Hybrid polymers in the marketplace

By: Barry Arkles
Gelest, Inc.
Tullytown, PA

chemical innovation

Coming in January!
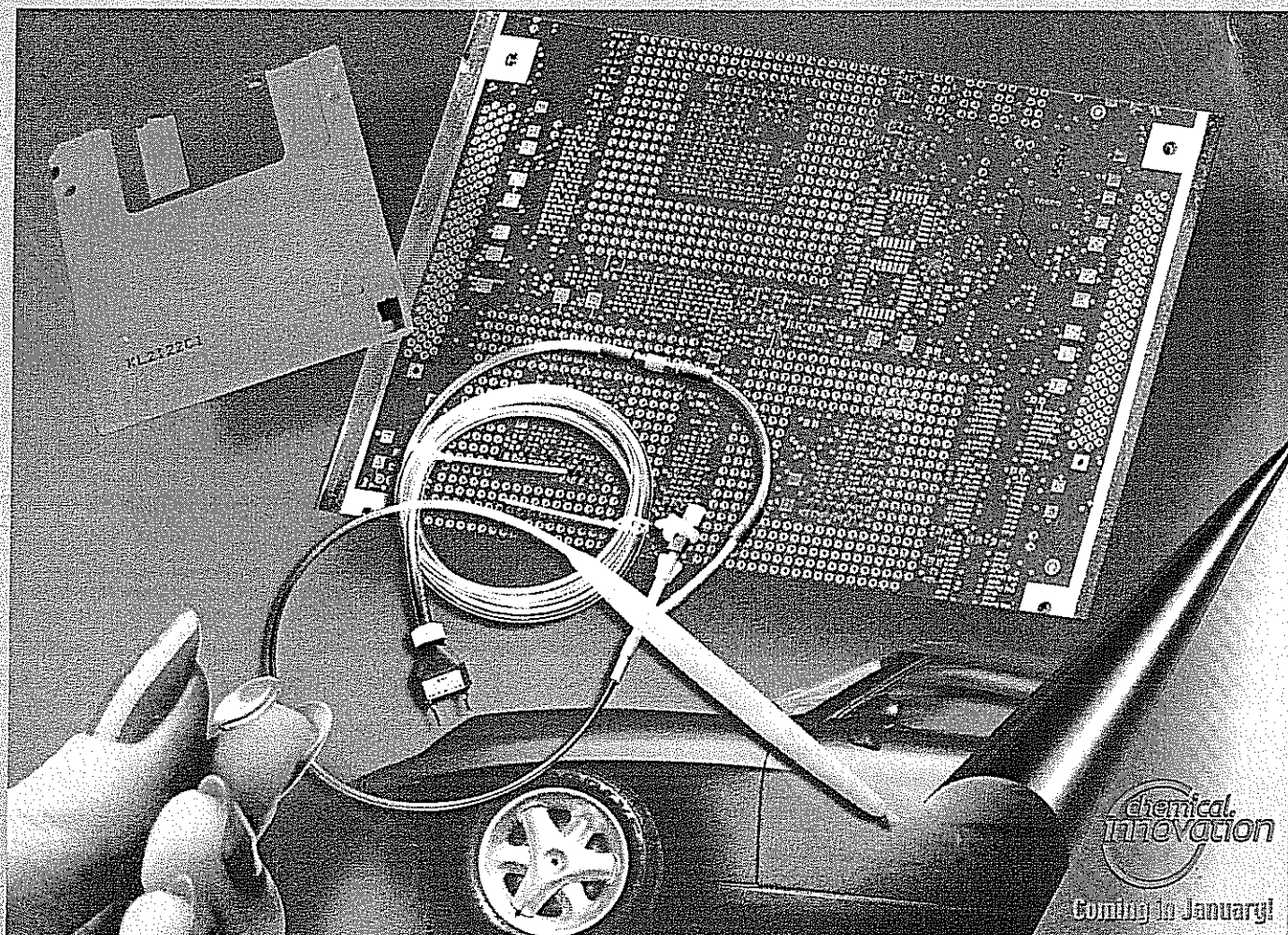
Hybrid polymers in the marketplace

Mix and match molecular building blocks to create better contact lenses, smoother-sailing ships, slippery surfaces, and more.

Barry Arkles

Recent attention directed to hybrid organic–inorganic polymers would lead one to believe that this field is new. Surprisingly, successful commercial hybrid organic–inorganic polymers have been part of manufacturing technology since the 1950s. As understanding of polymer chemistry and structure–property relationships has grown, chemists have learned to create hybrid materials that display unique properties. The current focus on hybrid organic–inorganic polymers promises to yield more new materials. To survive the crucible of the marketplace, materials must either offer unique properties that enable new end-use applications or provide significant benefits at much lower costs than materials commercially available. Hybrid polymers that have won niches in the current marketplace suggest directions for future winners.

No definition has been universally accepted for the bewildering variety of materials described as hybrid organic–inorganic polymers. A working definition is that hybrid organic–inorganic polymers consist of
■ discrete regions or morphologies in which organic structures (i.e., those that contain C, H, N, and O) dominate and
■ separate regions in which distinct structures imposed by heteroatoms dominate and in which we observe physical properties of the polymers that are not a linear or geometric average of the regions.

Two structural paradigms help us visualize hybrid sys-

tems. From an organic polymer perspective, the opportunity for hybrid systems clearly exists in copolymer, graft, block, and interpenetrating polymer network (IPN) morphologies.

The only inorganic polymers that have either achieved or been seriously considered for commercial application have been derived from group IVA and IVB elements, among which silicon is preeminent. Consequently, the inorganic polymer perspective proceeds from the introduction of organic substituents into an amorphous polyoxymetallate structure that is associated with silicates and siloxanes. A scheme for naming these structures derives from the number of oxygens bound to each metal atom. A resin in which each metal atom is bonded to four oxygens is termed a Q resin; if the "metal" is silicon, then the Q resin is SiO_2 (e.g., quartz). If each metal atom is bonded to three oxygens and one organic substituent, you get a T resin—silsesquioxanes, in the case of silicon. Two oxygens and two organic substituents per metal give a D resin (e.g., linear siloxanes).

Copolymer hybrids

Polyacrylates provide the backbone for tin- and silicon-based polymer uses as disparate as oxygen-permeable contact lenses and marine antifoulant coatings. Low-volume applications include photolithography agents for conventional graphics and microelectronics, oxygen-permeable films for membrane-enrichment technology and food packaging, and charge carriers and dispersants for pigments used in reprographics.

The author is with Gelest Inc.

Acrylate-functional silane copolymers: contact lenses. Contact lenses are a successful application of hybrid technology that continues to evolve in response to challenges in product design and function. Maximum wearer comfort is achieved with contact lens materials that allow the eye to "breathe". The primary design parameters that lead to selection of silicone materials are permeability and equivalent oxygen percentage (EOP), a finished lens measurement that considers the oxygen demand of ocular tissue. A minimum EOP of 5–7% has been proposed for finished lenses, equivalent to the oxygen available to the eye during sleep (when the eyelid covers the eye). An EOP of <2% causes corneal edema. Figure 1 shows how the EOP relates to permeability for various lens materials at different thicknesses (*1*).

Other parameters to consider in polymer design are wettability, dimensional stability, and refractive index. Enhanced oxygen permeability in siloxane lens systems is associated with high relative proportions of silicon–oxygen and silicon–carbon bonds. These bonds, which are longer than carbon–oxygen and carbon–carbon bonds lead to a free volume element that, in the case of poly-(dimethylsiloxane), is 5–6 times greater than for polymethacrylates (*2*).

The first methacrylate–silicone hybrid to achieve widespread commercialization was introduced by Syntex for rigid gas-permeable (RGP) lenses based on the technology disclosed by Gaylord (*3*). In the simplest example, methacryloxypropyltris(trimethylsiloxy)silane (**1**)

$$H_2C = C - C - O(CH_2)_3Si - OSi(CH_3)_3$$

1
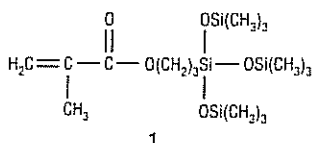
is copolymerized with othermethacrylate monomers (*4*), by which means the oxygen permeability of siloxanes is combined with the mechanical and optical properties of the methacrylates.

RGP lenses offer the highest oxygen permeability, visual acuity, and durability of any lens system. Their market share has dropped, however, because hydrogel systems based on hydrated cross-linked hydroxyethyl methacrylate (HEMA) require a much shorter break-in period. Despite greater wearer comfort with HEMA lenses initially, reduced oxygen permeability causes corneal edema when the lenses are worn for extended periods. It is more challenging to incorporate siloxanes into HEMA systems than into methyl methacrylate (MMA) because siloxanes and HEMA have very different solubility parameters, which frequently leads to polymer domain separation and opacity. Because of its ability to form hybrid block polymer systems, group transfer polymerization is a promising technology for the next generation of soft oxygen-permeable contact lenses. In the group transfer polymerization method, methacrylate monomers are added repeatedly to a "living" polymer chain bearing a silylated ketene acetal (**2**) (*5, 6*):

2
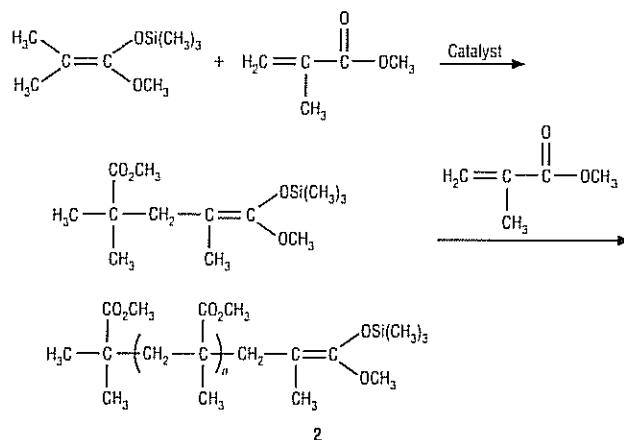
The technology disclosed by Seidner (*7*) uses methacryloxyethoxytrimethylsilane (blocked HEMA, **3**)

$$H_2C = C - C - OCH_2CH_2OSi(CH_3)_3$$

3
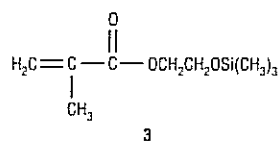
and methacryloxytris(trimethylsiloxy)silane as comonomers. Contact lenses based on group transfer polymerization technology are being introduced under the trade name Lifestyle (Permeable Technologies).

Acrylate-functional tin copolymers: marine coatings. Until recently, the largest volume hybrids were tributyltin–methacrylate copolymers, which are used as marine antifoulant coatings. The effectiveness of the tin hybrid polymers is demonstrated in Figure 2, which shows the near absence of marine organism growth on a treated metal coupon centered over an untreated control plate. To illustrate the potential savings from using antifoulant coatings, consider that a large cargo container ship operating at 15 knots for 300 days/year consumes more than $7 million of fuel. Increased drag caused by marine fouling can easily increase fuel consumption by 30%—more than $2 million per year.
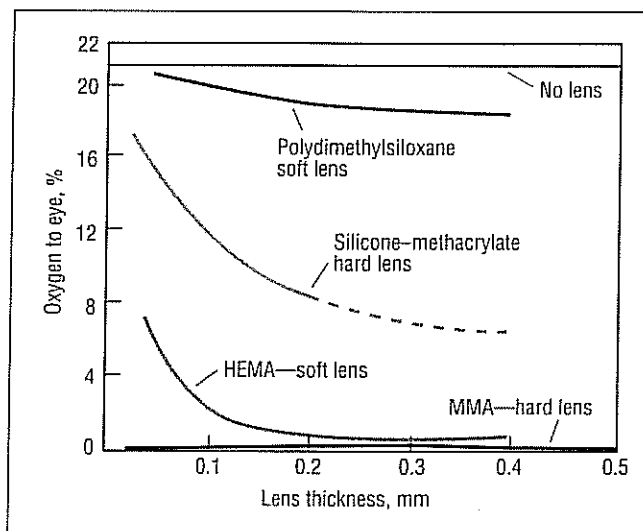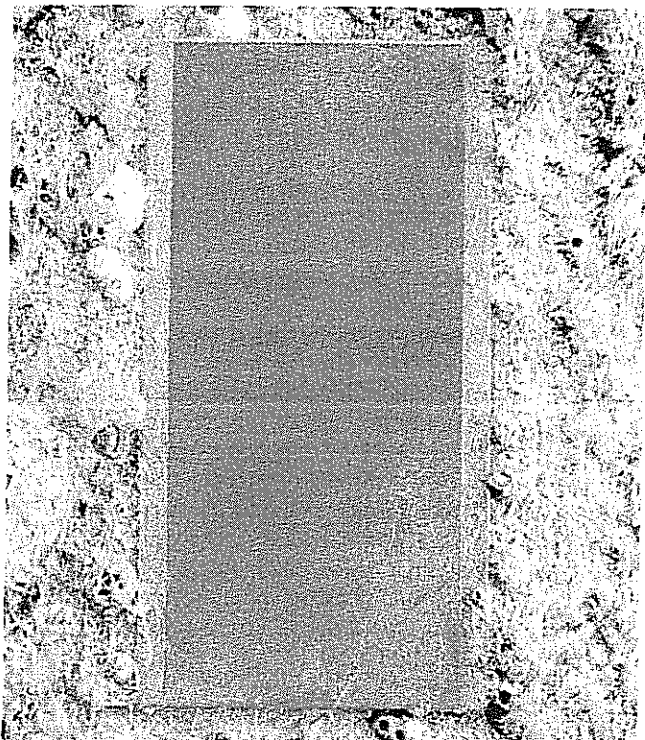
Figure 1. Equivalent oxygen permeability for contact lens materials. Air is 21% oxygen. HEMA, hydrated cross-linked hydroxyethylmethacrylate; MMA, methyl methacrylate.

Figure 2. **Tributyltin–methacrylate copolymers provide protection against marine biofouling.** This coated test coupon (middle) was mounted on an uncoated metal control and submerged in Biscayne Bay, FL, for 24 months. Source: Courtesy M. Gitlitz, Elf Atochem. Used by permission.

Although tin hybrid polymers were first patented in 1965 (8), their potential was not appreciated by manufacturers until the mid-1970s (9), and they were not approved by the U.S. Environmental Protection Agency until 1978. The enabling patent technology is credited to Milne (10). The success of organotin copolymers is attributed to the integrity of the dry polymer film coupled with the slow electrolyte-catalyzed hydrolysis of the tin–oxygen bond, which releases trialkyltin compounds. The trialkyltins behave as toxicants while forming a hydrophilic erodible layer. The erodible film is essential because after it is removed by the physical action of seawater, a fresh active surface is exposed to the marine environment (Figure 3).

The release of the tributyltin compounds is relatively linear over time. At the end of the release, the polymer film is totally removed, and vessels can be repainted without extensive surface preparation (11). This class of polymer is marketed under the trade name Biomet 300 (Elf Atochem). Although environmental regulations have curtailed the use of this technology recently, reevaluation indicates that the tributyltin–methacrylates may be the antibiofouling option that has the least environmental impact (12).

Hybrid grafts

Commercial hybrid grafts include structures in which organic polymers are grafted onto a polysiloxane chain, such as poly(ethylene oxide)-*graft*-poly(dimethylsiloxane) surfactants, or structures in which alkoxysilanes are grafted onto organic polymers, such as cross-linkable polyethylenes.
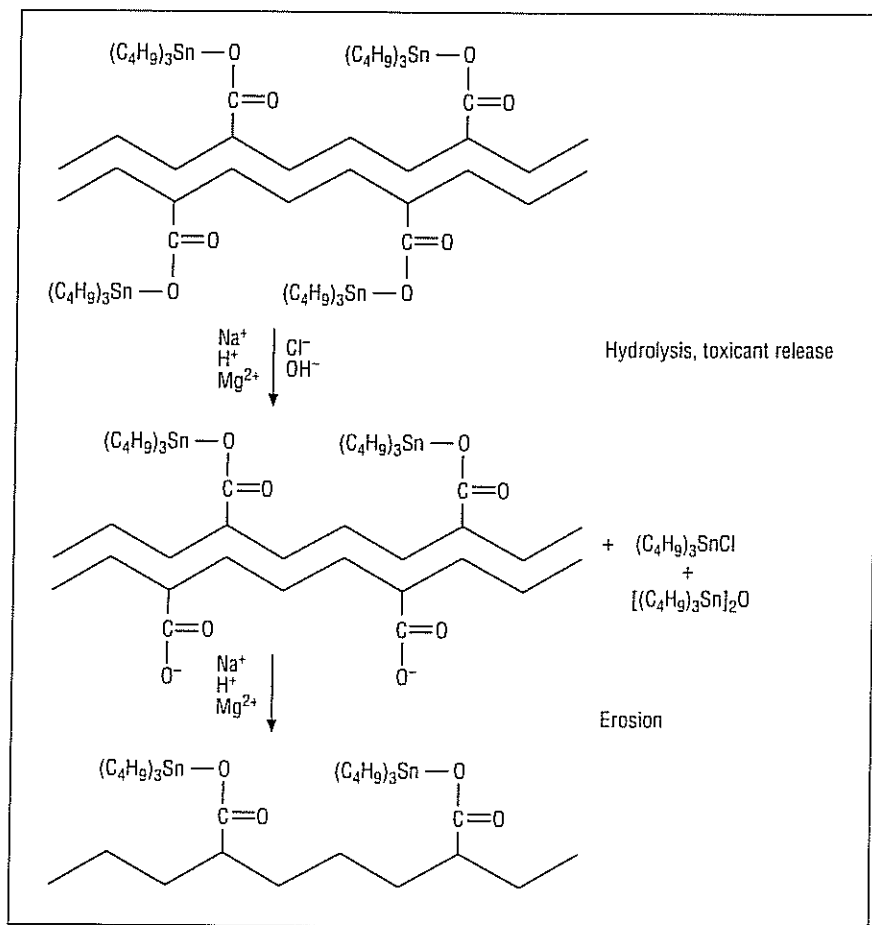

Figure 3. **Organotin antifouling coatings combine an organic polymer base film with hydrolyzable tin–oxygen layers,** which release toxic trialkyltin compounds. The erodible film is removed by the physical action of seawater, exposing a fresh active surface to the marine environment.

Surfactants and wetting agents. Poly(dimethylsilox-ane)s have many unique surface applications associated with the lowest surface tension of any nonfluorinated polymer and the high flexibility of the siloxane back-bone (13). Poly(dimethylsiloxane)s achieve high con-centrations at boundaries between phases, which makes them useful for applications such as release agents and defoamers. The combination of organic poly(alkylene oxide) pendants with the inorganic backbone of poly-(dimethylsiloxane) makes it possible to control wetting and surface tension. A typical structure (4) is alterna-tively referred to as a block, graft, or pendant copolymer system.

4
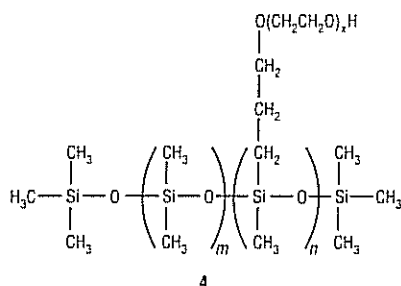
In earlier versions of the technology, a direct Si–O–C bond (which is not hydrolytically stable) was used instead of the propyl link between the alkylene oxide and polysiloxane.

Poly(dimethylsiloxane)s are widely used as surfactants, particularly in the emulsification and stabilization of poly-urethane foam. They orient at air–liquid and solid–liquid boundaries in a manner suitable for lubricating polymer interfaces.

Several short reviews of the synthetic chemistry (14, 15) and physical properties and technology for siloxane–alkylene oxide copolymers (16) are available. The synthe-sis usually proceeds through two steps, the production of poly(methylhydrosiloxane)–dimethylsiloxane copolymers and the subsequent platinum-catalyzed hydrosilylation of an allyl-terminated polyether.

Trisiloxanes are a special class of surfactants in which there are no dimethylsiloxane groups ($m = 0$ in Structure 4). Their orientation presents a "cloud" of seven methyl groups that give a projected surface energy of ~20 dyne/cm (~10 dyne/cm less than the hydrophobic sur-face energy component of hydrocarbon surfactants). The small size of the trisiloxane unit compared with hydro-carbons also allows the film to wet the surface and spread more rapidly. A significant body of enabling tech-nology for the hydrolytically stable siloxane–alkylene oxide copolymers is credited to Reid of Union Carbide (this business unit is now Witco–OSi) (17). The com-pany markets the products, which are used in paints and coatings, personal care products, textiles, and adjuvants for pesticides, under the name Silwet. Similar products are offered by Dow Corning, Goldschmidt, and others.

Cross-link polyethylene through siloxane bond for-mation. Polyethylene has a desirable balance of electrical, mechanical, and processing properties that has led to its application as a wire- and cable-insulation material. Perox-ide and radiation cross-linking raises the continuous oper-ating temperature of polyethylene from 70 to >90 °C.

These methods, which have shortcomings in production efficiency, product homogeneity, and process safety, have been largely supplanted by methods that incorporate pen-dant alkoxysilanes.

The alkoxysilanes cross-link by a hydrolytic mecha-nism to form silsesquioxane networks. The technology is widely used in insulation for wires and cables, including telephone and medium-voltage power cables. Hydrolytic cross-linking also has extended application areas for polyethylene to heat-shrinkable tubing and compression-resistant foam.

Two major technologies are used to cross-link poly-ethylenes with silanes. One is a graft technology in which vinyltrimethoxysilane is peroxide-grafted to a polyethylene backbone before or during cross-head extrusion of the cable. Grafting done before cross-head extrusion is called the Sioplas process, a two-step post-polymerization technology (18, 19). Grafting done dur-ing cross-head extrusion is called the Monosil process, a one-step postpolymerization technology (20, 21). Both processes are completed using moisture and a tin cata-lyst to cross-link the polymer after the final extrusion to produce structures like **5**.

5
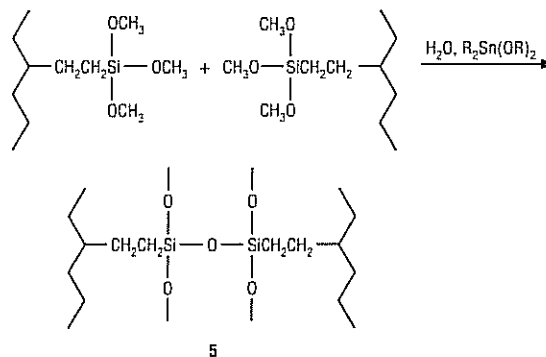
Equistar (formerly Quantum Chemicals) is one com-pany that uses graft technology. Cable processing compa-nies that use graft and cross-link technology include BICC, Alcan, and Okonite.

The success of silane graft technology for cross-link-able high-density polyethylene (HDPE) was based in part on the ability to manufacture product in conven-tional thermoplastic process equipment with relatively little new capital investment. As product benefits were recognized and markets grew, another copolymerization technology with a much greater capital barrier for com-mercialization became a viable contender. The enabling technology was patented by Mitsubishi (22). A peroxide-initiated polymerization at 2500 atm of 0.5–3% vinyltri-methoxysilane with ethylene generates copolymers with properties similar to those of graft copolymers. In some cases, high-temperature properties appear further enhanced; presumably, reactive tertiary carbon sites are eliminated. Companies that have commercialized copol-ymer technology include Neste (VISICO), Union Car-bide (SI-LINK), and AT Polymers (Aqua-Link).

Moisture-cure room temperature vulcanization (RTV) sealants. One technology that is parallel in concept to cross-linkable HDPE is based on an end-group func-tionalization of poly(propylene oxide) (23). The result is a
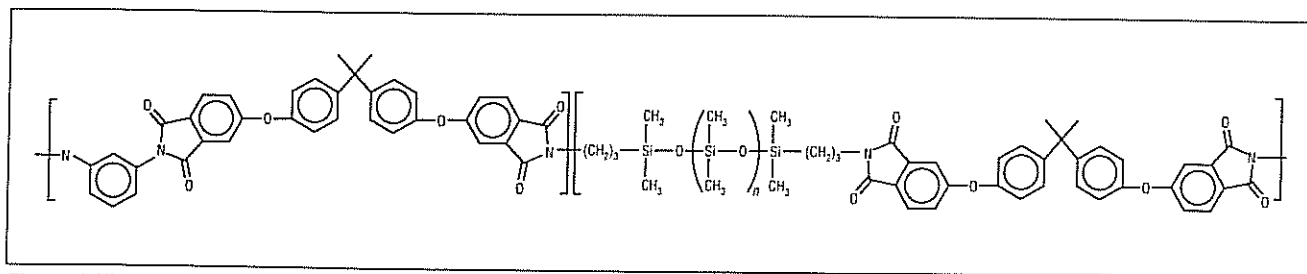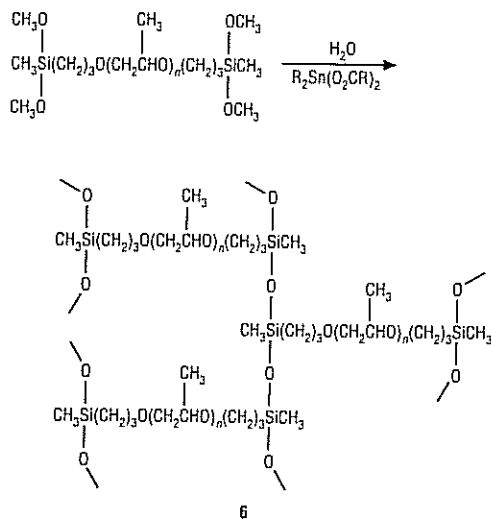
Figure 4. Thermoplastic silicone polyimides are used in the aerospace industry for making wire coatings and enamels.

liquid polymer that cures in the presence of moisture to form conformable low-cost sealants and caulks (6):

6

The technology has been commercialized by Kaneka.

Hybrid block and macromer copolymers

Silicone–polycarbonate block copolymers. The earliest well-characterized block copolymers to achieve commercial acceptance were the bisphenol A carbonate–dimethylsiloxane block copolymers (7) developed by Vaughn at General Electric (24).

7
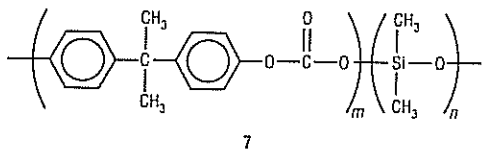
The resins exhibited a structure with a Si–O–C transition between inorganic and organic blocks. Under the trade name Copel LR Resin, silicone polycarbonates have been used in oxygen enrichment membranes (including those in heart–lung machines), in aerospace canopies, and as interlayers for bulletproof glazing. Silicone polycarbonates are prepared by the phosgenation of bisphenol A and chlorine-terminated poly(dimethylsiloxane) oligomer in methylene chloride with pyridine as a base acceptor.

These materials have been described as random block copolymers; the blocks are polydisperse and exhibit a fairly low degree of polymerization. They have outstanding physical properties. For example, a 50–55 wt%

bisphenol A copolymer has a tensile strength of 3000 psi (20.7 MPa), an elongation of 300%, and an oxygen permeability of 5.0×10^{-8} mL/cm/s, cm^2, cm HgΔP, and can be cast to films <5000 Å thick.

The one disadvantage of these polymers is their lack of long-term hydrolytic stability. More current versions of the technology eliminate the Si–O–C transition, replacing it with a stable urethane transition (25). Several versions of oxygen electrodes and other microelectrodes on chips have been incorporated into commercial devices, including medical diagnostic products, by companies such as I-Stat. Ion-selective electrodes have been fabricated by introducing pendant cyanoalkyl groups (which facilitate transport) into the silicone block (26).

Silicone polyimides. General Electric also developed a series of silicone polyimides (27). The technology did not find commercial application until National Starch acquired the technology in the mid-1980s and marketed a series of resins for microelectronics applications such as die-bonding adhesive and dielectric packaging through its Ablestik division. These applications have been sold under such trade names as Rely-Imide, Tabcoat, and Conductimer.

In early versions of the technology, the polymer structures were relatively simple, and their fully imidized forms were thermoset polymers (8).


8
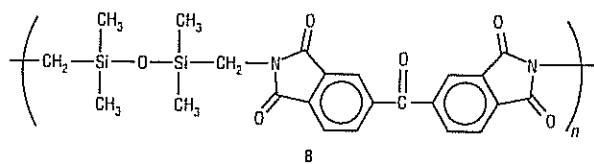
By carefully adjusting block size and comonomer composition, Cella at General Electric (28) developed a series of thermoplastic silicone polyimides with excellent electrical and thermal properties, as well as low smoke generation (Figure 4).

These materials are marketed as wire coatings and enamels under the trade name Siltem; they can be found in a variety of aerospace applications, including passenger aircraft.

Diene–hydrosiloxane resins. Diene–hydrosiloxane resins offer a radically different approach to hybrid organic–inorganic resins for electrical applications. The enabling technology was developed by Liebfried at Hercules (29) and was introduced to the market under the trade name Sycar. The technology uses multifunctional hydrosiloxanes and diene monomers in a two-stage reaction process that depends on hydrosilylation.

In the first stage, one of two olefin positions of the diene is reacted to give an "A-stage" resin (e.g., **9**), which contains approximately equal numbers of unsaturated groups and reactive silicon hydrides.

9
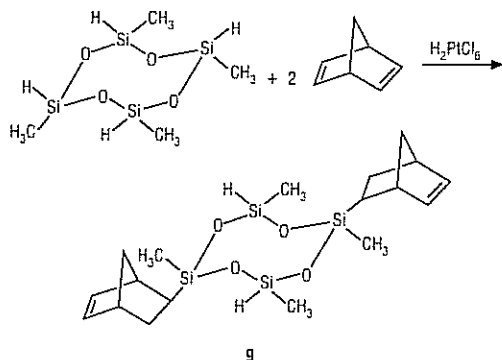
The surprising result is that this A-stage resin is a stable liquid. At elevated temperatures (>150 °C), the reaction goes to completion (i.e., the other double bond links to another siloxane to form a cross-linked polymer). Because the diene and siloxane monomers have low dipole moments, the result is an impregnating resin or encapsulant with a dielectric constant of 2.6 and water absorption of <0.05% after immersion in boiling water.

This technology was recently acquired by National Starch's Ablestik subsidiary. It is being used as a laminating resin for printed circuit boards and for chip-on-board direct encapsulation of chips without conventional packaging (*30*).

IPN technology

True IPNs: Silicone–urethanes. Various silicone–urethane hybrids satisfy the bioengineering criteria of fatigue strength, toughness, flexibility, and low interaction with plasma proteins. The earliest commercialization of hybrid organic–inorganic IPN technology was a bioengineering material introduced by Kontron Cardiovascular as Cardiothane 51. The material was originally described as an aromatic polyether–poly(dimethylsiloxane) copolymer (*31*), but it can be described more properly as an IPN that contains domains of pure silicone and urethane (*32*). Network formation is driven by an acetoxy-cure silicone reaction. The casting of medical device components such as blood pumps and intra-aortic balloons became the primary application for this material.

Semi-IPNs: Silicone–urethanes and silicone–polyamides. Classical or true IPNs are based on two thermosetting polymers that form cross-links without combining (except by entanglement). Semi-IPNs are based on combinations of cross-linkable and nonreactive linear polymers in which mutual entanglement is maintained by the cross-linked resin.

Silicone–thermoplastic semi-IPNs are formed by a reactive processing method in which a silicone is cross-linked in a linear thermoplastic with a high molecular weight. The enabling technology was disclosed by Arkles (*33*), and this polymer is offered under the trade name Rimplast by LNP Corp.

In the simplest embodiment of this method, vinyl- and hydride-functional siloxanes are extruded separately with a base resin. The materials are pelletized and mixed

together with a platinum catalyst to form a homogeneous blend. During subsequent extrusion or injection molding of fabricated parts, a vinyl-addition cross-linking reaction is activated. The result is a silicone semi-IPN with hybrid properties:
- the mechanical properties of a thermoplastic and
- the release, oxygen permeability, and blood–polymer interactions associated with silicones (*34*).

Catheter tubing is one application of silicone–urethane semi-IPNs. Applications of silicone–polyamide semi-IPNs include capstans for high-speed paper and tape transport and optical component devices in photographic equipment.
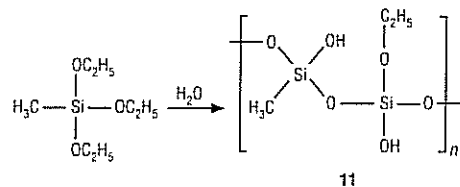
Hybrid organic–inorganic resins

Hybrid organic–inorganic resins may use copolymer, graft, or IPN technologies. They usually use all three elements. Interestingly, the most prominent examples of commercialization represent the earliest and latest embodiments of this hybrid organic–inorganic polymer technology.

In the early 1950s, Brady and co-workers at Dow Corning (*35*) produced a series of phenylsilsesquioxane–alkylsilsesquioxane copolymers (**10**) that had low molecular weight and high hydroxyl functionality.

10
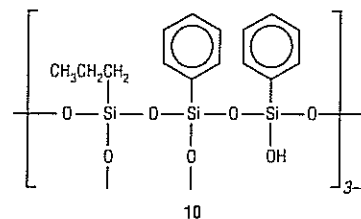
The phenylsilsesquioxane copolymers can be reacted with various standard alkyd resin formulations (*36*) to create a range of high-performance, weather-resistant coatings that are used on superstructures for naval aircraft. Similarly, alkoxy-functional silsesquioxane resins are incorporated into a variety of polyester formulations used in coil-coating applications (*37*).

Commercial abrasion-resistant coatings (ARCs) show a broad elaboration of silsesquioxane (or T-resin) technology. Simple unmodified methylsilsesquioxane resins of controlled molecular weight and hydroxyl content were the earliest examples of ARCs. These materials are rarely used in current ARC technology, but they retain important roles in electrical component coatings such as resistors, molding compounds, and spin-on dielectrics in microelectronic interlayer dielectric and planarization applications. Trade names include Techneglass (NEC) and Accu-Spin (Allied Signal). The materials (e.g., **11**) are prepared by controlled hydrolysis of alkyltrialkoxysilanes:


11

Although these materials cannot be defined as hybrid organic–inorganic polymers, many of their modifications are hybrids. For example, cohydrolysis of trialkoxysilanes with tetraethoxysilane incorporates Q units into silsesquioxanes. In other technologies, silica sols of low dimen-

sionality are generated, and alkyltrialkoxysilanes are reacted with them under hydrolytic conditions (38, 39). Alternatively, cohydrolysates with functional trialkoxysilanes can introduce specific reactivity or other physical properties.

The ceramic community conceptualizes these resins as organically modified silicas and has dubbed them "ormosils" (40). Several ormosils have been offered as scratch-resistant coatings and antireflection layers for eyewear (41–43). Many of the antireflection coatings substitute metals such as titanium for silicon in the Q portion of the structure. Companies that offer lens coatings include Essilor (Silor), SDC, American Optical, and Gentec. In other variations, ormosils modified by organic resins in a graft IPN technology (44) are offered as protective coatings by Ameron under the trade name PSX.

A new variant on the technology is a thermal- or UV-driven cure system, which allows the formation of hybrid systems (12) from modified T resins. The technology exploits the rearrangement reaction of siloxanes substituted at the β-position with electron-withdrawing groups:

12
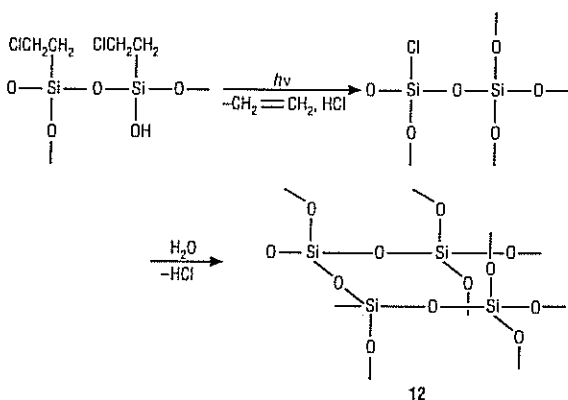
The technology disclosed by Arkles and Berry (45, 46) initially described thermally driven chloroethylsilsesquioxane rearrangements, but more recent work has focused on acetoxyethylsilsesquioxanes. Copolymer versions of the technology lead readily to hybrid structures. Pure or modified silicon dioxide patterns can be written by thermal-cure microcontact printing or UV laser (47). The technology, introduced to the market under the trade name Seramic SI, is finding applications in the formation of dielectric structures for technologies such as flat-panel displays.

Clear, scratch-resistant automotive coatings

A dramatic new high-volume application for hybrid organic–inorganic polymers is large-volume automotive coatings. In current automotive finish technology, coloration is provided in a pigmented base coat. A clear, scratch-resistant overcoat is applied that must not only satisfy optical and mechanical requirements but increasingly must provide protection from environmental factors such as UV radiation and chemical attack.

In a technology introduced by DuPont as Generation 4, these tasks are accomplished by using two hybrid polymer systems that cross-link simultaneously during cure to form a partly grafted, partly interpenetrating polymer network. Hazan and Rummel disclosed the enabling technology (48). A high–cross-link–density acrylate tetrapolymer core

that includes an alkoxysilane substitution, typically methacryloxypropyltrimethoxysilane and residual unsaturation is generated. The core polymer is dispersed in a terpolymer having a low cross-link density that also contains an alkoxysilane, which primarily provides film-forming properties. Melamine–formaldehyde resins and catalysts are blended into the polymer dispersion, allowing the independent cross-linking reactions shown schematically in Figure 5 (page 14).

The superior scratch resistance and environmental etch resistance of these coatings led to their acceptance as topcoats for 8 of the 10 top-selling automobiles for 1997, including Ford Taurus, Toyota Camry, and Honda Civic del Sol.

Evolving with polymer technology

The understanding of organic and inorganic polymer chemistry and the development of new hybrid polymer technologies reflect the available technology and knowledge of structure–property relationships that exist at any given time. As our understanding has grown over time, we have learned to create hybrid materials that display unique properties. The development of new hybrids depends on the ability to establish and understand structure–property and reactivity relationships. The viability of hybrids in the marketplace depends on achieving a set of properties that make the polymers unique and more economical than those currently available.

Because of the increasing research focus on hybrids and a marketplace that has developed exceedingly complex demands, hybrid polymer systems are expected to have ever-increasing impact.

References

(1) Hill, R. Contact Lens Manufacturers Association. 1981, Paper 10-81, p 240.
(2) Ziegel, K.; Erich, F. J. Polym. Sci., Part A: Polym. Chem. 1970, 8, 2015.
(3) Gaylord, N. U.S. Patent 3,808,178, 1974; U.S. Patent 4,120,570, 1978.
(4) Arkles, B. CHEMTECH 1983, 13, 542–555.
(5) Webster, O.; Sogah, D. In Silicon Chemistry; Corey, J., Corey, E., Gaspar, P., Eds.; Horwood-Wiley: Chichester, U.K., 1988; pp 41–48.
(6) Hertler, W. In Silicon in Polymer Synthesis; Kricheldorf, H., Ed.; Springer–Verlag: New York, 1996; pp 69–105.
(7) Seidner, L.; Spinelli, H.; Ali, M; Weintraub, L. U.S. Patent 5,244,981, 1993.
(8) Leebrick, J. U.S. Patent 3,167,473, 1965.
(9) Atherton, O.; Verbogt, J.; Winkeler, M. J. Coat. Technol. 1978, 51 (657), 88.
(10) Milne, A. U.S. Patent 4,021,392, 1977.
(11) Gitlitz, M. J. Coat. Technol. 1981, 53 (678), 46.
(12) Rouhi, M. Chem. Eng. News 1998, 76 (41), 17.
(13) Owen, M. In Siloxane Polymers; Clarson, S., Semlyen, J., Eds.; Horwood-Prentice Hall: New York, 1993; pp 309–372.
(14) Burger, C. Kreuzer, F. In Silicon in Polymer Synthesis; Kricheldorf, H., Ed.; Springer–Verlag: New York, 1996; p 138.
(15) Noshay, A.; McGrath, J. Block Copolymers; Academic Press: New York, 1977; p 400.
(16) Hill, R. In Specialty Surfactants; Robb, I., Ed.; Blackie Publishers: London, 1997; pp 143–168.
(17) Kanner, B.; Reid, W.; Peterson, I. Ind. Eng. Chem. Prod. Res. Dev. 1967, 6, 88.
(18) Scott, H. U.S. Patent 3,646,155, 1972.
(19) Bryan, T., Bowrey, M. Wire J. 1977, 10 (5), 88.
(20) Swarbrick, P.; Green, W. J.; Maillefer, C. U.S. Patent 4,117,195, 1978.
(21) Kertscher, M. Rev. Gen. Caoutch. Plast. 1978, 55, 57–63.
(22) Isaka, T.; Ishioka, M.; Shimada, T.; Inoue, T. U.S. Patent 4,413,066, 1983.
(23) Watabe, T.; Tsuruoka, K.; Doi, T. Jpn. Kokai Tokkyo Koho JP 09124922; CAS 127:35652.
(24) Vaughn, H. U.S. Patent 3,189,662, 1965; U.S. Patent 3,419,634, 1968; U.S. Patent 3,419,635, 1968.
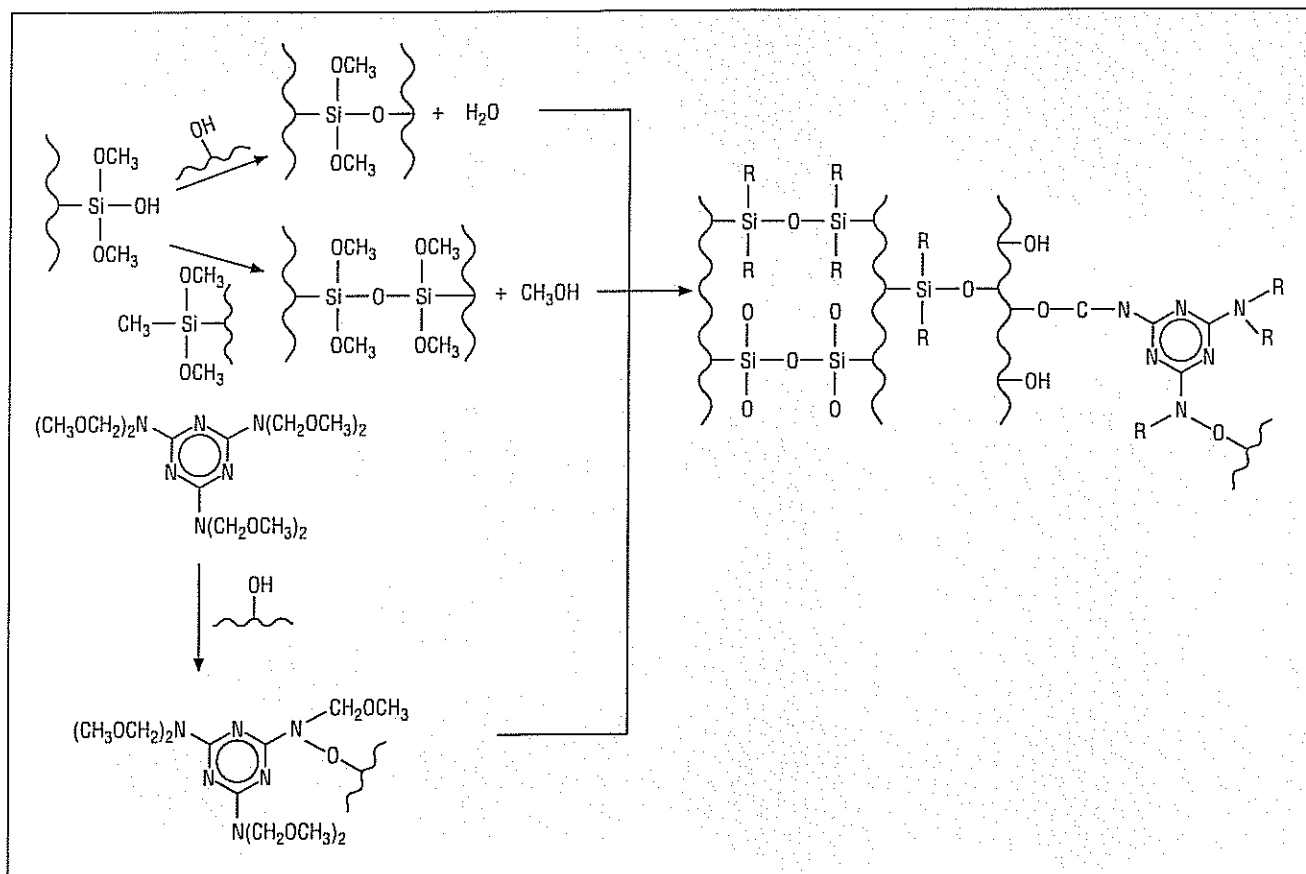
Figure 5. **Clear, scratch-resistant automotive coatings combine two hybrid polymer systems** that cross-link simultaneously during cure to form a partly grafted, partly interpenetrating polymer network.

(25) Riffle, J.; Freelin, R.; Banthia, A.; McGrath, J. *J. Macromol. Sci. Chem.* **1981,** *A15,* 967.

(26) Kinson, P., Orland, C., Klebe, J. Chemical Modification of Siloxane Copolymers for Use as Membranes in pH or K⁺ Electrodes. Presented at the 11th Organosilicon Symposium, Kansas City, MO, 1977.

(27) Berger, A. U.S. Patent 3,274,155, 1966.

(28) Celia, J. U.S. Patent 4,808,686, 1989.

(29) Liebfried, R. U.S. Patent 4,900,779, 1990.

(30) Bard, J.; Brady, R. In *Proceedings of the 42nd ETC Conference, May 1992;* p 1018.

(31) Nyilas, E. U.S. Patent 3,562,352, 1971.

(32) Ward, R.; Nyilas, E. In *Organometallic Polymers;* Carraher, C., Sheats, J., Pittman, C., Eds.; Academic Press: New York, 1978.

(33) Arkles, B. U.S. Patent 4,714,739, 1987; U.S. Patent 4,970,263, 1990.

(34) Arkles, B.; Crosby, J. In *Silicon-Based Polymer Science;* Zeigler, J., Fearon, F., Eds.; American Chemical Society: Washington, DC, 1990; pp 181–199.

(35) Warrick, E. *Forty Years of Firsts;* McGraw-Hill: New York, 1990; p 212.

(36) Brown, L. In *Treatise on Coatings;* Myers, R., Ed.; Marcel Dekker: New York, 1973; Vol. 1, Part III, p 513.

(37) Finzel, W.; Vincent, H. *Silicones in Coatings;* Federation of Societies for Coatings Technology, Blue Bell, PA, 1996.

(38) Clark, H. U.S. Patent 4,027,073, 1977.

(39) Olsen, D. R.; Webb, K. K. U.S. Patent 4,491,508, 1985.

(40) Schmidt, H. In *Better Ceramics Through Chemistry;* Brinker, C., Clark, D., Ulrich, D., Eds.; North-Holland: New York, 1984; p 327.

(41) Phillip, G.; Schmidt, H. U.S. Patent 4,746,366, 1988; In *Ultrastructure Processing of Advanced Ceramics;* Mackenzie, J., Ulrich, D., Eds; Wiley & Sons: New York, 1988; p 651.

(42) Mori, K.; Shimoyama, N.; Tamiguchi, T. U.S. Patent 4,895,767, 1990.

(43) Yajima, E. U.S. Patent 5,165,992, 1992.

(44) Foscante, R. E.; Gysegem, A. P.; Martinich, P. J.; Law, G. H. U.S. Patent 4,250,074, 1981; Ternoir, L. R.; Foscante, R. E.; Gasmena, R. L. U.S. Patent 5,275,645, 1994; Mowrer, N. R.; Foscante, R. E.; Rojas, J. L. U.S. Patent 5,618,860, 1997; Mowrer, N. R.; Foscante, R. E.; Rojas, J. L. U.S. Patent 5,804,616, 1998.

(45) Arkles, B.; Berry, D.; Figge, L. U.S. Patent 5,853,808, 1998.

(46) Arkles, B.; Berry, D.; Figge, L.; Composto, R.; Chiou, T.; Colazzo, H. *J. Sol–Gel Sci. Technol.* **1997,** *8,* 465–469; *Thin Solid Films* **1999,** *345,* 244–254.

(47) Sharma, J.; Berry, D.; Composto, R.; Dai, H. *J. Mater. Res.* **1999,** *14,* 990.

(48) Hazan, I.; Rummel, M. U.S. Patent 5,162,426, 1992.

Barry Arkles is the president and founder of Gelest Inc., a manufacturer of organosilicon and organometallic materials (612 William Leigh Dr., Tullytown, PA 19007; 215-547-1015; info@gelest.com). Previously, he was cofounder and president of Petrarch Systems (now Sivento). He started his industrial career at LNP Engineering Plastics, where he became manager of technical development. He received his B.S. degree and Ph.D. at Temple University. Arkles has published more than 100 papers in the areas of polymer and organometallic materials science. He has received the Industrial Research IR-100 Award, Temple University's Diamond Achievement Award in Natural Science, and the Leo Friend Award from the Industrial and Engineering Chemistry Division of the ACS. His current research interests are thin-film materials and surface modification for electronic, optical, and separation technologies.

Gelest, Inc.

Telephone:

General: 215-547-1015

Order Entry: 888-734-8344

Technical Service: 215-547-1016

FAX   215-547-2484

Internet: gelest.com

Correspondence:

612 William Leigh Drive

Tullytown, PA 19007-6308 USA