text{R}_4\text{N})_2\text{Ni}(\text{CN})_4$ and $\text{Ni}(\text{CN})_2$ complexes could produce high molecular weight polyketones in hexafluoroisopropanol solvent using acid cocatalysts such as $\text{CF}_3\text{SO}_3\text{H}$ and 4- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$.¹⁵

While perfectly alternating copolymers could be prepared from the above catalytic routes, they were all extremely inefficient, suffering from low activities and yields. Polymerization rates ranged from only about 1-300 grams of polymer/gram catalyst/hour. The resulting polymers with their high catalyst residues also suffered from stability problems and could be characterized as “thermoset-like” since they quickly crosslinked above their melting points, *vide infra*. By 1982, catalyst advances by Sen showed that Pd catalysts with non-coordinating anions, $[\text{Pd}(\text{PPh}_3)_n(\text{CH}_3\text{CN})_{4-n}](\text{BF}_4)_2$ ($n = 1-3$), could produce polyketone polymers under extremely mild conditions (25°C), however, they too suffered from extremely low reaction rates.¹⁶

EARLY ALIPHATIC POLYKETONES

The development of polyketone polymers within Shell started in the early 70's after Nozaki began preparing high MW polymers using newly developed palladium catalysts described above. Processing instability, however, quickly surfaced as a primary developmental hurdle. Attempts to melt process these early E/CO copolymers generally led to crosslinking of the melt, yielding only brown crumb or material resembling “pencil sharpener shavings.” Compression molding of early polyketone polymers was even problematic. Very poor consolidated specimens were obtained of dark brown color and populated with brown-red particulates. Table 1 shows the material properties determined for copolymers in 1975.¹⁷ Tensile strength, impact, and elongation were observed to be very low. The heat deflection temperature was high, but this was suspected to be the result of polymer crosslinking. Polymer crosslinking was evident from the lack of polymer solubility in hexafluoroisopropanol (one of the few solvents for linear aliphatic polyketones) and the disappearance of any melting endotherm by differential scanning calorimetry. Decreasing mold fill-out with increasing melt temperatures was also indicative of crosslinking in the melt. As a result of these problems, Shell terminated its development of polyketone polymers in 1975.

In 1980, polyketone research “phoenixed” within Shell with the efforts of W.

TABLE I
Chronological development of aliphatic polyketone polymer properties

	<i>1982 Drent Invention</i>			
	1975 Copolymer	1980 Copolymer	1990's Copolymer	1990's Terpolymer ^a
Tensile Strength, psi	5700	>8000	12000	9000
Flex Modulus, psi	-	300,000	350,000	240,000
Izod impact, ^b ft-lb/in	1	3	3-5	3-5
HDT ^c (264 psi), °C	150	130-150	180	105
Break strain, %	3	>20	90	>300
Specific gravity	1.28	1.28	1.28	1.24
Properties after initial melting				
Melting point, °C	None	210-240	255	220
Solubility in HFIPA ^d	Limited	Limited	Complete	Complete

^a Terpolymer contains a small amount of propylene, MP = 220°C.

^b Notched izod, ASTM method D256.

^c HDT, heat distortion temperature.

^d HFIPA, hexafluoroisopropanol, one of the few solvents known for aliphatic polyketones.

Hart and coworkers.¹⁸ Convinced that E/CO copolymers were not inherently unstable, Hart was able to demonstrate melt processability after extracting Pd catalyst residues from the polymer and blending it with other polymers such as styrene/acrylonitrile copolymer. From these studies, it was shown that engineering properties were possible (Table 1), rivaling those of commercial engineering thermoplastics. While linear polyketones were now shown to possess truly desirable attributes, an economically viable synthesis route was still needed.

HIGH ACTIVITY CATALYST INVENTION

In 1982, while conducting non-polymer related carbonylation research, Shell discovered a new class of efficient Pd(II) catalysts capable of copolymerizing carbon monoxide and ethylene into linear, perfectly alternating polyketone polymers of high molecular weight.¹⁹ These catalysts, developed at Koninklijke/Shell Laboratorium Amsterdam (KSLA) by E. Drent, could now produce polyketones with essentially 100% selectivity at surprisingly high catalytic activities (>6000 g/g Pd/hr) and yields under modest synthesis conditions (ca. 45 bar, 85°C). For the first time, these new catalysts made commercialization economically attractive and provided much more stable polymers with catalyst residues now measured by ppm rather than percent. These catalysts also provided the possibility to co- and terpolymerize CO with other α -olefins such as propylene. In fact, the first commercial polyketone by Shell will be a terpolymer with a melting point of 220°C, containing the random incorporation of a small amount of propylene.

Figure 2 shows that Drent's initial focus concerned the alkoxycarbonylation of

ethylene. Palladium diacetate was shown to effectively yield methylpropionate with high selectivity (>98%) and moderate rates (80 g/g Pd/h) when triphenylphosphine and an acid (e.g., HCl) were used as catalysts. Surprisingly, the same methylpropionate could be made at very high rates (5000 g/g Pd/h) if HCl was exchanged with an acid whose conjugate anion was non-coordinating with the Pd metal center, e.g. $\text{CF}_3\text{SO}_3\text{H}$ or $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$. Even more amazingly, it was observed that when the monodentate phosphine ligand was exchanged with a bidentate phosphine ligand, the chemoselectivity of the catalyst was surprisingly changed. Now instead of liquid methylpropionate, a white powder filled the autoclave. The polymer was first thought to be polyethylene, but its insolubility in ordinary organic solvents and its high melting point (257°C) proved otherwise. Nuclear magnetic resonance analysis led to the conclusion that the polymer was a linear, perfectly alternating ethylene/carbon monoxide copolymer with ethylketone and methylester endgroups.

The type of phosphine ligand was shown to be important in directing the chemoselectivity of the catalyst, while the type of anion influenced the overall catalyst rate. Careful examination of the products reveals that the difference between methylpropionate and polyketone polymer is essentially the number of repeat units in the backbone: $\text{H}(\text{CH}_2\text{CH}_2\text{CO})_n\text{OCH}_3$, $n = 1$ for methylpropionate. Therefore, while the overall reactions on Pd must be similar, termination by methanol is extremely facile in Pd catalysts which produce methylpropionate, compared to Pd catalysts which produce polyketones by the propagation with repeated olefin/CO insertions. Attempts to explain this are shown in Figure 3. While *cis* and *trans* configurations exist in equilibrium in d^8 , square planar Pd complexes with monodentate ligands, the *trans* orientation of phosphine ligands is preferred. This avoids the unfavorable situation of a Pd-P bond *trans* to a Pd-C bond. This *trans* orientation of growing chain and open coordination site opposes the insertion of new monomer and leads to eventual termination by methanol to form methylpropionate. However, bidentate phosphine ligands function to lock these positions *cis* to one another. This favors monomer migratory insertion reactions and leads to polymer propagation, Figure 3. Most importantly, the insertion steps alternate invariably between ethylene and CO to create a perfectly alternating polymer even when monomer ratios are grossly different from 1.0. Catalyst activity is related to the availability of open sites at the catalyst center. Therefore, counteranions which are non-coordinating toward Pd have been found to strongly promote the rate of polymerization.

ALIPHATIC POLYKETONE THERMOPLASTICS TODAY

The discovery of efficient Pd catalysts for producing high molecular weight, linear, alternating olefin/carbon monoxide polymers for the first time made commercial production economically attractive. However, even with this discovery in 1982, further development of aliphatic polyketones was in order for their successful utilization in a wide variety of market applications. Collaborative research efforts within Shell have subsequently provided advances in polymer stabilization, synthesis processes, fabrication and compounding. These efforts have resulted in a

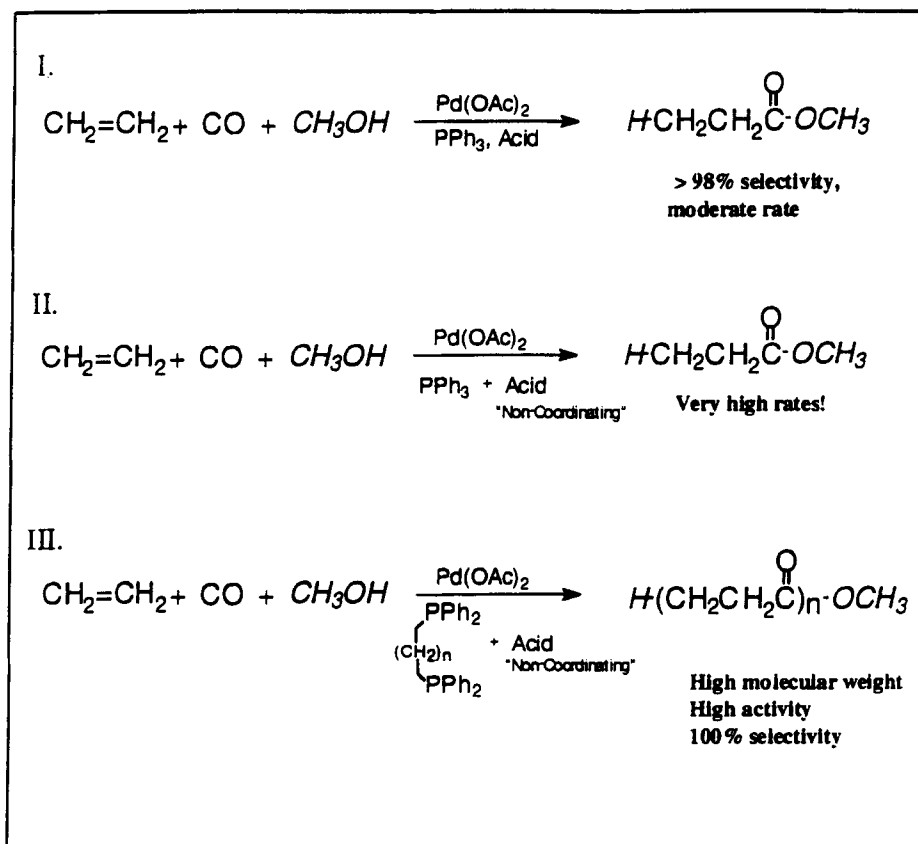


FIGURE 2 High activity Pd(II) catalyst invention for aliphatic polyketones.

broad patent coverage and have now moved aliphatic polyketones toward commercial reality with the first commercial plant being built in the UK.²⁰ Typical properties of current aliphatic polyketones are shown in Table 1.

Aliphatic polyketone thermoplastics have been developed to be easily melt processable. They can be melt fabricated by a variety of conventional methods, e.g., extrusion, injection molding, blow molding, rotational molding, etc. They also exhibit fast mold cycle times with good mold definition characteristics. In addition, scrap polymer generated during fabrication is reusable. Aliphatic polyketones benefit from being largely insensitive to moisture both in unmolded and in finished parts. As a result, post-mold conditioning of parts is not required before use.

As stated earlier, semicrystalline, aliphatic polyketones possess a unique, balanced set of properties not found in other commercial polymers. For example, polyketones exhibit a desirable combination of strength, stiffness, and impact resistance, over a broad range of temperatures. As shown in Figure 4, aliphatic polyketones show excellent toughness while possessing good stiffness characteristics compared to other engineering thermoplastic polymers. As shown in Figure 5, aliphatic polyketones also exhibit excellent strength while at the same time being capable of undergoing unusually high elongation before yielding. This capability

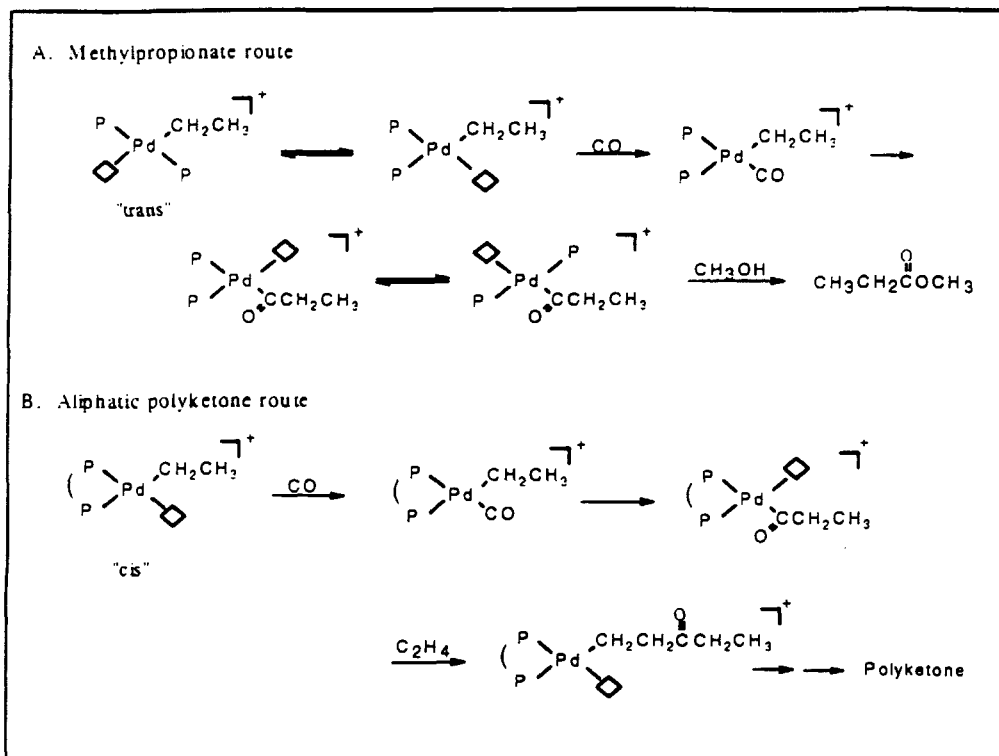


FIGURE 3 Effect of mono- and bidentate phosphorus ligands in Pd(II) carbonylation chemistry.

results in a capacity to store relatively large quantities of elastic energy. Polyketone polymers, therefore, show excellent impact, resilience, creep, and fatigue properties.

Aliphatic polyketones also exhibit excellent tribological (friction and wear) properties. As can be seen in Table II, polyketones rotated against steel show excellent wear resistance (low wear factor) and an excellent ability to sustain heat input from increasing pressure and velocity (high limiting PV), even while exhibiting relatively high frictional characteristics. The excellent wear resistance of aliphatic polyketones is again exhibited in Figure 6 where polymer wear is measured in polymer against polymer spur gear testing. Therefore, polyketones exhibit a unique, balanced set of tribological properties. These combined characteristics are useful in considering a wide variety of tribological related applications such as gears, bearings, cams, guides, lever, pulleys, ratchets, rollers, seals, slurry transfer pipes, etc.

Further, aliphatic polyketone polymers exhibit excellent chemical resistance. Polyketone polymers are not soluble in ordinary organic solvents and they are not adversely plasticized by most reagents. As a result, they are resistant to a wide variety of automotive fluids, solvents, and other industrial and household chemicals. They benefit from their crystalline nature (30–50%) and the fact that the chemical backbone of aliphatic polyketones does not undergo hydrolysis. As a result, they stand up to a variety of aqueous environments, such as weak acids or inorganic salt environments, which would otherwise detrimentally affect the mechanical prop-

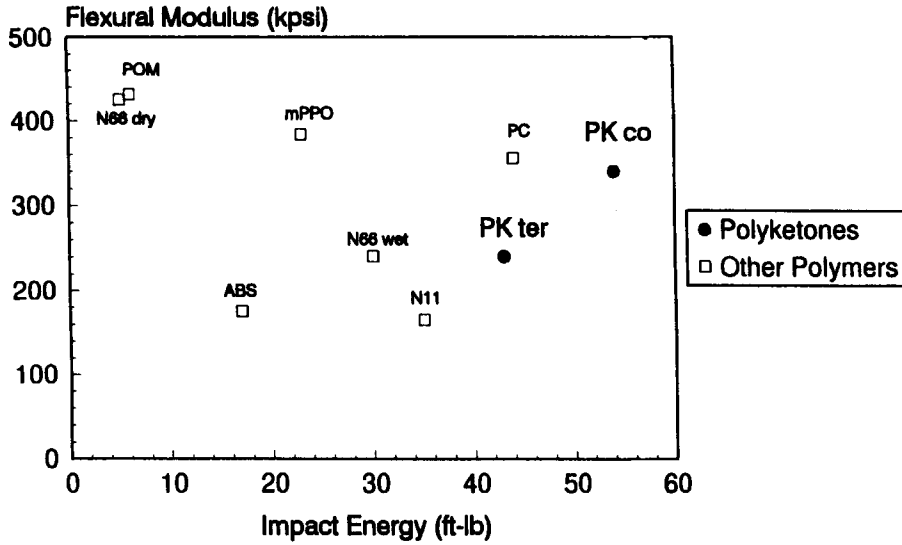


FIGURE 4 Stiffness/toughness balance of polyketone polymers, co- and terpolymers, versus other engineering thermoplastics.

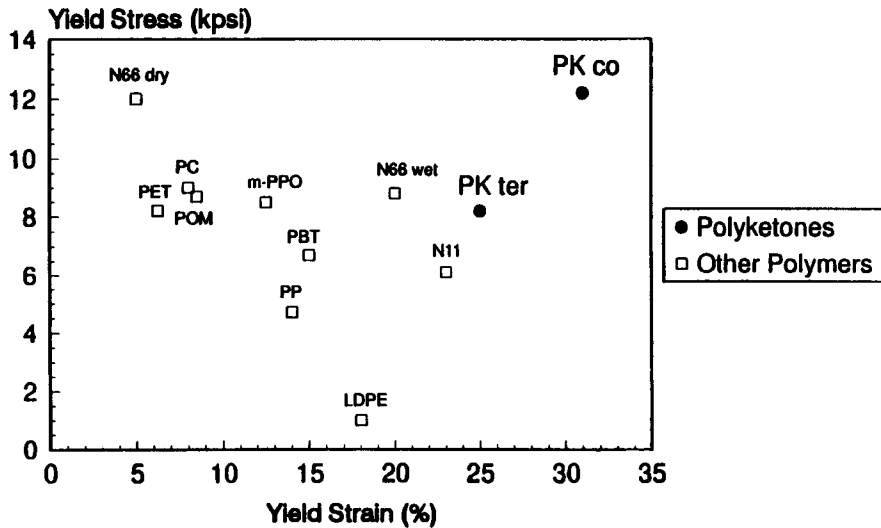


FIGURE 5 Strength/elongation balance of polyketone polymers, co- and terpolymers, versus other thermoplastics.

TABLE II
Tribological properties of polymer thrust washers against steel

Polymer	Wear Factor [@ 40 psi, 50 fpm] 10^{-10} in ³ -min/lb-ft-hr (10^{-10} in ³ -min/lb-ft-hr)	Static Coefficient of Friction [@ 25 psi]	Dynamic Coefficient of Friction [@ 300 psi, 10 fpm]	Limiting PV [@ 100 FPM] lb-ft/in ² -min
Polyketone Terpolymer	215 (43)	0.07	0.86	32,000
Polyketone Copolymer	75 (15)	N.A.	0.83	65,000
Nylon 6, 6	795 (159)	0.09	0.64	30,000
Acetal Copolymer	650 (130)	0.04	0.33	20,000
Acetal Homopolymer	210 (42)	0.04	0.45	15,000

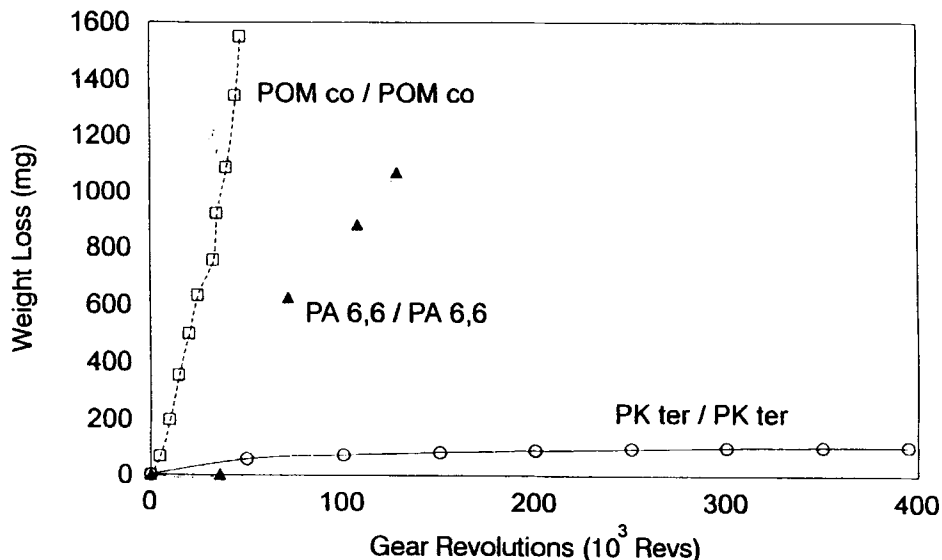


FIGURE 6 Wear resistance comparison of polyacetal (POM co), polyamide (PA 6,6), and polyketone (PK ter) polymers using polymer-on-polymer spur gears.

erties of polymers such as polyamides, polyesters, polycarbonates, etc. In addition, aliphatic polyketones combine chemical resistance with excellent barrier properties to hydrocarbons and gases such as oxygen. Figure 7 illustrates the high barrier properties of aliphatic polyketones towards gasoline, while Table III shows the low oxygen permeability of polyketone polymers compared to other high barrier polymers. The combined polymer properties of chemical resistance and low permeability should be attractive to applications such as protective coatings and chemical containment. The latter is especially important for applications where reducing volatile organic compound emissions (VOC's) to the environment is of concern.

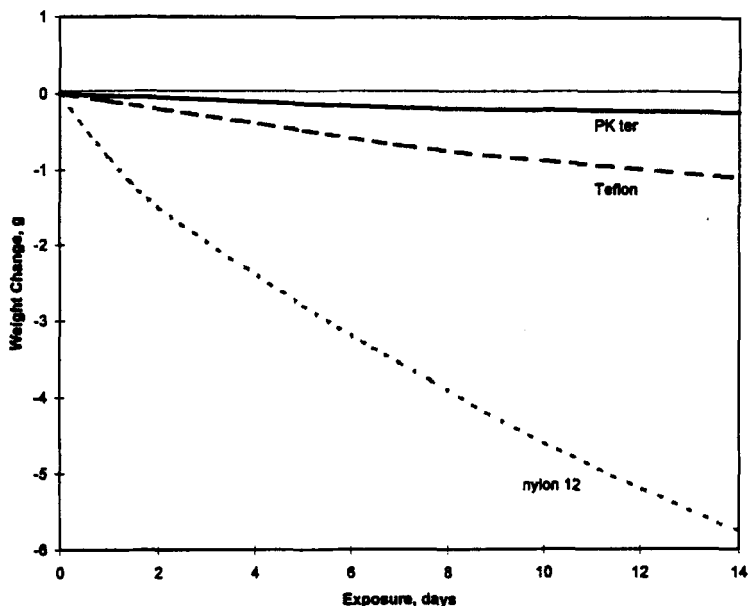


FIGURE 7 Permeability of unleaded gasoline at 93C through containers made from polyketone (terpolymer), teflon, and nylon 12 polymers. *Measured according to GM SPEC 9061-P.

TABLE III

Comparison of oxygen permeability properties of alternating aliphatic polyketones and other high barrier polymers

Polymer	O ₂ Permeability (cc mil/ 100 in ² day atm) @ 23°C	
	0% relative humidity	75% relative humidity
Poly(ethylene terephthalate)	3.5	3.5
Nylon 6,6	1.8	2.0
EVAL-E	0.1	0.1
Polyketone (terpolymer) ^a	0.1	1.0
Polyketone (terpol., exp.) ^b	0.1	0.3

^aTerpolymer contains a small amount of propylene. MP = 220°C.

^bTerpolymer, experimental grade.

Aliphatic polyketones should be useful as well in chemical transfer applications (e.g., pipe and hose) which many times require combined chemical resistance and low permeability with high mechanical resilience and abrasion resistance, especially in abrasive slurry applications.

To further extend the utility of polyketone polymers, filled (e.g., inorganic particulates, glass fiber, carbon fiber, etc.) and flame retarded grades have been prepared. Particularly useful are short glass reinforced polymer grades which provide increased strength, stiffness, and use temperatures. For example, polyketone terpolymer containing 30% glass reinforcement has >19000 psi tensile strength,

>1,000,000 psi flexural modulus and 218°C heat deflection temperature (@ 264 psi). Flame retarded grades can also be prepared without the use of hazardous halogenated or phosphorus compounds.

Aliphatic polyketones provide a broad set of excellent properties originating from the simple constituents of olefin and carbon monoxide. While other polyketones are currently in the marketplace, they should not be confused with the new aliphatic polyketones. In contrast, current commercial polyketones contain aromatic rings in their backbone. These so-called aromatic polyketones exhibit extremely high melting (ca. 335°C), processing, and use temperatures. Aromatic polyketones are classified as advanced thermoplastic polymers and provide very high performance characteristics.²¹ However, their high monomer costs and manufacturing costs make these polymers expensive and limited in use to specialty polymer or niche applications where specific performance properties are required. Aliphatic polyketones possess a broader set of properties which make them suited for consideration in a wider variety of applications. These potential applications include:

- Industrial pipe, pipe fittings, pump, liners for chemical transfer and containment systems
- Automotive components for fuel and other fluid handling systems and under-hood functional components
- Gears, bearings, and washers
- Electrical connectors and enclosures
- Food and industrial packaging
- Protective coatings
- High strength fibers

Interestingly in the area of polyketone fibers, highly oriented, gel-spun fibers have been shown to exhibit creep resistance superior to high modulus polyethylene and polyethylene terephthalate yarns with tensile strengths approaching that of aramid systems.²²

CONCLUSIONS

The ability to efficiently copolymerize ethylene and other olefins with carbon monoxide in a perfectly alternating manner has led to the development of a new chemical family of thermoplastic polymers, known as aliphatic polyketones (PK). While these semicrystalline polymers are made from simple starting materials, they possess high thermal properties combined with an exceptional balance of engineering properties which include: high strength, stiffness, impact resistance, lubricity, mechanical resilience, chemical resistance, and low permeability. Aliphatic polyketones have been developed to be easily melt processable using a variety of conventional fabrication techniques. These attributes make aliphatic polyketones well suited for consideration in a wide variety of engineering thermoplastic applications.

Acknowledgment

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