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Color changes mark Polymer reactions

Polydiacetylenes are unusual among polymer families: They have conjugated backbones. And this property produces effects that have led one researcher working with the substances to foresee their value as an educational tool.

The effect produced by the polymer backbone is color change. When polydiacetylenes undergo various chemical and physical processes, they change color, making the processes visible.

A group of 15 or 20 short experiments thus could demonstrate visibly all the processes that monomers and polymers undergo. And the visible nature of the changes brought on by the processes would reinforce understanding of the theory.

The idea of using polydiacetylenes as an educational aid comes from Gordhan N. Patel, staff chemist at Allied Chemical's corporate research center, Morristown, N.J. Allied researchers are working on the compounds with a number of potential commercial uses in mind.

The educational use of polydiacetylenes is an offshoot of that work and not something Allied is pursuing. But Patel believes it would have academic value. "What we see is what we believe," he says.

Polydiacetylenes are unusual substances. The polymerization of diacetylene became known about 80 years ago. But nothing much happened until Gerhard Wegner of Albert Ludwigs University in Freiburg, West Germany, revived interest in this area in 1969. A number of researchers are now working on polydiacetylenes, including groups at the University of Pennsylvania, Case Western Reserve University, and Brown University in the U.S.

At Allied, researchers have synthesized about 200 polydiacetylenes having different substituent groups. So far, nine patents have been granted, 10 allowed, and filings have been made for five more.

Most diacetylenes, $R-C\equiv C-C\equiv C-R$ colorless solids. They polymerize in the solid state via 1,4- trans addition reactions, either upon thermal annealing or exposure to high-energy radiation, such as ultraviolet. Typically, the partially polymerized diacetylenes are either blue, purple, or red. Fully polymerized polydiacetylenes are metallic gold or copper colored as a result of extensive delocalization of electrons along the conjugated backbone. The polymers are poorly conductive, however.

The color of the backbone and therefore the polymer is determined mainly by its planarity (effective conjugation length). A highly planar backbone is blue, a slightly planar one is red, and a highly nonplanar one yellow. It is this feature that leads to the color changes as the polymers undergo conformational transitions in different processes.

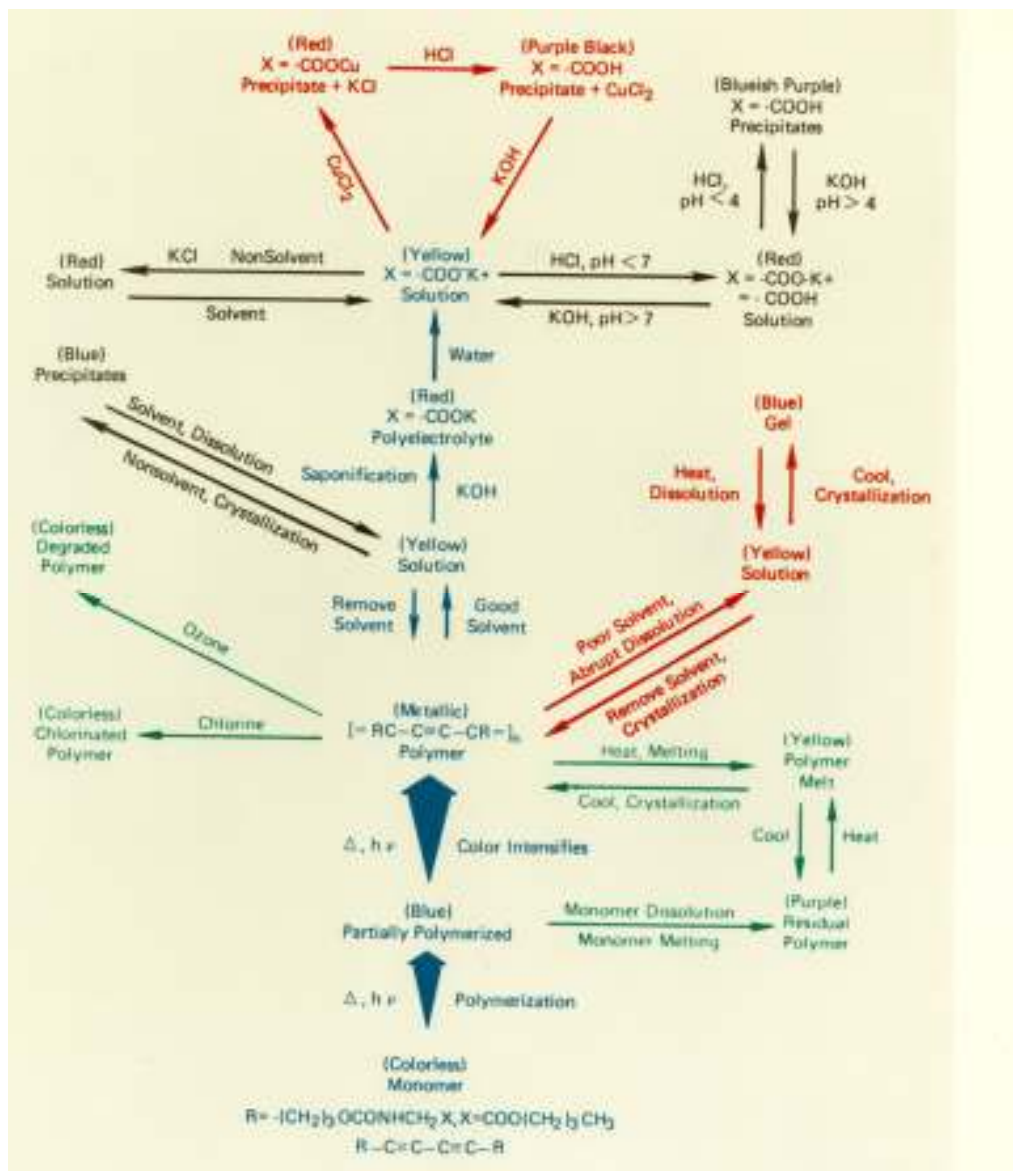
To highlight the educational use of these color changes, Patel has made a movie demonstrating a “process tree” he devised that shows most of the processes the polymer can undergo and the color changes that take place. The process tree is based on a polydiacetylene with butoxy carbonyl methylene urethane substituents—a polymer synthesized by Patel in 1976 that undergoes a color change in all of the processes.

For example, it’s possible to see the polymer melting and crystallizing. Polydiacetylenes show intermolecular and intramolecular melting, Patel explains. On intermolecular melting the color changes from metallic to red, and on intramolecular melting from red to yellow. These changes, reversible, usually take place within 5°C.

If polydiacetylenes can thus be used to demonstrate processes visually, other aspects lend themselves to more advanced experimentation.

For example, Patel notes that there are no experiments in laboratory manuals for determining important energetic parameters such as activation energy of polymerization, heat of polymerization, heat of dissolution of polymers, and heat of conformational transitions. Since most monomers are liquids or gases, determining polymerization energetic parameters is an involved procedure. But since diacetylenes are solids, such parameters are easily determined by differential scanning calorimetry.

As for heat of dissolution, some polydiacetylenes dissolve abruptly—within a few degrees C and in less than a minute. Thus, differential scanning calorimetry can be used for determining this parameter as well.



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