PERSPECTIVES: POLYMER SCIENCE

Shape Persistence of Synthetic Polymers

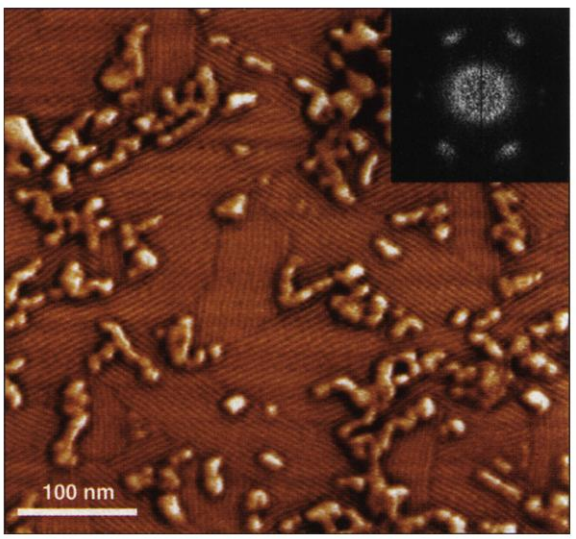
Christopher K. Ober

Biological macromolecules have marvelously complex structures, made possible by precise molecular shapes and sizes whose three-dimensional arrangement is formed by many weak bonding sites. It is this control over all aspects of macromolecular architecture that enables many life processes. The world of the man-made macromolecule is quite different. Synthetic polymers tend to have variable molecular sizes and typically lack a well-defined molecular architecture. Fortunately, in many applications, physical strength is more important than molecular precision, and despite the lack of control over chain conformation and function, synthetic polymers are extremely useful, forming the basis of a multibillion dollar industry.

Enhanced online at www.sciencemag.org/cgi/content/full/288/5465/448

Recent years have seen substantial progress toward controlling synthetic polymer function, size, and shape. Rigid polymers such as Kevlar can possess the strength of steel, whereas flexible polymers can stretch like rubber bands. Stiff conjugated polymers, combined with precise molecular placement, are enabling the construction of microelectronics made from plastics. A recent meeting at the Max-Planck-Institut für Polymerforschung (MPIP) in Mainz, Germany, held in honor of Gerhard Wegner on the occasion of his 60th birthday (*1*), focused on synthetic polymer design strategies that provide much greater control over polymer size and shape than hitherto possible in commercial polymers.

If made sufficiently stiff, a polymer can extend for micrometers (*2*). This situation contrasts dramatically with the ubiquitous "random walk" conformation that provides flexible synthetic polymers of the same molecular length with a roughly spherical shape only a few nanometers in diameter. Several strategies for increasing persistence length or stiffness in a polymer chain were reported at the meeting. In one method, the polymer backbone is made out of rigid, interconnected groups. Conjugated polymers such as poly(phenylene) (*3*) typically fall in this category, and their conjugation enables the creation of optical and electronic devices. Researchers associated with the MPIP have pioneered many of these studies. Chain stiffness of conjugated polymers persists even in solution, permitting the uncoupling of backbone conformation from the possible effects of charged groups on a polymer. Ballauf (Universität Karlsruhe) presented scattering studies of poly(p-phenylene) substituted with ionic groups to demonstrate that ions remain more closely associated with the conjugated polymer chain than previously thought. Khokhlov (Moscow State University) examined similar polymers (*4*) and found that their stiffness and aggregation behavior lead to effective trapping in a gel network from which flexible polymers easily escaped.



Aligning stiff polymers. Phase contrast scanning force microscopy image of an ultrathin layer of a dendronized polymer deposited on graphite. The rows can be attributed to molecules that are predominantly oriented parallel to the surface. The Fourier transform is shown in the inset. [From (*10*)]

Molecular stiffness enables the precise placement and functional control of shape-persistent polymers. This can, for example, be done by building molecular logs, floating them on water, and compressing them to construct organized films with Langmuir trough methods. Armstrong (University of Arizona) described optoelectronic devices that exhibit enhanced charge transport efficiency when assembled from stiff polymers in this manner (*5*). Disclike phthalocyanine groups were strung together to produce a rigid-rod poly(phthalocyanine) with enhanced charge transport properties. Wenz (Universität Karlsruhe) showed that, alternatively, molecular rings, such as cyclodextrin, could be threaded on a flexible polymer chain (*6*) to form molecular rods that might also serve as chemical sensors.

An alternative strategy for making stiff polymers is to place so many side groups on a polymer backbone that a normally flexible structure can no longer bend, thus stiffening the chain. If the side groups are big enough, such polymers adopt a shape resembling a "bottle brush" where the side groups act as the bristles. Individual polymers chains of this kind were imaged by two research teams. Polymers derived from long side group alkyl methacrylates were shown by Schmidt (Universität Mainz) to possess extended chains stretching for hundreds of nanometers, with surprising 120° kinks as revealed by atomic force microscopy studies of individual chains deposited on graphite (*7*). The team of Schlüter (Freie Universität Berlin) and Rabe (Humboldt Universität, Berlin) has synthesized poly(phenylene) substituted with monodendron side groups, creating a macromolecule characterized by both chain stiffness and steric crowding (see the figure). Scanning tunneling microscopy revealed the dramatic stiffening of the polymer backbone in images of single polymer chains.

The interplay between interfaces and chain conformation was also discussed. Stupp (Northwestern University) has used rod-coil block copolymers to direct supramolecular size and dimensionality. The shape-persistent rod segment has fewer degrees of conformational freedom and therefore influences the organization of flexible segments stretching across the microstructure interface. Thomas (Massachusetts Institute of Technology) described recent successful efforts in using self-assembly to produce optical wavelength photonic band gap materials by the formation of large-scale layered microstructures. The surface of a polymer film can also affect polymer conformation and even redirect the orientation of polymer chains, as observed by myself in studies of

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semifluorinated block copolymers. This rearrangement is critical to the formation of the extremely hydrophobic surfaces produced by these polymers.

Gerhard Wegner has pioneered many approaches to investigating shape persistence. As he has said, "Supramolecular structures derived from shape-persistent ("stiff") macromolecules may be used as examples to demonstrate the correlation between chemical structure, order phenomena and performance in applications concerning advanced or developing technologies" (*8*). Starting with his groundbreaking studies of the topotactic polymerization of diacetylenes (*9*), he was one of the first to realize that shape persistence or chain stiffness offers a method of controlling the spatial arrangements of a polymer chain. In subsequent studies at the University of Freiburg and later as one of the two founding directors of the MPIP, he probed many other aspects of shape persistence in polymer science, including studies of conducting polymers, hairy rod polymers, and ultrathin films. His insightful work has influenced many scientists around the world and has led to his being honored with many scientific awards and visiting professorships. All who attended the meeting look forward to his further contributions to the science of polymers.

References

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PERSPECTIVES: LANGUAGE

Movement Patterns in Spoken Language

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If language is a product of the human mind, it is also, as Studdert-Kennedy once wrote, "a mode of action" (*1*). Words are put into play by movements of the human body. To fully appreciate the nature of spoken language, it is therefore necessary to ask whether, and in what ways, linguistic structure reflects the physical activity that yields fluently articulate vocalization. This is what MacNeilage and Davis (*2*) have done in their report on page 527 of this issue. By analyzing the babbling sounds and first words of infants in an English-speaking environment (and subsequently in environments where other languages are spoken), they found four (possibly universal) sound patterns that suggest how the spoken forms of words originate.

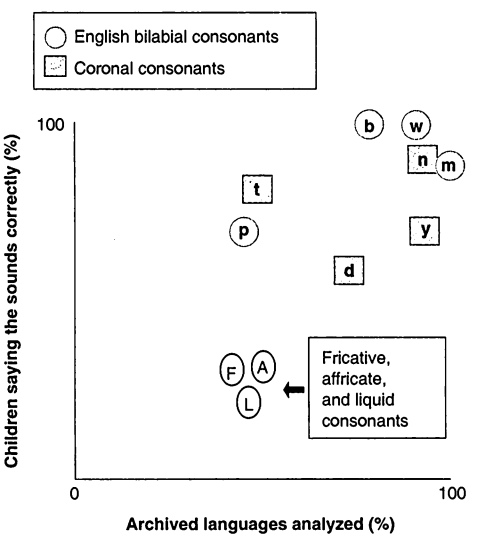
Dictionaries are considered prescriptive, but they also record the verbal habits of the educated and powerful. At one time, prominent Americans produced an aspirate /hw/ when they said the initial consonant in "wheel" and "which," but subsequent generations said /w/, causing lexicographers to revise earlier transcriptions.

Whether aware of it or not, people have always had control of the phonetic reins of language. Speakers who wish to charge "five bucks" sometimes request "fibe bucks"; others who are "supposed to," say they are "sposta." These smoothing operations make speech easier and more fluent. If repeated enough times, they can alter the structure of individual words as well as the sound system of established languages.

Phoneticians have offered various physiological and other explanations for the precise form assumed by speech sounds and syllables, as well as differences in the frequency of vowels and consonants within and across languages (*3*). In the 1970s and 1980s, several teams of linguists conducted systematic searches for phonological universals—patterns that appear in all or most of the languages that have been analyzed. They found that all languages include stop consonants such as /t/ and /d/, but not all have fricatives such as /s/ and /z/; and that all languages have single consonants, but some do not contain clusters such as /pr/ and /gl/. A particularly interesting finding was that every one of the archived languages had consonant-vowel syllables, although many lacked syllables with the reverse order (*4, 5*).

The new study continues in this vein (*2*). Peering inside particular languages, MacNeilage and Davis find that physical, or phonetic, effects may be more pervasive—and languages less arbitrary in structure—than linguists have previously supposed. But their studies begin not with languages in search of an explanation but with individuals in search of a language: preverbal infants who spontaneously emit speech-like sounds but know few words.

Infants usually begin to alternately lower and raise the jaw while vocalizing at about 7 to 10 months of age. With passive bunching of the tongue tip, this activity yields syllable sequences such as "yaya" or, if the tongue is flat, "wawa." If constrictions are



Infant babble, child speech and languages. Sounds that are babbled frequently are produced more accurately by English-learning 2-year-olds, and appear more often in the languages of the world, than other sounds (*5*). The four bilabial (lip) consonants of English are shown in circles; coronal consonants (produced by the tongue at the front of the mouth) articulated in a similar manner appear in boxes. Together, these items constitute about 60 to 80% of all consonant-like sounds in the babbling of preverbal infants. Note the high frequency of the labials (except /p/, which requires momentary interruption of laryngeal vibration) in children's speech and established languages. The coronals are about as frequent in archived languages but take longer to acquire. Fricative (F), affricate (A), and liquid (L) consonants, shown in ovals, are rarely babbled and are found at a reduced frequency in both children's speech and the languages of the world.

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