

Trends in Polymer Development

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The modern era of polymer research began in the 1930's with pioneering work in the groups of H. Staudinger and W. Carothers. Since that time, many thousands of new polymeric organic compositions have been characterized by researchers in laboratories all over the world. The novelty varies from small differences in structure in well-known families of polymers to compositions representing new families of polymers. The research has been done for many pur-

posed intractable can be formed for study and use. Research on polymer flow, or rheology, has aided understanding of processing requirements.

3) Studies relating structure and processing to final use properties—for example, tensile strength, stiffness, and toughness—have allowed optimization of both polymers and the processes used to prepare them.

4) New synthetic methods provide improved structural control. Many mono-

Summary. Polymer science and technology has flourished as polymers with many new compositions have been synthesized. The range of properties attainable has been continually extended, providing materials with higher strength, better reinforcing capabilities, and greater resistance to extreme thermal and corrosive environments. Examples of evolutionary developments in the polyamides, the fluorocarbon resins, and the aromatic engineering plastics are used to illustrate the trends. It is expected that this process will continue in order to meet changing needs and that emphasis will be put on selective polymer design for specific applications.

poses, ranging from academic investigations of structural possibilities, through subtle modifications to vary processing or physical properties in a useful way, to the preparation of polymers with specific compositions that are expected to have premium properties or combinations of properties.

Interest in polymer research is sustained by steady advances in all phases of polymer science:

1) New and improved analytical techniques are providing more detailed information about molecular structure, molecular weights, end groups, and structural faults in polymers, as well as increasing knowledge of the crystalline and amorphous regions in the supermolecular structure or morphology.

2) Fabrication technology has advanced so that polymers once consid-

ers can be copolymerized either randomly or in blocks as desired. New monomers provide many new structural possibilities. Polymers and copolymers have been developed that contain functional groups needed for cross-linking or other reactions carried out subsequent to synthesis. The chemist can almost routinely prepare structures that seemed impossible only a few years ago.

The field is much narrower when commercially useful, or potentially useful, polymers are considered. Nevertheless, very large technologies involving many structure variations have developed around the polymers made in billion-pound quantities. Many of the commercial polymers made in lower volume are also modified to form numerous new products. These new polymers can range from a polyethylene type useful in cer-

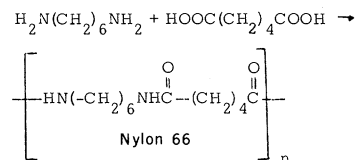
tain packaging applications, to quite new rubbery structures able to withstand extremes of temperatures, to exceptionally strong, stiff organic fibers with many potential uses.

Within the limitations of space and of our own knowledge of the voluminous literature, we have chosen examples that illustrate the extensions of an existing family of polymers, the polyamides; the manipulation of structures in the fluoropolymers; and the development of new aromatic engineering plastics. Our examples are commercial or nearly commercial polymers, particularly those with premium properties or resistance to difficult environments. The reader can consult recent publications for more examples and greater detail (1, 2).

Polyamides

Polyamides are a microcosm of the polymer field, illustrating the range of properties attainable by selective changes in structure. After the introduction of nylon 66 in the late 1930's, chemists continued to explore structure-property relationships in other polyamides (3). This has recently culminated in the development of the high-strength, high-modulus fibers, probably the most important advance in organic polymers in the last decade.

Nylon 66 is prepared from hexamethylenediamine and adipic acid and is used both as a fiber and as an engineering



plastic. (The number 66 is a code designating the polymer structure; it refers to the number of carbon atoms in the diamine and the diacid, respectively.)

Nylon 66 is a semicrystalline polymer. Parts of the polymer chain exist in ordered crystalline regions that have definite melting points and parts are in dis-

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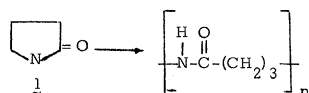
Nylon	MP °C	Equilibrium moisture absn. 100% RH, 73°F	Flexural modulus (GPa)		
			Dry	50% RH	100% RH
4 $\left[\text{NH}(\text{CH}_2)_4\text{C}(=\text{O}) \right]_n$	—	> 10	—	—	—
66 $\left[\text{HN}(\text{CH}_2)_6\text{NH}-\text{C}(=\text{O})-(\text{CH}_2)_4\text{C}(=\text{O}) \right]_n$	250-260	9.0	2.82	1.21	—
612 $\left[\text{HN}(\text{CH}_2)_6\text{NHC}(=\text{O})-(\text{CH}_2)_{10}\text{C}(=\text{O}) \right]_n$	206-215	3.0	2.00	1.24	0.82
11 $\left[\text{HN}-(\text{CH}_2)_{10}\text{C}(=\text{O}) \right]_n$	180-190	1.9	1.17	1.03	0.95

Fig. 1. Characteristics of different polyamides. Abbreviations: *MP*, melting point; *absn.*, absorption; and *RH*, relative humidity.

ordered or amorphous regions. The chains in these amorphous regions are rigid if the temperature is below the glass transition temperature (T_g) of the segments, but behave as liquids above T_g . The degree and kind of crystallinity of the ordered phase and the T_g of the amorphous phase profoundly affect the physical properties.

Nylon 66 is moisture-sensitive, primarily because of absorption of water by the amide groups in the amorphous regions; the water acts as a plasticizer, lowering T_g and increasing the mobility of the polymer chains. As a result, physical properties such as modulus, tensile strength, and toughness and structural dimensions in molded parts are sensitive to the relative humidity of the environment. For specialty uses, polyamides that offer a different balance of water absorption, melting points, and crystallinity have been developed; examples are shown in Fig. 1.

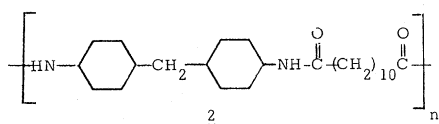
Nylon 4, derived by ring-opening polymerization of pyrrolidone, 1, has a



higher ratio of amide to hydrocarbon groups and absorbs more water. This results in textile characteristics that are more cottonlike than those of nylon 66.

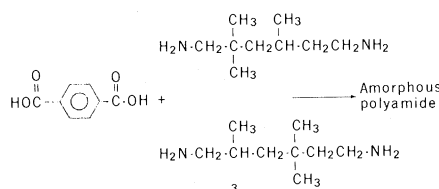
Polyamides with lower moisture sensitivity and greater dimensional stability are also needed. This can be achieved by increasing the ratio of hydrocarbon to amide groups; thus nylon 612 and nylon 11 absorb less water and show less change in modulus than nylon 66 in hu-

mid environments (Fig. 1). The polyamide 2 from bis(4-aminocyclohexyl)methane and dodecanedioic acid has two structural features that contribute to



dimensional stability: (i) the frequency of the amide group is lower than in nylon 66 and (ii) the large cyclohexyl rings substantially reduce the mobility of the chain, resulting in a much higher T_g , and the polymer is only moderately plasticized by absorption of water (4). Fibers from 2 show little change in properties on exposure to moisture and have unusually good wash and wear properties.

Completely amorphous or glassy polyamides are another structural variation. They can be prepared by using monomers with an irregular chain structure so that the long-range order necessary for crystallinity cannot develop. The use temperature of such amorphous polymers is determined mainly by the T_g . An example is the polyamide from terephthalic acid and mixed trimethylhexamethylenediamines, 3, which is market-



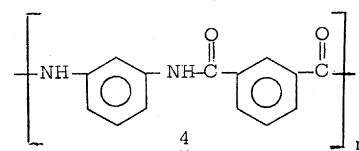
ed as Trogamid T (5). In common with other glassy polymers, this polyamide is transparent, an important advantage in

many applications, and it has much better retention of mechanical properties at elevated temperatures than many crystalline polyamides of lower T_g .

Aromatic Polyamides and New

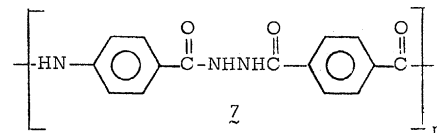
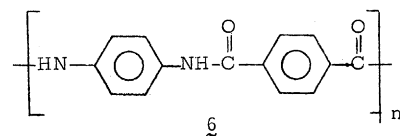
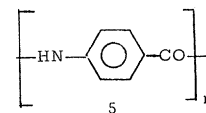
High-Strength, High-Modulus Fibers

Aromatic polyamides or aramids were introduced in the early 1960's to meet the need for fibers with more heat and flammability resistance. These polymers melt at too high a temperature to be made by the melt polymerization processes used for aliphatic polyamides. New low-temperature polymerization techniques involving solution or interfacial reaction of a diacid chloride and a diamine in the presence of certain salts were developed so that polymers with the high molecular weights required for useful physical properties could be reproducibly prepared (6). The first example is poly(*m*-phenyleneisophthalamide), 4. The flam-



mability resistance and thermal stability of this polymer have led to its extensive use in protective clothing, electrical applications, and as a replacement for asbestos.

The next step in the evolution of aramids has been the development of high-strength, high-modulus fibers. The fibers are derived from very highly crystalline rigid-chain polymers that form extended chain crystals. These rigid-chain polymers are based on *para*-substituted aromatic polyamides, including 5, 6, and 7.



The commercial material is DuPont's Kevlar aramid fibers. The development of these fibers is a truly revolutionary advance in polymer technology. They greatly extend the range of physical properties attainable in synthetic poly-

mers, provide new insights into polymer crystallinity and properties, and have stimulated research on polymeric liquid crystals (7-10).

The fibers are stiffer—that is, have a higher modulus—than glass or steel and are stronger on an equal-weight basis. Figure 2 compares the strength and modulus of Kevlar to properties of other reinforcing fibers (glass, graphite, and so on) on an equal-weight basis. Modulus values as high as 128 gigapascals (18.5×10^6 pounds per square inch) have been obtained with these *para*-oriented aromatic polyamides. This is more than 90 percent of the calculated theoretical value. Tensile strengths approach 20 percent of the theoretical value—substantially higher than achieved with nylon 66 or polyester fibers (8). The combination of high strength, high modulus, and low density makes these fibers useful for reinforcement of composite structures including tires. Cables as strong as steel with one-fifth the weight of steel are being used to anchor oceanic drilling platforms. Lightweight bulletproof vests have opened a new dimension in protective clothing.

Research to fully understand the structure of these fibers and their structure-property relationships is being actively pursued. Current results suggest that the polymers differ both in their high level of crystallinity and in the arrangements of the crystals. The fiber from poly(*p*-benzamide), **5**, is almost completely crystalline and the chains are believed to be extended. A small fraction of randomly oriented but crystalline material is present, which forms defect zones between regular crystalline lamellae. There is a high fraction of extended chains which pass through these defect regions, maintaining a long-range order that is absent in most fibers (11).

Another important characteristic of polymers such as **5** is a propensity to form liquid crystals in concentrated solutions in certain solvents. The polymer chain is sufficiently rigid and the polymer conformation sufficiently rodlike in solution that the chains associate in ordered arrays (liquid crystals) above a critical concentration. The solutions are visually anisotropic and the solution viscosity is substantially lower than expected for random-coil polymer chains. The orientation in these ordered arrays can be maintained during spinning, so that a fiber is obtained with oriented extended-chain crystals without subsequent orientation. This behavior is very important for the economic manufacture of these fibers.

Research in this field is extensive, par-

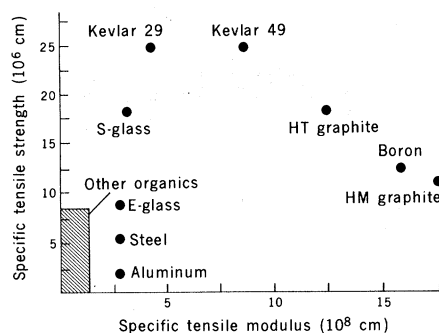


Fig. 2. Specific tensile strength and specific tensile modulus of reinforcing fibers (tensile strength or modulus divided by density).

ticularly on synthetic polymeric liquid crystals. Liquid crystal behavior has been reported in melts of some aromatic polyesters (12), indicating that more examples remain to be discovered.

Fluoropolymers

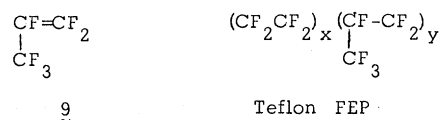
In the 1940's the preparation of polymers from fluorinated monomers, beginning with polytetrafluoroethylene (PTFE), opened a new area of polymer technology by providing combinations of properties that were unavailable in other materials. Polytetrafluoroethylene resin—for example, Teflon fluorocarbon resin—is a homopolymer of tetrafluoroethylene (TFE), **8**; its chemical resist-



ance is unique and its thermal stability and low-friction characteristics are very useful. The original homopolymer, however, had characteristics that limited its application. PTFE has an extremely high molecular weight and is very difficult to fabricate in complex shapes. It cannot be used under very high loads because of the ease with which the crystals deform and slip.

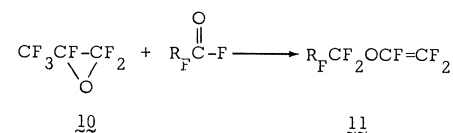
The use of copolymerization technology to obtain desirable property and processing characteristics in fluoroplastics illustrates the evolutionary modification of this family of plastics very well.

Many monomers can be copolymerized with TFE, but most of the copolymers have reduced thermal stability. Hexafluoropropylene (HFP), **9**, was the first fully fluorinated comonomer, which was used to modify the properties of



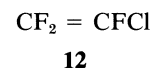
PTFE. Hexafluoropropylene does not copolymerize readily with TFE, so only a limited range of copolymer compositions is readily accessible. A copolymer containing ~10 mole percent HFP was introduced in 1960 as Teflon FEP. Teflon FEP can be melt-fabricated and extruded directly on wires; however, the use temperature is reduced from 250° to 205°C and electrical losses are slightly higher than in PTFE.

Extensive exploratory research at DuPont led to the discovery that fluorovinyl ethers, **11**, copolymerize with tetrafluoroethylene and related fluoroolefins over a wide range of compositions. This discovery and the existence of a practical synthetic route for the vinyl ethers from hexafluoropropylene oxide, **10**, have led to the development of a variety of new perfluoroplastics and elastomers.



Teflon PFA (perfluoroalkoxy) fluorocarbon resins are copolymers of TFE with small amounts of vinyl ethers such as **11**. Because long fluoroalkyl side chains can be introduced, only a small amount of the comonomer is needed to reduce crystallinity and modify the morphology. This gives a melt-processable fluoroplastic that can be injection-molded or extruded and has high-temperature properties very close to or better than those of the original PTFE (13).

The PFA resins are expensive and their use is not commercially justified in many applications. Other approaches to more processable fluoropolymers have involved the preparation of copolymers with simple olefins. Two such materials are copolymers of ethylene with TFE, **8**, or chlorotrifluoroethylene, **12**. Although

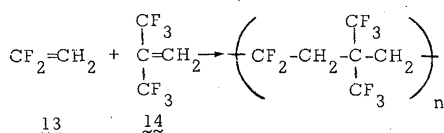


these polymers do not have the heat stability or the high use temperature of PTFE, their chemical resistance and electrical properties are remarkably similar. This is undoubtedly because the hydrocarbon units alternate with the tetrafluoroethylene units and these isolated units are less susceptible to oxidative attack. Both materials are less expensive and easier to fabricate than PFA resins. The ethylene-TFE (ETFE) copolymers have found particular use in wire coatings in electrical equipment and computers. In addition to the necessary insulation properties, they have low flam-

mability, and in the event of a fire their combustion products are not as corrosive as those of the materials they replace.

The ETFE copolymers have been known experimentally for many years. Their recent commercialization is mainly due to improvements in several key physical properties. Unmodified copolymers become brittle above 150°C. The problem was managed by careful control of the polymerization conditions and by the introduction of a small amount of a third monomer to modify the crystalline structure. With the increased amorphous content of the polymer, embrittlement was reduced to an acceptable level.

A related melt-processable plastic is derived by copolymerization of vinylidene fluoride, **13**, and hexafluoroisobutylene, **14**. This is an alternating co-

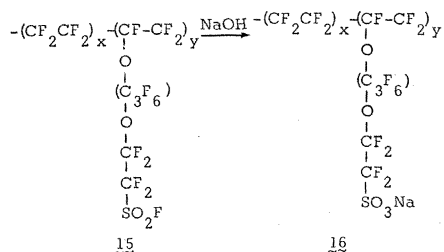


polymer in which the CH₂ groups are shielded from oxidative attack by the large electronegative CF₃ groups. The copolymer is highly crystalline, with a melting point of 327°C and a use temperature up to 280°C. Like other fluoropolymers it has low surface energy, and compared to PTFE it has higher surface hardness, better abrasion resistance, and better scratch resistance. Because of this combination of properties, uses of this material for hard, low-friction, chemically resistant coatings are being investigated (14).

A recent advance has been the development of a fluoroplastic reinforced with graphite fibers. The composite structure has outstanding rigidity and resistance to creep and can be used in gaskets for extremely corrosive environments.

Fluorocarbon Ionomers

Other new materials that have evolved from the chemistry of perfluorovinyl ethers are copolymers of tetrafluoroethylene with ether monomers containing perfluorinated sulfonyl fluoride functional groups, **15**. These polymers can be

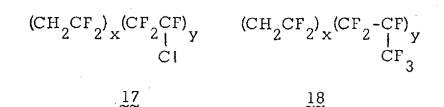


converted to the sulfonic acid form and then to an acid salt or ionomer, **16**.

The ionic groups aggregate in the low-dielectric medium of the fluoropolymer to give highly polar domains that swell in water. These perfluorinated ionomers combine the excellent resistance to chemical attack characteristic of fluoropolymers with selective permeability to certain ions. The sulfonic acid polymers as well as similar ones with carboxyl functional groups are being investigated as membranes in cells for making chlorine and caustic by electrolysis of salt solutions (1, 15).

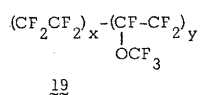
Fluoroelastomers

The need for thermally and chemically resistant elastomers grew rapidly after World War II, especially for aerospace and military applications. The first fluorinated elastomer was a copolymer, **17**, of vinylidene fluoride and chlorotrifluoroethylene, but it was rapidly replaced by superior copolymers of vinylidene fluoride with hexafluoropropylene, **18**. In



each case a large group (Cl or CF₃) was introduced to destroy the crystallinity of the polyvinylidene fluoride. These hydrofluoroelastomers provided a new level of thermal resistance for cured elastomers, having an almost indefinite life at 200°C. Elaboration of the basic structure and extensive curing chemistry has resulted in a family of very useful heat- and solvent-resistant commercial rubbers (16).

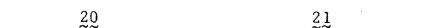
Elastomers useful at even higher temperatures have recently become available from copolymers of TFE with the perfluoroalkylvinyl ethers previously discussed. These materials are the most completely fluorinated elastomeric polymers and can be considered elastomeric analogs of PTFE.



Copolymers, **19**, of TFE with 20 to 50 percent (by weight) perfluoromethylvinyl ether are amorphous, again illustrating the general principle of eliminating the crystallinity of PTFE by introduction of chain irregularity. To fully realize the chemical and thermal resistance of this system, special comonomers had to be developed so that

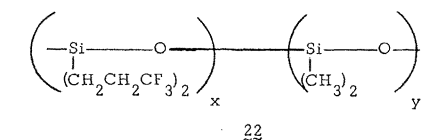
the copolymers could be cured. Examples are shown below.

Terpolymers containing the nitrile **20** can be cross-linked, probably with the



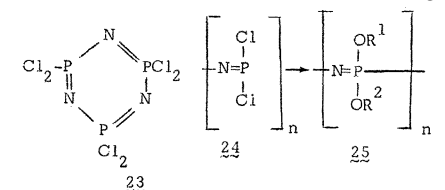
ultimate formation of triazines. Terpolymers containing **21** can be cross-linked by reaction with bisphenols. Cured elastomeric parts have a continuous-use temperature of 260°C and are exceptionally resistant to most organic solvents. The parts can be used, for example, in sour gas and oil wells, where temperatures are above 200°C and extremely corrosive environments are encountered.

Chemically resistant elastomers are also needed which are both more flexible at low temperatures than the examples above and stable at high temperatures. The current materials of choice are the fluorosilicones, **22**; the silicone chain re-



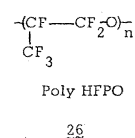
tains flexibility to -100°C and the CF₃ groups confer useful solvent resistance.

A new family of low-temperature rubbers with excellent oil resistance is the polyorganophosphazines. The base polymer is made by polymerization of the cyclic chlorophosphazine **23** to the linear analog **24**. The chlorines can be displaced by alkoxy or fluoroalkoxy groups. By use of a mixture of alkoxy substituents with longer alkyl chains, crystallization can be avoided, providing an amorphous rubber, **25**, with a low *T_g*.



The polymers can be subsequently cross-linked by use of peroxides or radiation (1).

Perhaps the ultimate in a fluorinated rubber with both high- and low-temperature properties will be obtained by polymerization of hexafluoropropylene oxide (HFPO), **10**, to poly-HFPO, **26**. The oxy-



gen atom greatly increases the flexibility of the main chain so that the polymer remains flexible at -50°C, and excellent

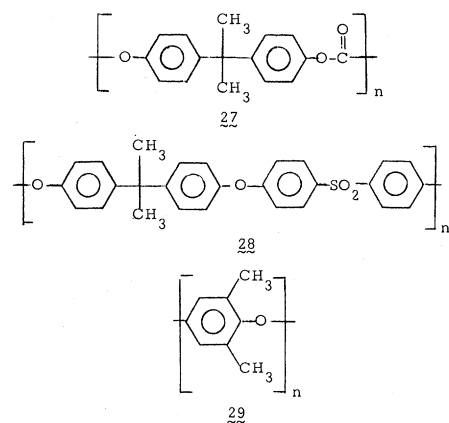
thermal stability has been reported. HFPO polymers with low molecular weights (1 to 2000) are commercially available as thermally stable fluorinated oils and greases. To date, only modest success has been achieved in converting HFPO to a high molecular weight that can be cross-linked (17). Successful completion of this research would extend even further the impressive development of fluorinated elastomers.

Engineering Plastics Based on Aromatics

Engineering plastics are used for structural and mechanical functions, frequently replacing parts once made of metal. They replace metals because they can be fabricated in complex shapes more readily and inexpensively, have better resistance to corrosion, are lighter in weight, or offer a wider range of physical properties. The first and still one of the most important engineering plastics is nylon 66.

The early engineering plastics, however, lacked the strength and stability at higher temperatures to replace metal in many applications. Recent research on the synthesis of aromatic polymers has provided many candidates to meet this need. The aromatic rings confer the structural rigidity, thermal and oxidative stability, and high softening temperatures required for demanding applications.

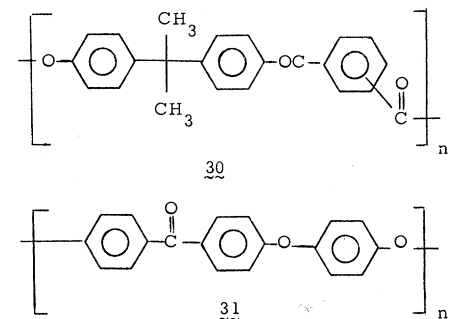
Examples are the polycarbonates, 27, introduced in 1959 by General Electric and Bayer; the polyether sulfones, 28, introduced in 1965 by Union Carbide; and the polyphenylene ethers, 29, in-



roduced in 1964 by General Electric. All these polymers are glassy or amorphous, with glass transition points between 150° and > 200°C. They are generally more difficult to process than the crystalline plastics because they have higher melt viscosities. Special fabrication equipment and procedures had to be developed for these materials. The poly-

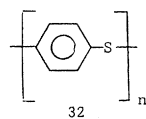
phenylene oxide resins are sufficiently difficult to process that their largest uses are in blends with polystyrene that have lower melt viscosities but also lower use temperatures.

New aromatic polymers continue to extend the range of properties attainable. The aromatic polyesters, 30 (1974), resemble the polycarbonates in chemical



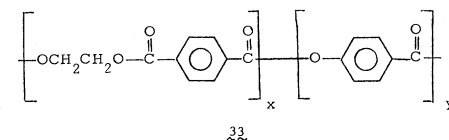
stability but add 30° to 40°C to the maximum use temperature. The polyether ketones, 31, are crystalline and have a wider range of chemical resistance than amorphous polymers.

Polyphenylene sulfides, 32, combine



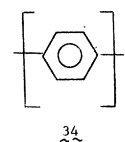
crystallinity and higher use temperatures. Early efforts to prepare useful polyphenylene sulfide by a variety of techniques were unsuccessful; the molecular weights were not reproducible and gelation was a frequent problem. Workers at Phillips Petroleum found that well-defined linear polymers could be prepared by reaction of *p*-dichlorobenzene with Na₂S in a solvent. The polymer is highly crystalline with a melting point above 288°C and is insoluble in most solvents below 200°C. It is exceptionally thermally stable, showing no weight loss up to 500°C and only a modest change in physical properties after 30 weeks at 204°C. While difficult to melt-fabricate, it is finding uses in corrosive environments where high-temperature solvent resistance is needed.

A partially anisotropic aromatic-aliphatic polyester, 33, has recently been



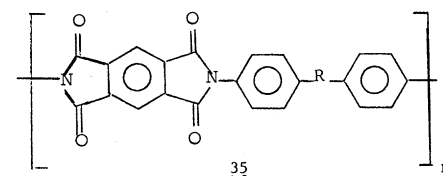
introduced as an experimental high-performance plastic (12). The anisotropy may contribute to easier processing. Broadening of this technology could again increase the maximum use temperature of polyesters.

Probably the ultimate structure in an aromatic polymer is poly(*p*-phenylene), 34, which has a theoretical melting point



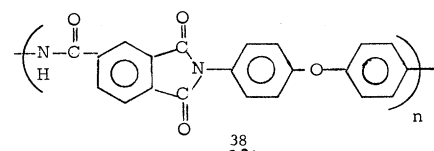
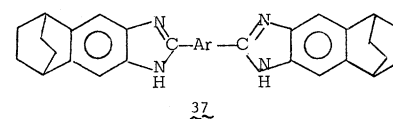
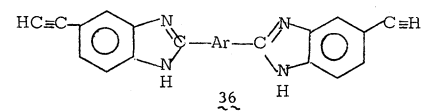
above 1000°C. This material can be fabricated by sintering the fine powders slightly below the decomposition temperature of 625°C (18).

An alternative method for achieving high-temperature performance is to create cross-linked or thermosetting polymers. Epoxy plastics are well-known thermosets that are adequate for long-term use at temperatures of 100° to 125°C. For higher use temperatures, polyimides such as 35, which are ex-



ceptionally thermally stable, are preferred. Because these polyimides are intractable, two techniques have been used to convert them to usable shapes. In one, a soluble prepolymer is formed into a film or coating and then chemically and thermally converted to the polyimide. In the other, methods developed in powder metallurgy are used. A powder with a high surface area is formed into a part at high pressures and then sintered at high temperatures, during which powder coalescence, imide formation, and cross-linking all occur.

Several modified polyimides are being tested that are designed to combine the thermal stability of the polyimide with greater flexibility in processing. Polyimides 36 and 37 (where Ar rep-



resents an aromatic group) have low enough molecular weights to be melt-processed; they are then cross-linked by addition polymerization of the acety-

lene or norbornene groups. Polyimide amides, **38**, represent another approach. Although a structure such as **38** can be melt-processed, it also has a reduced high-temperature capability; for example, **38** has a heat distortion temperature (at 1.86 MPa) of 260°C compared to 360°C for **35**.

Conclusion

The field of polymer chemistry has already reached a high degree of excellence and a certain maturity. The available fibers, plastics, elastomers, and coatings provide a wide range of properties at costs competitive with those of alternative materials. Thus it is increasingly difficult to extend the range of properties or find a niche not filled by existing polymers, especially with the current high costs of market introduction.

Nevertheless, some current developments and world trends provide opportunities for further useful invention. These include:

1) The ability to synthesize and engineer new structures with property combinations ideally suited to specific needs.

2) The need to conserve energy by weight reduction, particularly in automobiles.

3) Increasing environmental concern and regulation, which will favor products that can be recycled and are biodegradable.

4) Changing expectations of society, which will favor more durable materials.

5) The development of new raw material sources, which will present opportunities to replace more expensive polymers with less expensive ones.

We foresee polymer science meeting the challenge of the changing future needs. It seems certain that new compositions will ultimately extend the range of properties available in the high-strength, high-modulus polymers, the fluoropolymers, and the high temperature-resistant engineering plastics. In addition, many modifications of existing polymer types can be expected to improve specific characteristics.

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