

The Discovery and Commercialization of Group Transfer Polymerization

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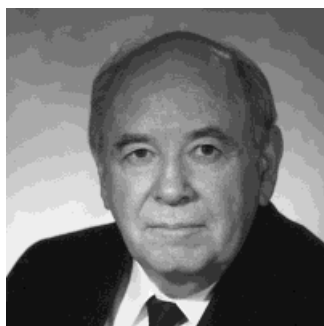
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ABSTRACT: Group transfer polymerization (GTP) is a fundamentally new method for polymerization of acrylic monomers, discovered at DuPont over 20 years ago. It allows one to make block and other specialized polymer chain architecture at above ambient temperature. The method uses silyl ketene acetals

as initiators and requires a nucleophilic catalyst. DuPont uses the process to make dispersing agents for pigmented inks and automobile finishes. The development of GTP from its discovery to introduction of commercial products is presented. © 2000 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 38: 2855–2860, 2000

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Owen W. Webster is currently Adjunct Professor of Chemistry at the University of Pennsylvania. He retired from DuPont Central Research in 1995 where he was one of 25 DuPont fellows. Dr. Webster holds a B. S. in Chemistry and an honorary Dr. of Science degree from the University of North Dakota. He has a Ph.D. in Organic Chemistry from Penn State University. He joined DuPont in 1955 as a research chemist in their Central Research Department. After working 20 years on various organic synthesis projects, he switched to polymer chemistry. His most notable achievement in this area was the discovery of group transfer polymerization (GTP), a new process for controlled polymerization of acrylic monomers. GTP is presently used by DuPont to manufacture block polymer dispersing agents for jet printer inks. Dr. Webster has published 59 scientific papers and reviews and has lectured around the world. He has 35 patents. Dr. Webster is past chairman of the Delaware Section of the American Chemical Society and has received both the ACS Delaware Section Award and the National ACS Award in Applied polymer chemistry.



Scheme 1

INTRODUCTION

Group transfer polymerization (GTP) was discovered over 20 years ago under DuPont's exploratory research project. This project provided funds for staff chemists to work on ideas unrelated to their assigned areas. We were encouraged to spend at least 10% of our time on bootleg research. GTP has proved to be a rich mine of technology. To date Chem. Abstracts lists 872 journal articles, 108 reviews, and 398 patents resulting from investigations of the method. To some extent it may have kindled the surge of activity in the "living" polymerization area that began in the mid 1980s. Debates on the mechanism of GTP (dissociative or associative) drew large crowds at most national and international polymer synthesis meetings.

In this review I will recount how GTP was discovered and the pathway from a fragile research result to a substantial business for DuPont making inks for jet printers.

I was involved early in the inventions and discovery process for GTP in my own lab but soon retreated to manage the GTP group and give talks at universities and scientific meetings. Dotsi Sogah gradually took over the day-to-day management of the GTP group. In my write-up I will use a historical approach noting the names of the many coworkers and their contributions. As with any write-up of this kind memories are also fragile and I apologize if I have left out any crucial contributors. Data relating to the ink jet enterprise is especially sparse since I was not involved with this group in a substantial manner.

THE DISCOVERY

In the mid 1970s DuPont Automotive Products and DuPont Central Research had made a series of methacrylate block polymers with promising properties for dispersing pigments and rheology control in automobile finishes. These polymers had been made at $-80\text{ }^{\circ}\text{C}$ by sequential polymerization of different methacrylate monomers under "living" anionic conditions.¹

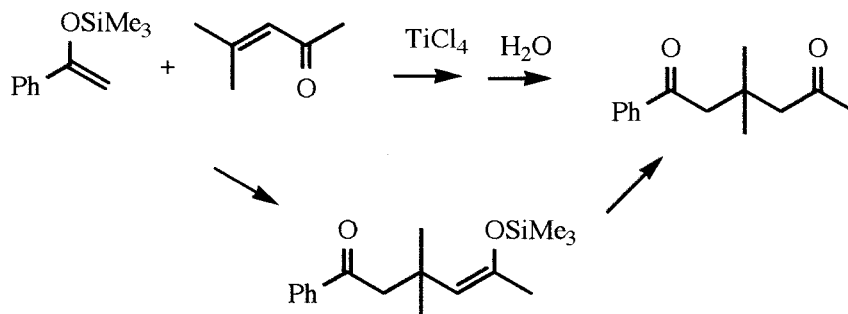
Research in the area was stopped when our process engineers determined that the cost of the process including maintaining reactors at $-80\text{ }^{\circ}\text{C}$ would be too great to make commercially viable products. (Methacrylates have

a heat of polymerization of about 14 Kcal/mole.) At this point in my career at DuPont, I was a year into an assignment change from synthetic organic chemistry to polymer chemistry. I had a small group of new chemists reporting to me but also maintained a laboratory and technician to do my own research. As his first project, Jerry Andrews, a new member of the group, was to make telechelic dihydroxy poly(methyl methacrylate). To do this he initiated the "living" anionic polymerization of methyl methacrylate with a 1,1-diphenylhexyl anion containing a silyl protected hydroxy group.² His plans were to couple the anion ended polymer to arrive at the α , ω -dihydroxy derivative. In his first effort he planned to make a trimethylsilyl ketene acetal ended polymer and couple it with TiCl_3 a well-known literature method for coupling silyl ketene acetals (Scheme 1).

To check the literature reaction, Andrews had made a sample of trimethylsilyl ketene acetal, **1**. He had some of it left over from his research so I asked him if I could use it to see if it would react with MMA to give polymer by a repetitive Mukaiyama reaction. I had obtained my Ph.D. thesis at Penn State under the late Professor Leo Summer, the famous organosilicon chemist, and although my research was straight organic synthesis some organosilicon technology rubbed off on me. I remembered that a silyl ketene acetal would add to activated double bonds under Lewis acid catalysis, the Mukaiyama Reaction,³ (Scheme 2).

I reasoned that the product of one to one addition of MMA to **1** would generate a dimer that still had a silyl ketene acetal function ripe for further addition of MMA (Scheme 3). [In Mukaiyama's work he had hydrolyzed the assumed silyl enoate with water during the work-up (see Scheme 2).]

Since all of the polymer chains would be growing at the same time the molecular weight would be controlled by the ratio of the initiator, **1**, to MMA and the polydispersity should be close to 1, a living polymerization. It was 1979 and the anionic polymerizations of styrene,⁴ butadiene,⁴ and methacrylates were the only reported living polymerization systems. Kennedy's isobutylene polymerization⁵ was not "truly living" at the time and Sawamoto and Hagashimura's living polymerization of vinyl ethers would be announced in 1984.⁶ After talking over my plans with Bill Sharkey and Burt Anderson, my supervisors, I tried a few unsuccessful reactions with Lewis acids such as BF_3 etherate that I had on the shelf.



Assumed intermediate

Scheme 2

I mentioned my efforts to Barry Trost, a DuPont consultant, and he suggested that I try ZnBr_2 as a catalyst.⁷ With ZnBr_2 as catalyst we had our first production of PMMA by group transfer polymerization.⁸ The molecular weight was twice theory but the polydispersity was near one as judged by analytical results based on methods used for polystyrene.

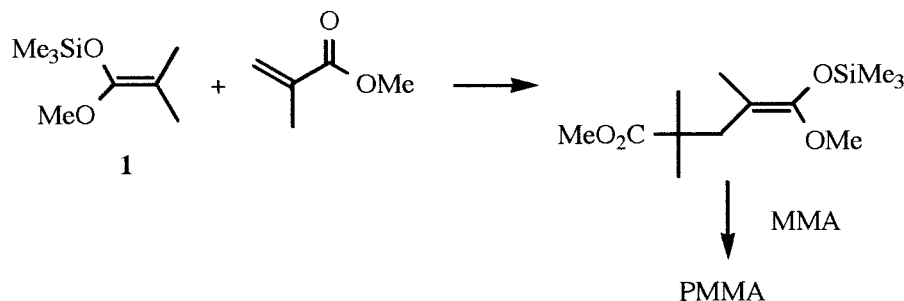
FINE TUNING

In its early stages GTP was very fickle and although we started getting better correspondence of molecular weight with monomer/initiator ratios, we only formed polymer in one out of two runs. After I had wrestled with the conditions for six months, Anderson thought the demonstration was valuable enough to justify more effort and asked Wally Hertler to work on the project. Wally, an excellent problem solver, soon found that he could get polymer every time by making the ZnBr_2 from diethyl zinc and bromine. Zinc bromide from the bottle just wasn't good enough.

While Wally was continuing his search for better reaction conditions, Dotsi Sogah arrived from UCLA and was assigned a project to make block and telechelic polymers by GTP. Meanwhile T. V. RajanBabu in the

Chemical Division of CRD was studying the chemistry of trisdimethylaminosulfonium difluorotrimethylsiliconate, TASF, **2**. Just to see what would happen he added a little TASF to a solution of MMA and **1** at low temperature. The MMA polymerized instantly. He told Bill Farnham also in the Chemical Division and Sogah about his experiment and they decided to look into TASF as a catalyst for GTP. Until then no one had used nucleophilic catalysts for the Mukaiyama reaction. Sogah stored his TASF in an old dry box (he was a new employee and had not yet gotten one of the new highly efficient boxes like the one Farnham had). This lucky break led us to the first "leave-in" catalyst for GTP. Farnham's good sample of TASF did not give a living GTP at room temperature, while the sample Sogah used worked perfectly. Very small amounts gave living polymer at room temperature. Elemental analysis of Sogah sample showed it to be low in silicon. Bill and Dotsi reached the same conclusion when their results were reported. Water was reacting with the TASF to produce bifluoride (Scheme 4).

With this serendipitous breakthrough GTP was finally established as having real commercial potential. Bifluoride efficiently catalyzed GTP at less than 0.01% concentration versus initiator while levels of ZnBr_2 in the 10% range were previously needed. At this low level of



Scheme 3



2

Scheme 4

use, bifluoride could be left in and the polymer solution used directly in auto finishes without costly purification steps. We had a living polymerization of methacrylates that worked at room temperature.⁹ After about two years the number of projects on GTP technology had expanded rapidly. Farnham and RajanBabu were working on new catalysts and the polymerization mechanism. I. M. Dicker, W. S. Brittain, and G. M. Cohen came on board and Sogah was named group leader reporting to me and on up the line to F. P. Boettcher and R. Pariser. Although the group goal was to commercialize GTP, each chemist had his own project and goals: other monomers, new catalysts, new initiators, and so forth. Telechelic polymers, block polymers, star polymers, and other new architectural forms of polymethacrylates began to fill our library of new structures.

MECHANISM STUDIES

The group met for half-day long sessions with our organic and polymer consultants, B.M. Trost, J. D. Roberts, the late Speed Marvel, O. Vogl, Hans Reich, and the late J. Stille, to name a few, to go over mechanisms and other problems. It was at one of these sessions that Trost suggested the name group transfer polymerization (GTP) since our early mechanism studies indicated the trimethylsilyl group remained with the chain it started with during polymerization.¹⁰ In other words it transferred to

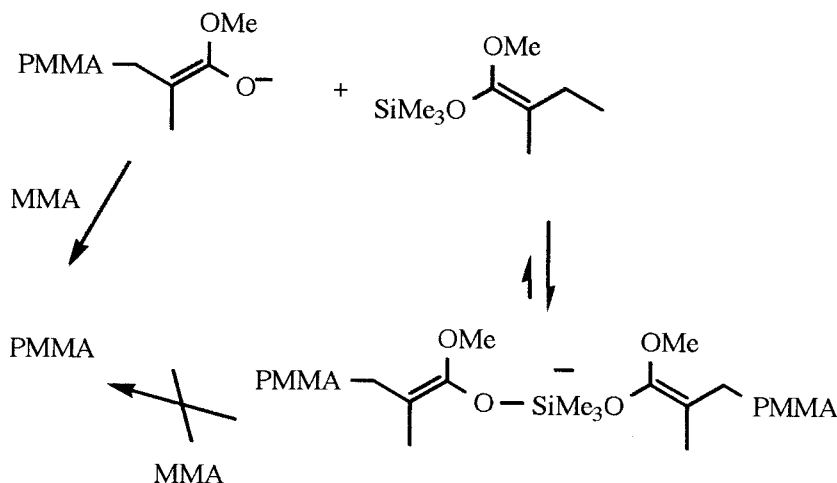
incoming monomer. This mechanism later came under fire by Rod Quirk, Akron University, A. Jenkins, University of Sussex, and Stan Bywater, of NRC Ottawa. Quirk's work was seminal. Instead of using traditional GTP anionic catalysts, he used a known anionic initiator for MMA, one known to give living PMMA but only at -80°C . In the presence of trimethylsilyl ketene acetal, the polymerization proceeded smoothly at room temperature.¹¹ The enolate end groups were being stabilized by coordination with the silyl ketene acetal ended polymer (Scheme 5).

To clinch the result Axel Müller, University of Mainz, had shown that increasing the amount of silyl ketene acetal would retard the polymerization, a necessary result to show that the complex itself is not adding MMA.¹²

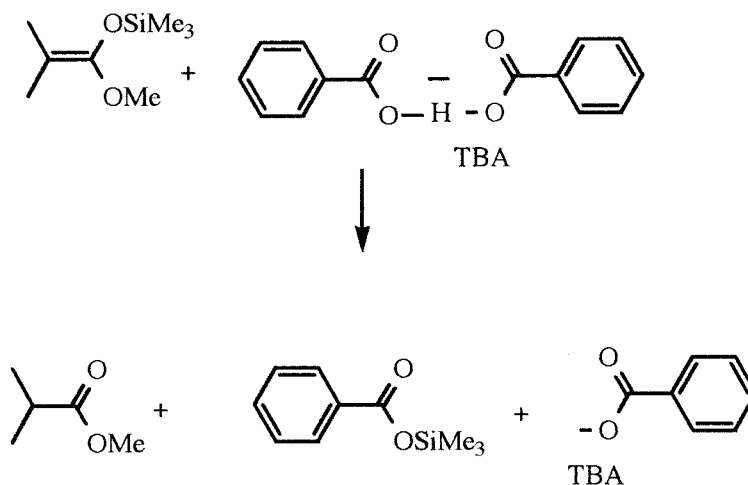
The dissociative mechanism also explained the long induction periods many GTP runs had. The true catalyst was being generated during the induction period by addition to the methacrylate double bond or by complexation with and removal of small amounts of trimethylsilyl function. In addition the dissociative mechanism fits well with the fact that too much catalyst kills the GTP process. Excess catalyst would generate too much unstable bare enolate.

TECHNOLOGY TRANSFER

Two years into the development of the GTP effort Burt Anderson transferred to the Automotive Products De-



Scheme 5



Scheme 6

partment as Assistant Director of Research. This was a break for GTP technology transfer since in his new position, Burt could assign people who knew how to make products and also process engineers to GTP projects. H. J. Spinelli, J. A. Simms, C. S. Hutchins, Waifong Anton, L. A. Page, M. S. West, A. C. Shor, L. V. Schneider, and D. C. Carbaugh were eventually assigned under the able direction of Chuck De Boer. GTP also had several higher management advocates at the Marshall Research Laboratories, especially Al Armour and Carol Senkler. The GTP group met on a monthly basis to report progress on new potential products and process scale up studies.

One of the first things we found out was that a room temperature process was better than $-80\text{ }^{\circ}\text{C}$ but still would require refrigeration to cool the reactor. Carbaugh, the process engineer, told us to find conditions that would allow river-water-cooled reflux condensers to cool the reactor or the process would not be cost effective. Ira Dicker, Luke Schneider, and Mike West were told to come up with a process operating at $80\text{ }^{\circ}\text{C}$. In a few months they came through. The trick was to use a tetrabutylammonium aromatic carboxylic acid salt as the catalyst. These less active catalysts worked at $80\text{ }^{\circ}\text{C}$ but not at lower temperatures.¹³

Bibenzoates gave particularly good results since the extra mole of acid generated small amounts of trimethylsilyl benzoate, which helped control the enolate at low levels (Scheme 6).¹⁴ GTP was ready for the 10-gal reactor that Carbaugh had fabricated.

PUBLICATION

A decision was made to publicize the new technology to show our customers that we had something new in

the pipeline for auto finish technology. The GTP patents were about to issue so the new technology would be public knowledge anyway. I presented the first paper on GTP at the annual organosilicon meeting, which that year was held at Fargo, North Dakota, June 3, 1983. We told the organizers to keep our GTP talk confidential since we wanted to make a more general presentation at the national ACS meeting in Washington that fall. Not being polymer-oriented they said "no problem." Hertler and Sogah presented their work in two posters at the ACS meeting August 29, 1983.¹⁵ The ACS agreed to hold one of their usual press conferences on GTP. Usually *Chem Week*, and *C&E News* came to these meeting press conferences. However Claudette Whiting in DuPont public affairs had a connection with the *Wall Street Journal* and told them about the press conference. The news of a new PMMA breakthrough at DuPont spread quickly and as a result the press conference had reporters from *The New York Times*, *The Wall Street Journal*, *The Philadelphia Inquirer* and *The Washington Post*, as well as others. The day of the conference the value of Rohm & Haas stock dropped six points (They made PMMA resins) and DuPont went up two. Geraldine Sanderson, ACS news Service, told us this ACS news conference was the largest they ever had. In a room jammed with reporters, Hertler, Sogah, and I sat at a table and answered questions about GTP. Although the conference was supposed to be on the science of GTP the reporters were more interested in DuPont business plans. These questions were answered by Dick Quisenberry, Director of Research for Automobile Products, and Rudy Pariser, CRD Material Science Director from the floor. After the press conference reporters were invited to a reception at one of the local hotels. In spite of the excitement we still had no

commercial products ready for the market. However the automobile products team had several promising leads in hand. A. C. Shor and C. S. Hutchins had come up with a block polymer dispersing agent that is still being used to disperse pigments in auto finishes.¹⁶ The cost of the initiator made GTP products too expensive to be used as a finish resin but the high tech block polymer dispersing agents made by GTP allowed one to get the same intensity of color with less pigment. Pigments are expensive ingredients in finishes. John Simms made a coating that was both hard and flexible by crosslinking GTP star polymer into a regular finish resin.¹⁷ The high projected cost of the product killed its further development, however. A toner for copying machines was developed by D. G. Madelein and offered for sale but this product line was dropped due to lack of interest. Plans for a fuel oil sludge inhibitor were also dropped early in the development stage. The big product breakthrough came in the area of dispersants for water-based printing ink for jet printers, an area that did not even exist when GTP was discovered. In the late 1980s Hewlett Packard asked Ray Work in our Printing and Publishing department if DuPont could make pigmented inks for their jet printers. (Pigmented inks are more stable to sunlight and do not wick as badly as the dye-based inks then in use.) Ray said he was sure we could do it. He came to the DuPont automotive finishes with the request. Spinelli, Hertler, and Sheau-Hwa Ma tackled this problem and came up with suitable black ink in a short time. They next tackled the colored pigments. Today DuPont's ink jet enterprise is a thriving business and their plant in Fort Madison, Iowa, is running at full capacity.

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