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The Photopolymer Science and Technology Award

The Photopolymer Science and Technology Award No.091100, the Outstanding Achievement Award 2009, was presented to James V. Crivello (Professor, Rensselaer Polytechnic Institute) for his outstanding achievement in photopolymer science and technology, "Invention of photoacid generators and its contribution to advancement of microlithography".

James V. Crivello

Dr. Crivello received his Ph.D. in organic chemistry from the University of Notre Dame in 1966. He joined the General Electric Corporate Research and Development Center in 1966 and for several years was a research project manager. In 1980, he was elected a Coolidge Fellow by the staff at GE Corporate Research and Development and spent the 1986-1987 year in the Federal Republic of Germany working with Prof H. Ringsdorf. He joined the faculty at the Rensselaer Polytechnic Institute in 1988 as Professor and currently he directs a number of graduate students and postdoctoral associates in various aspects of research in the synthesis of polymers and copolymers by cationic, free radical and transition metal catalysis. At the 2007 American Chemical Society Meeting in Chicago, Professor Crivello was honored as a fellow of the Polymer Materials Science and Engineering Division for his work in photoinitiated cationic polymerizations.

Professor J.V. Crivello's fields of activity include: organic nitrations, oxidations, arylations, polyimides, silicones, and new photo- and thermal initiators for cationic and free radical polymerizations. Among these, his discovery of photoacid generating systems was a key contribution to the success of nanolithographic resists. Chemically amplified resist systems were invented by Dr. H. Ito and his IBM coworkers and are presently used as nanolithographic resists. These resists consist of polymer having functional groups which on removal of a blocking group becomes developable in alkaline solution and photoacid generating materials as the essential key components. The only photosensitive component in this system is a photoacid generator that serves to generate a strong acid on exposure to a deep UV light that subsequently causes deblocking of the polymer. Dr. Crivello discovered a series of novel photosensitive diaryliodonium and triarylsulfonium salts that generate strong or Brønsted acids. These two classes of onium salts are highly photosensitive with quantum yields that range from 0.5-0.9. A large number of modified derivatives of the original sulfonium salts have been synthesized and several are now widely employed for the production of semiconductor devices by KrF and ArF nanolithography. The contribution of the invention of onium salts was undoubtedly significant and accelerated the success of the chemical amplification resist systems.

In addition to the nanolithographic resist technology, onium salts are efficient photoinitiators for the polymerization of various monomers. Depending on the specific application, one can utilize these photoinitiators to conduct either free radical or cationic polymerizations. The photolysis of onium salts produces a variety of active species that react further with proton donors to generate protonic acids. By choice of the appropriate anion, MtX_n^-, of a diaryliodonium or triarylsulfonium salt, the strengths of the photochemically generated acid can be varied from weak acids to powerful super acids. For this reason, these onium salts are widely employed in high performance negative working epoxy-novolak photoresists, where high relief images are required and

for a wide variety of UV-curing applications. When onium salts are used in positive microlithographic photoresists where their function is to provide acids for catalytic photodeblocking reactions, anions such as perfluoroalkylsulfonates are usually employed. In addition to the above mentioned photoinitiators, a wide number of structurally diverse compounds have been designed and prepared to absorb in specific regions of the UV spectrum. Current intense research activity in this area suggests that onium salts will be a continued forcus of the future effort to develop ever more sensitive photoresists with higher resolution capabilities. At the same time, onium salts are finding applications in many fields including: coatings, adhesives, printing inks as well as in many other aspects of thin film polymer and imaging technology.

As described above, Dr. Crivello's invention of photosensitive onium salts is one of the epoch-making events in the field of photopolymer technology which is currently attracting many engineers and scientists.

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Tsuguo Yamaoka
Chiba University