The Technical Association of Photopolymers, Japan

フォトポリマー懇話会　ニュースレター

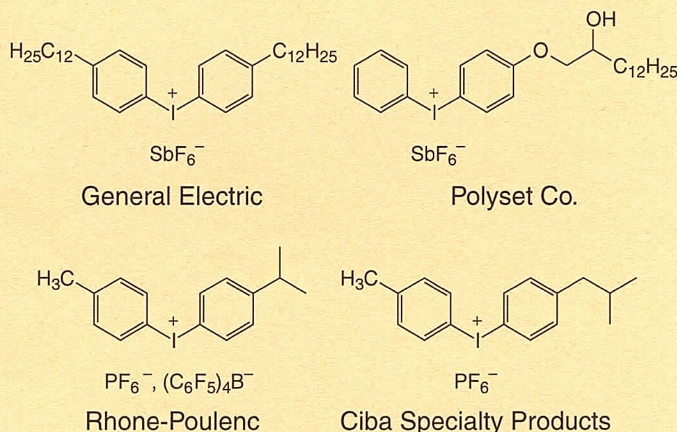
No.23　July 2003

Diaryliodonium Salt Photoinitiators for Cationic Polymerization

Department of Chemistry, Rensselaer Polytechnic Institute

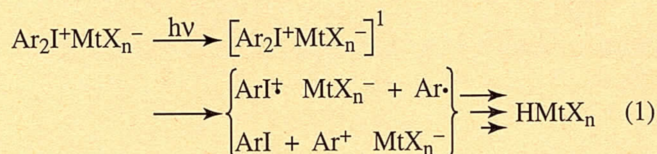
James V. Crivello

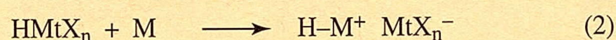
Photoinitiated polymerizations are of increasing interest today because they address a number of energy, economic, environmental and social issues currently of major importance in the world. These polymerizations are employed in many industrial applications and can essentially eliminate air and water pollution since solvents are not required. Further, their consumption of energy is only a small fraction of that required for traditional thermally induced polymerizations. Work in this laboratory has focused on the development of novel classes of photoinitiators that make it possible to carry out cationic polymerizations at high speeds under UV irradiation. A key discovery [1,2] made in this laboratory was the observation that diaryliodonium salts are efficient cationic photoinitiators. These hypervalent iodine compounds are easily prepared and modified using a variety of straightforward synthetic methods. This makes it possible to tailor at will their physical properties such as melting points, solubilities, as well as their UV absorption characteristics. Diaryliodonium salts not only possess excellent photochemical quantum yields but paradoxically also have good thermal stabilities. This enables users to prepare shelf-stable solutions of diaryliodonium salt photoinitiators in a wide variety of highly reactive monomers. Currently, the diaryliodonium salt photoinitiators shown below are available from several commercial sources. These compounds are finding many applications, for example, in photocurable coatings, printing inks, adhesives, among many others. They are widely employed as photoacid generators for use in the most sensitive photoresists used for integrated circuit fabrication and also in stereolithography for the construction of three-dimensional models.

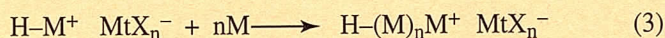


Diaryliodonium salts are a series of stable, colorless, crystalline, ionic salts that are readily soluble in many organic solvents, but nearly insoluble in water. Especially useful is their excellent solubility in a wide variety of polar cationically polymerizable monomers. It was observed that all

diaryliodonium salts are photosensitive [3], however, only those bearing non-nucleophilic anions of the type MtX_n^- as indicated above are useful as photoinitiators of cationic polymerization. Considerable attention has been devoted to the elucidation of the mechanism of the photolysis of diaryliodonium salts [4,5]. The actual mechanism is quite complex and an abbreviated version is shown in equation 1 of Scheme 1.



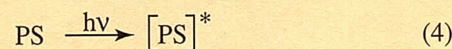


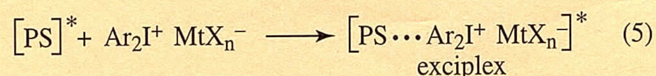


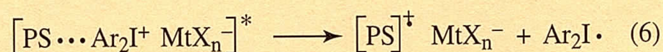
Scheme 1

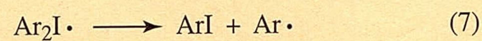
The photolysis of a diraryliodonium salt produces the excited singlet that rapidly decomposes by both heterolytic and homolytic cleavage reactions to provide cations, radicals and cation-radicals. The quantum yield of this process is quite high and of the order of 0.7. The cations and cation-radicals interact with the surrounding environment, i.e. solvent, monomer or impurities, to generate the protonic acid, $HMtX_n$. If the anion, MtX_n^-, is selected such that a super acid (Hammett acidity -12 or lower) is formed, protonation of virtually any cationically polymerizable monomer, M, will take place (eq. 2) and subsequent polymerization (eq. 3) will occur.

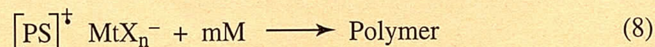
Phenyl-substituted diaryliodonium salts have their primary absorption bands in the wavelength region (220-250 nm). For this reason, they respond well to such emission sources such as medium pressure mercury arc lamps that emit in this region. However, for applications involving imaging, it is often necessary to employ longer wavelength emission sources such as lasers and light emitting diodes. Achieving spectral sensitivity at these wavelengths has been possible through the use of electron-transfer photosensitizers, PS. For example, polynuclear hydrocarbons such as anthracene, pyrene and perylene and their derivatives have been employed to provide sensitivity in the 300-530 nm region [6,7]. The mechanism of electron-transfer photosensitization is depicted in Scheme 2.



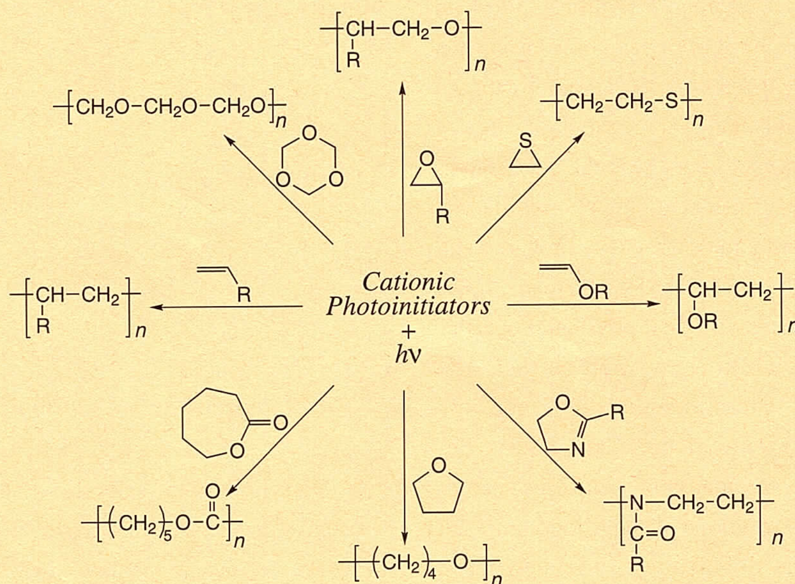








Scheme 2



Scheme 3

On the absorption of light, the photosensitizer, PS, gives the corresponding excited species [PS]* (eq. 4). An excited state complex (exciplex) is often formed as an intermediate between the onium salt and the excited photosensitizer (eq. 5). Next, the onium salt is reduced by a formal one electron-transfer between the two reaction partners (eq. 6). The rapid decomposition of the resulting unstable diaryliodine free radical (eq. 7) prevents back electron-transfer and renders the overall process irreversible. Lastly, (eq. 8), the photosensitizer cation-radical induces the cationic polymerization of the monomer.

Diaryliodonium salt photoinitiators can be used to conduct the polymerization of virtually every known type of cationically polymerizable monomer. Scheme 3 shows some typical examples of vinyl and heterocyclic monomers that have been photopolymerized.

Work in this laboratory has focused on three major classes of cationically polymerizable monomers included in Scheme 3: epoxides, oxetanes and vinyl ethers. These specific monomers are of interest since they undergo the most rapid rates of polymerization. A wide range of epoxide monomers is available commercially and many of these monomers are suitable for coatings, adhesives and printing inks. More recently, several new series of epoxide monomers have been prepared with high reactivities and excellent properties [8]. Oxetane monomers have many properties that are similar to epoxides [9]. Vinyl ethers display exceptionally high reactivity in photoinitiated cationic polymerization by diaryliodonium salts and are most suited to high-speed printing ink applications.

Diaryliodonium salts have also found considerable use as photoacid generators in chemically amplified microelectronic photoresists [10]. Poly(4-*t*-butoxycarbonyloxystyrene) on exposure to UV light in the presence of a diaryliodonium salt gives poly(4-hydroxystyrene), carbon dioxide and isobutylene. The photoresist is then developed using aqueous base to give a positive image.

1. Crivello, J. V.; Lam, J. H. W. *Macromolecules* **1977**, *10*, 1307.
2. Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci.*, Symp. No. 56 **1976**, 383.
3. Khanna, R. K.; Gokel, G. W. *J. Org. Chem.* **1981**, *46*, 2153.
4. DeVoe, R. J.; Sahyun, M. R. V.; Serpone, N.; Sharma, D. K. *Can. J. Chem.* **1987**, *65*, 2342.
5. Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, *55*, 639.
6. Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci. Part A: Polym. Chem.* **1979**, *17*, 1059.
7. Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci. Part A: Polym. Chem.* **1976**, *16*, 2441.
8. Rajaraman, S. K.; Mowers, W. A.; Crivello, J. V. *Macromolecules*, **1999**, *32*, 36.
9. Sasaki, H.;. Crivello, J. V. *J. Macromol. Sci.*, *Pure Appl. Chem.*, **1992**, *A29*(10), 915.
10. Ito, H.; Willson, C. G.; Frechet, J. M. J. *SPE Regional Technical Conference*, Ellenville, New York, Nov. 1982.

【会告】

第13回フォトポリマー講習会
協賛　日本化学会
会期　2003年8月19日(火)～20日(水)
会場　理窓会館（東京理科大学）　新宿区神楽坂
プログラム

Ⅰ　基礎編　(8月19日)
1) 有機および高分子の光化学　理科大　山下 俊 氏
2) フォトポリマーの材料設計とリソグラフィ　松下電器産業　遠藤政孝 氏
3) 微細加工用レジスト材料と評価　シャープ　森 重恭 氏
4) 感光性ポリイミド　東工大　上田 充 氏

Ⅱ　応用編　(8月20日)
5) ラジカルおよびカチオン硬化型樹脂とその応用　JSR　宇加地孝志 氏
6) 微細加工用レジスト　信越化学工業　河合義夫 氏
7) 配線板用の材料動向　住友ベークライト　飯田隆久 氏
8) コーティング用フォトポリマー（仮）　未定
9) 光化学と分子増幅　理科大　市村國宏氏

参加費　会員および協賛会員　30,000円
非会員　40,000円、学生　20,000円
いずれも要旨集（テキスト）代を含む
参加申込方法　FAXで事務局 (043-290-3462) まで
定員　95名（定員になり次第締め切ります）

第144回フォトポリマー見学会・講演会
会期　9月16日(火)
見学先　NHK技術研究所
参加資格　当会会員のみ
参加申込方法　E-mail (miya@faculty.chiba-u.jp) にて事務局まで。会員番号・参加者氏名・ご年令・所属・ご連絡先を明記のこと。定員になり次第締切。申し込まれた方に、後日、詳細な案内を送付いたします。

【平成15年度総会報告】

日時　2003年4月17日(木)　13時00から
会場　理窓会館3F会議室
出席者数　会員16名、運営委員15名(委任状含む)
議案
1．平成14年度事業報告承認の件
2．平成14年度収支決算ならびに年度末貸借対照表承認の件
3．平成15年度事業計画および収支予算承認の件
4．その他の事項
議事
会則に基づき、会長を議長として開会。懇話会会則第11条により総会は成立。議案1、2、および3について承認、議決された。

【研究室紹介】

韓国最大の化学企業、LG Chemical Ltd.
A Photosensitive Materials Program's Activity in the Development of Photosensitive Coating Materials for the TFT-LCDs

Dr. Kim, Kyung-Jun

Photosensitive Materials Program,
Information & Electronic Materials Research and Development(IEMRD)
LG Chemical Ltd. / Research Park / Daejon / Korea

Our Team, opened in June, 1996 belongs to the IEMRD (Information & Electronic Materials R & D) which is pursuing the development of high performance products in the fields of Displays / Circuit Board Materials / Reprographics / Optical Materials through the technology integration and fusion. At present, 20 researchers with respecting and understanding mind to share their creativity and challenging spirit are conducting research on the development of coating materials for LCD in our team.

Since we started the development of pigment-dispersed color filter resist for full color TFT-LCD in 1996, we have extended research items to all kinds of negative photo-sensitive coating materials such as:

1) acryl-based color filter photoresists for notebook, monitor and TV (commercialized in 1999)
2) highly transparent overcoat photoresist for protection and planarization of the color filter layer(commer–cialized in 2002)
3) highly photosensitive column spacer photoresist for the patterned spacer to keep a constant and reliable cell gap uniformity of LCD panel(commercialized in 2002)
4) black photoresist for the resin black matrix with high electric resistivity and high optical density
5) thermally stable advanced overcoating materials for TOC(TFT-array on Color Filter) and thermally curable transparent overcoat materials as well as positive-mode photoresists including transparent insulating materials for a TFT-array and photoresists for microlithography.

We have been focusing on the acquirement of essential technologies concerned with photoresists and coating materials, and is now securing the world-class core technologies as follows;

1) design and synthesis of matrix polymer(transparent thermoplastic, thermosetting and photo-curable polymer)
2) design and synthesis of photo-active compounds such as photo-radical initiators, photoacid generators (PAG) and photoreactive compounds, etc.
3) organic pigment dispersion using special dispersants and functional additives
4) product solution formulation, characterization and evaluation
5) control of various product properties
6) surface treatment and analysis
7) fine chemical analysis
8) ink-jet technology

and now, we constructed very reliable mass production plants in Daejeon and Chung-ju.

Since we have established excellent R & D group related with LCD materials and very reliable mass production system, we can help our customers by solving any technical problems concerned with development and production of TFT-LCDs. (http://www.rnd.lgchem.co.kr)

【ピックアップスケジュール】

応用物理学会2003年秋季講演会
会期 2003年8月30日（土）～9月2日（火）
会場 福岡大学七隈キャンパス（福岡市城南区）
問い合わせ先
URL: http://www.jsap.or.jp/

第52回高分子討論会
会期 2003年9月24日(水) ～ 26日(金)
会場 山口大学吉田キャンパス（山口市吉田）
問い合わせ先 （社）高分子学会 第52回高分子討論会係
Phone: 03-5540-3770, -3771 FAX: 03-5540-3737
URL: http://www.spsj.or.jp

2003年日本液晶学会講演会・討論会
会期 2003年10月14日(水) ～ 19日(金)
会場 青森市文化会館（青森市）
問い合わせ先　あおもり産業総合支援センター
八戸工大コア Phone: 0178-21-8727,
e-mail: jlcs2003@hi-tech.ac.jp

The 13th International Conference on Photopolymers & the 8th International Conference on Advances in Polymers for Microelectronics
会期 2003年10月20日(月)～22日(水)
会場 Termiment Resort & Conference Center, Termiment, Pennsylvania, USA
問い合わせ先
Dr. Hiroshi Ito, e-mail: hiroshi@almaden.ibm.com
URL: http://www.research.ibm.com/chemistry/retec2003

Ninth Microoptics Conference (MOC ' 03)
会期 2003年10月29日(水)～31日(金)
会場 TOKYO International Exchange Center, Waterfront/ Odaiba, Tokyo, Japan
問い合わせ先 Prof. Hirochika Nakajima
e-mail: hiro@pic.phys.waseda.ac.jp
URL: http://www.din.or.jp/~microopt/moc03/

光化学討論会
会期 2003年11月22日(土)～24日(月)
会場 島根県民会館 （松江市)
問い合わせ先 2003年光化学討論会事務局
Phone: 0852-32-6422
e-mail: pc2003@riko.shimane-u.ac.jp
URL: http://www.pc2003.shimane-u.ac.jp/

8th Pacific Polymer Conference
会期 2003年11月24日(月)～27日(木)
会場 Queen Sirikit National Convention Center, Bangkok, Thailand
問い合わせ先 Dr. Vipavee P. Hoven,
e-mail: ppc8@chula.ac.th
URL: http://www.ppc8.thai.net/

第１２回ポリマー材料フォーラム
会期 2003年11月27日(木)～28日(金)
会場 千里ライフサイエンスセンター（豊中市）
問い合わせ先　（社）高分子学会
URL: http://www.spsj.or.jp/c8/pmf/12pmf.htm

【事務局から】

○平成16年度の懇話会事業計画は企画委員会において検討されていますが、会員の皆様の中で例会のテーマとして取り上げたいトピック、講演を聴いてみたい講師の方がおありでしたら、事務局までご一報下さい。企画委員会において検討いたします。昨年に引き続き会員の皆様のニーズにお応えできるような懇話会にしたいと思っております。

【編集コーナーから】

○23号より新しい編集スタッフでお届けします。23号は4月発行の予定が原稿不着で7月発行号と合併して23号といたします。編集スタッフは次のようです。いろいろとご意見をお聞かせ下さい。
　編集委員会　　坪井當昌（編集長）、 矢部 明、 前田龍吾
　フォトポリマー懇話会事務局　宮川信一（長）、 歸山喜代子
○本ニュースレターで新商品あるいは新技術を紹介したいとお考えの方は下記事務局までご連絡下さい。お待ちしております。（掲載費用は無料です）

編集者　坪井當昌　　2003年7月1日発行
発行人　加藤政雄
発行所　フォトポリマー懇話会事務局
〒263-8522　千葉市稲毛区弥生町 1-33
千葉大学工学部情報画像工学科　山岡研究室内
電話/FAX　043-290-3462
E-mail：poffice@ppi.tp.chiba-u.ac.jp
ＵＲＬ：http://ppi.tp.chiba-u.ac.jp/tapj/