

Abstracts of Books and Reviews (2003)

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Preparation of Topological Gel Using Cyclic Macromonomer [in Japanese], Masataka KUBO, and Takahito ITOH: *Polymer Applications*, 52, pp. 27-31, 2003.

Since the discovery of network formation via in situ self threading of functionalized macrocycles, a new methodology referred to as a mechanically cross-linking has been developing. This review describes preparations of mechanically cross-linked vinyl polymers (topological gels) by radical copolymerization of a vinyl monomer with a cyclic monomer (cyclic macromonomer) as a non-bonding cross-linking agent. Mechanically cross-linking is achieved by the threading of the ring by a segment of another polymer chain during the copolymerization. This method offers a network polymer with an enhanced swelling property due to the high degrees of freedom in the segmental movement.

Basic Experiments in Bioorganic Chemistry [in Japanese], Makoto SHIMIZU, The Fifth Series of Experimental Chemistry, Maruzen (Tokyo), pp. 297-330, 2003.

Scope for the basic experiments in bioorganic chemistry was described, which involved lipase-catalyzed asymmetric hydrolysis of esters, baker's yeast reduction of ketones, and other reduction and oxidation methodologies mediated by bio-catalysts. In particular, details were explained for the experimental procedures of these biotransformations.

The Characterization and Reactivity of Photochemically Generated Phenylene Bis(diradical) Species Revealed by Matrix Spectroscopy and Computational Chemistry, Athanassios NICOLAIDES and Hideo TOMIOKA, In "Photochemistry of Organic Molecules in Isotropic and Anisotropic Media", Edited by V.Ramamurthy, K. S. Schanze, Marcell Dekker, New York, Vol. 9/10, Chapter 3, pp. 133-184, 2003.

Phenylene-linked bis(diradicals), where the diradical is a carbene or a nitrene, are relatively simple, experimentally accessible and it is possible to vary the carbene site by chemical substitution. Thus, such compounds are reasonable models for the spin-spin interactions across conjugated systems and in particular across aromatic rings. This chapter is devoted in the recent efforts to generate and study such systems in order to progress our understanding of more complex cases. More specifically, para, meta and ortho-phenylene carbeno(nitrenes) are analyzed in terms of the relative stabilities of multiplicities (singlet, triplet and quintet) and electronic configurations (σ^2 , $\sigma\pi$ and p^2) by theoretical calculations and then these species are actually generated by photolysis of proper precursors and characterized by matrix-isolation spectroscopic techniques in order to verify the theoretical predictions.

Approach to A Persistent Triplet Carbene, Hideo TOMIOKA, In "Carbene Chemistry – From Fleeting Intermediates to Powerful Reagents", Edited by G. Bertrand, Marcell Dekker / Fontis Media, New York / Lausanne, pp. 103-152, 2002.

Our attempts to stabilize triplet carbenes have been reviewed. The review starts with the background story of the idea, followed by the strategy we have used to realize a stable triplet carbene with its integrity intact. Persistent triplet diarylcarbenes, where aryl groups are changed from phenyl, naphthyl and anthryl rings, are discussed in terms of ESR zero-field splitting parameters, UV/vis absorption spectra and kinetics in solution at room temperature (lifetime and rate constants with typical triplet quenchers, such as oxygen and 1,4-cyclohexadiene). Our attempts to use these persistent triplet carbenes as a spin source to construct a high-spin polycarbene as a model for organic ferro-magnetic materials are also mentioned.

m-Phenylene-linked Bis(biradicals). Generation, Characterization and Computational Studies, Athanassios NICOLAIDES and Hideo TOMIOKA: J. Photoscience 10, pp. 165-173, 2003.

m-Phenylene-linked biscarbenes, bisnitrenes and carbenonitrenes can be formed photochemically from appropriate nitrogenous precursors. Generation of such reactive intermediates under matrix-isolation conditions allows for their characterization by spectroscopic techniques such as ESR, UV/vis and IR. Computational chemistry methods complement experimental IR data, aiding, thus, in identification of such compounds. In addition electronic structure calculations help in developing qualitative and semi-quantitative models, which can be useful in predicting ground-state multiplicities. The parent systems of *m*-phenylene-linked carbenes and nitrenes have high-spin ground states, but a switching to lower multiplicity can be achieved by chemical substitution. The ground state and various low-lying excited states of *m*-phenylenecarbenonitrenes can be reasonably approximated by simple valence-bond depictions. Finally, *m*-phenylenecarbenonitrenes are photoreactive in the inert matrix isomerizing to cyclopropene derivatives.

Electrochemical Reduction of CO₂ at Cu Electrode in Methanol at Low Temperature, Satoshi KANECO, Hideyuki KATSUMATA, Tohru SUZUKI and Kiyohisa OHTA: "Utilization of Green house Gases", edited by C. Liu, R. G. Mallinson and M. Aresta, American Chemical Society Symposium Series 852, ACS Division of Fuel Chemistry, Chapter 11, pp. 169-182, 2003.

The electrochemical CO₂-to-hydrocarbons reduction system with high Faradaic efficiency at copper electrode using methanol media has been developed. Since the cold methanol has been inductively used as the physical absorbent of CO₂ in Rectisol method, a combination technology of the Rectisol CO₂ absorption process and the electrochemical CO₂ conversion method will be able to apply the large scale plant.

Slurry Sampling Electrothermal Atomic Absorption Spectrometry with a Metal Tube Atomizer for the Analysis of Human Consumable Materials, Md. Nurul AMIN, Satoshi KANECO, Tohru SUZUKI and Kiyohisa OHTA: Res. Rep. Fac. Mie. Univ., 28, pp. 9-24, 2003.

A slurry sampling technique for the analysis of human consumable materials by electrothermal atomization atomic absorption spectrometry (ETA-AAS) with a metal tube atomizer is reviewed. An ultrasonic agitation method was used for the slurry sampling ETA-AAS. The slurry sampling ETA-AAS was applied to the human consumable materials such as calcium drug, herbal medicine and Bangladeshi vegetable samples. The merits of the slurry sampling ETA-AAS are simplicity, rapid calibration fast analysis and low cost.

A Message from Biomembrane Systems: Supramolecular Biosystems and System-Specific Principles, Tetsuro YOSHIMURA and Kanta TSUMOTO: Rec. Res. Develop. Biophys. Biochem., 3, pp. 585-597, 2003

Recently, along with the proposal on a concept of "complex systems", it has been suggested that "reductive" approaches appear to be unsuccessful and "constructive" approaches are important for understanding and construction of life. We also proposed a concept of "supramolecular biosystems". Based on these two concepts, we found that there are system-specific principles in the intrinsic functions of biomembrane systems and proposed a working hypothesis that the concept of system-specific principles is involved in all biological

functions, suggesting that the supramolecular biosystem and system-specific principle concepts are implicated as a methodology in the field of system biology.

Folding Transition of DNA and Gene Activity [in Japanese], Hidehiro OANA*, Kanta TSUMOTO and Kenichi YOSHIKAWA*: Bioscience & Industry, 61, pp. 11-16, 2003.

Large DNA molecules that are more than several tens of kilo base pairs long undergo a discrete transition in the higher-order structure as the solution environment changes. Such a behavior as a large DNA molecule exhibits implies that this transition may switch on/off gene activity. Here, we present our recent studies on the correlation between DNA folding transition and gene activity, and the feasible development and application to bioindustry of this research will be discussed.

Viscous Fingering in Complex Fluids Containing Cellulose Derivatives [in Japanese], Masami KAWAGUCHI: Cellulose Commun., 10, pp. 114-118, 2003.

Viscous fingering in complex fluids is reviewed focusing on pattern morphology and pattern growth in terms of rheological properties of the complex fluids. The complex fluids prepared are aqueous solutions of hydroxyl propyl methyl cellulose (HPMC), silica particle suspension in an aqueous solution of HPMC, and silicone oil emulsified by HPMC in water.

Structure Study of Amorphous and Crystalline Silica in Plant-Biological System – An Access to Biomimetic Fabrication of Silica Glass or Quartz under Ambient Condition, Kanichi KAMIYA, Tadanori HASHIMOTO, Hidenori AKAMATSU, Yutaka UMETANI and Hiroyuki NASU: Extended Abstracts of Third International Symposium on Biomimetic Materials Processing, P. 94, 2003.

Silica particles were extracted from rice-hulls and bamboo leaves and subjected to X-ray structure analyses. It was found that the atomic-scale structure of such bio-silicas is very close to silica glass even though they have been formed under the ambient condition. On the other hand, silica extracted from “so-called calcic plants” was crystalline or α -quartz. These results suggested the possibility of “in-vitro” formation of the silica glass and α -quartz under the ambient condition.