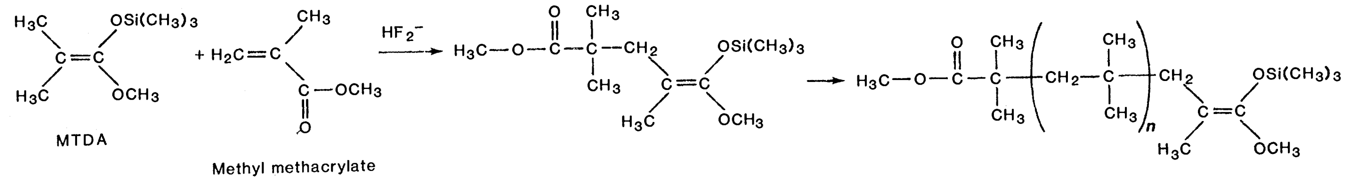
New Way to Catalyze Polymerization

Group transfer polymerization gives excellent control of molecular weight of acrylic polymers, allows introduction of functional groups

A new way to catalyze the synthesis of polymers was reported at the recent meeting of the American Chemical Society* by investigators from the Du Pont Company headed by Owen W. Webster. The new process, called group transfer polymerization (GTP), has so far been used only with acrylic polymers, but it has the potential to be used with other types of monomers. Barry M. Trost of the University of Wisconsin, who has consulted with the Du Pont group, calls GTP "the first new approach to polymers to occur in several decades." The chief advantage of the process is that it gives more precise control of the polymerization process and of the size of polymers formed.



One initiator of polymerization in GTP is methyl trimethylsilyl dimethylketene acetal (MTDA). Related acetals may also be used. Additionally, the process requires a nucleophilic catalyst. The Du Pont group has most often used bifluoride ion, but other effective catalysts include difluorotrimethyl silicate, cyanide, and azide, as well as such Lewis acids as zinc halides and alkylaluminum chlorides.

In the initiation step for GTP of methyl methacrylate, for example, the trimethylsilyl group of MTDA is added to the carbonyl oxygen of the monomer; the rest of the MTDA molecule then is joined to the monomer at its β carbon. These steps are repeated for each new monomer added to the growing chain and continue until all monomer is used up.

This process has several important aspects, says Webster. First and foremost, he says, the growing polymer is "living"—that is, as long as the trimethylsiloxy group is present, the polymer retains the capacity to add more monomer. The Du Pont group has shown that the living polymer retains this capacity even after storage for 2 days at room temperature. The trimethylsiloxy is typically removed only by reaction with protic solvents, so there is no premature chain shortening arising from transfer of the initiator to another chain or any other loss of the initiator; all the polymer chains thus have very nearly the same length and weight. In addition, block copolymers can be readily formed by feeding different monomers sequentially.

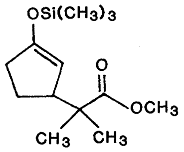
Different initiators can be used to control the identity of the end group on the polymer chain. With MTDA, the end group is an ester. If the methoxy group of MTDA is replaced with an alkyl trimethylsiloxy group, it is possible to obtain a polymer with a free hydroxyl group at the end. If a trimethysilyl group is used instead of methoxy, a carboxylic acid is obtained. Any of these can be readily dimerized in virtually 100 percent yield to produce new polymers with a hydroxyl, carboxyl, or ester group at each end.

The only other polymerization technique that even approaches GTP in efficiency and selectivity is anionic polymerization, which also produces polymers with a very narrow size distribution. Anionic polymerization, however, gives only about a 90 percent yield of functionalized end groups—not sufficient for many applications. Furthermore, it must be carried out at -78°C and can be used with only a few monomers. GTP, in contrast, proceeds smoothly at room temperature and its use can probably be extended to a much larger number of monomers, particularly α,β-unsaturated ketones, nitriles, and carboxamides. The reaction conditions are so mild and specific, moreover, that GTP can be used for copolymerization of such reactive monomers as allyl acrylate (used for making elastomers) and glycidyl acrylate (for epoxies) without the premature cross-linking reactions that occur during most other polymerization processes.

GTP will probably first be used in the production of acrylic automobile finishes and related products. Because of the uniformity of polymer size, says Richard Quisenberry of Du Pont, coatings can contain 60 percent solids rather than the 20 percent that is now common. This means that less solvent is required; there will thus be fewer atmospheric emissions during application. The absence of unreacted monomer also reduces pollution.

Acrylic finishes produced by GTP can also be cured at temperatures as low as 180°F, says Quisenberry, compared to the normal range of 240° to 260°F, resulting in a saving of energy. The new technique could also find application for the fabrication of silicon chips in the semiconductor industry, in the production of coatings for optical fibers, and in the production of "composites" that could be substitutes for metals.

The GTP technique can also be used in synthetic organic chemistry. T. V. Rajanbabu of Du Pont reported that it is particularly useful for minimizing side reactions in the Michael reaction, the addition of carbanions across the 1- and 4-positions of α,β-unsaturated carbonyl compounds. Rajanbabu reacted MTDA with 2-cyclopentenone, for example, to obtain the trimethylsilyl enolate addition product in 91 percent yield. The enolate was then hydrolyzed to give methyl 2-(3-oxocyclopentyl) propanoate in 82 percent yield.



Studies on the mechanism of these reactions suggest that the nucleophilic catalyst activates the silicon atom of MTDA (or of the living polymer) by coordinating with it. A monomer then forms a hexacoordinate silicon by binding to it through the carbonyl oxygen. In the final step, the trimethylsilyl group forms a covalent link to the monomer oxygen, the catalyst is expelled, and the monomer forms a carbon-carbon bond to the former end of the chain. The reaction is probably concerted.

—**Thomas H. Maugh II**

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*186th National meeting of the American Chemical Society, held 28 August to 2 September 1983 in Washington, D.C.