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Contents

Articles

W. James Feast, Miquel Gimeno, Ezat Khosravi

Journal of Molecular Catalysis A: Chemical 213 (2004) 9

Approaches to highly polar polymers with low glass transition temperatures. 2. Fluorinated polymers via ring-opening metathesis copolymerisation and hydrogenation Diels Alder adducts of fluorinated olefins with cyclopentadiene undergo ring opening metathesis copolymerisation with cyclopentene. Hydrogenation of the resultant unsaturated polymers gives saturated fluoroelastomers with variable fluorine content and low $T_{\rm g}$ values; e.g. 27% fluorine (60 mol% incorporation) and a $T_{\rm g}$ of -22° C.



Walter Kaminsky, Christian Piel

Journal of Molecular Catalysis A: Chemical 213 (2004) 15

Tailoring polyolefins by metallocene catalysis: kinetic and mechanistic aspects

The $C_{\rm s}$ -symmetric zirconocene complex was used for the copolymerisation of ethene and 1-octene and showed extremely high activities of up to 200,000 kg_{polymer}/(mol_{Zi}hc_{monomer}). The molecular weight of the obtained copolymers reached values of 900 kg/mol.



Stucture of $[Ph_2C(2,7-di^{-tert}BuFlu)(Cp)]ZrCl_2$

Richard R. Schrock

Journal of Molecular Catalysis A: Chemical 213 (2004) 21

Recent advances in olefin metathesis by molybdenum and tungsten imido alkylidene complexes Recent advances in olefin metathesis studies include the preparation of catalysts "in situ," supported catalysts, and tungsten-based catalysts, and observation of molybdacyclobutane complexes, molybdacyclopentane complexes, base-free methylene complexes, and ethylene complexes such as $Mo(N-2,6-Cl_2C_6H_3)(CH_2=CH_2)$ [*rac*-Biphen](Et₂O).



Ricardo Castarlenas, Cédric Fischmeister, Christian Bruneau, Pierre H. Dixneuf

Journal of Molecular Catalysis A: Chemical 213 (2004) 31

Allenylidene-ruthenium complexes as versatile precatalysts for alkene metathesis reactions





J.C. Mol

Journal of Molecular Catalysis A: Chemical 213 (2004) 39

Industrial applications of olefin metathesis

 $CH_2=CH_2 + CH_3CH_2=CH_2CH_3 \rightleftharpoons 2 CH_3CH_2=CH_2$

Olefin metathesis opens up new industrial routes to petrochemicals, polymers, specialty chemicals, etc. The most important applications are the production of propene, detergent-range olefins, and polymers via

C. Thieuleux, C. Copéret, V. Dufaud, C. Marangelli, E. Kuntz, J.M. Basset

Journal of Molecular Catalysis A: Chemical 213 (2004) 47

Heterogeneous well-defined catalysts for metathesis of inert and not so inert bonds Three catalysts were conceptually designed and prepared by a Surface Organometallic Chemistry approach in order to achieve: olefin metathesis ([(\equiv Si-O)-Re(\equiv C-*t*-Bu)(=CH-*t*-Bu)(CH₂-*t*-Bu)]), -Ziegler–Natta depolymerisation/alkane hydrogenolysis ([(\equiv SiO)₂ZrH₂], [(\equiv SiO)₃Zr–H]) and - alkane metathesis ([(\equiv SiO)₂Ta–H]).

ring-opening polymerization of cyclo-olefins.



Tomoya Miura, Hiroaki Murata, Koichi Kiyota, Hiroyuki Kusama, Nobuharu Iwasawa

Journal of Molecular Catalysis A: Chemical 213 (2004) 59

W(CO)₅(L)-promoted cyclization of 1-iodo-1alkynes via iodovinylidene tungsten complexes Iodovinylidene tungsten complexes are generated from 1-iodo-1-alkynes and W(CO)₅(thf), and are employed for two types of synthetically useful reaction, that is, 6π -electrocyclization for o-(iodoethynyl)styrenes, and endo-selective cyclization for ω -iodoacetylenic silyl enol ethers and 1-iodo-5-en-1-yne.



Miwako Mori

Journal of Molecular Catalysis A: Chemical 213 (2004) 73

Ruthenium-catalyzed ROM, RCM and CM of enyne

In ROM–RCM of cycloalkene-yne, various cyclized compounds were reconstructed from the corresponding cycloalkene having alkyne in a tether.



Masahiro Yamazaki

Journal of Molecular Catalysis A: Chemical 213 (2004) 81

Industrialization and application development of cyclo-olefin polymer

Cyclo-olefin polymers (ZEONEX[®], ZEONOR[®]) for optical resins) exhibit excellent optical transparency, extremely low impurity and volatile chemical content, low water absorbency, heat resistance, excellent high-frequency insulation property, and outstanding molding properties as thermoplastic resins. These resins are necessary for optical and electronic applications in information technology area.



Udo Anders, Oskar Nuyken, Michael R. Buchmeiser

Journal of Molecular Catalysis A: Chemical 213 (2004) 89

Regio- and stereospecific cyclopolymerization of 1,6-heptadiynes

The synthesis of poly(ene)s exclusively consisting of one single repetitive unit, i.e. 1,2-cyclopent-2-enylenvinylenes, from 1,6-heptadiynes is described. Polymers were obtained by low-temperature-initiated or quinuclidine-assisted cyclopolymerization using Schrock-type initiators, e.g. $Mo(N-2,6-Me_2-C_6H_3)(CHCMe_2Ph)(OC(CH_3)_3)_2$. Complementary to the use of well-defined Schrock initiators, these poly(ene)s were accessible by applying the quaternary polymerization systems $MoCl_5-n$ -Bu₄Sn–EtOH–quinuclidine, respectively.



T.E. Hopkins, K.B. Wagener

Journal of Molecular Catalysis A: Chemical 213 (2004) 93

Bio-olefins via condensation metathesis chemistry



Acyclic Diene Metathesis (ADMET) has been used to prepare bio-olefins, which are highly functio-

Masayoshi Nishiura, Zhaomin Hou

This mini review describes recent advances in the application of organolanthanide complexes toward dimerization of terminal alkynes and polymerization of aromatic diynes. The regio- and stereoselectivity in these reactions can be controlled by tuning the ancillary ligands and the central metals of the catalysts.

Journal of Molecular Catalysis A: Chemical 213 (2004) 101

Organolanthanide catalyzed regio- and stereoselective dimerization of terminal alkynes and polymerization of aromatic diynes



Christian Slugovc, Sandra Demel, Silvia Riegler, Josefine Hobisch, Franz Stelzer

In ROMP reactions molecular weights and molecular weight distributions are strongly affected by the functional groups present in the reaction mixture. Thus, polymer properties can be effectively adjusted by addition of donor solvents to the reaction mixture.

Journal of Molecular Catalysis A: Chemical 213 (2004) 107

Influence of functional groups on ring opening metathesis polymerisation and polymer properties



Additive: MeCN, PhCN, HNEt2, NEt3, pyridine, etc.

Y.S. Gal, S.H. Jin, S.K. Choi

Journal of Molecular Catalysis A: Chemical 213 (2004) 115

Poly(1,6-heptadiyne)-based functional materials by metathesis polymerization

Poly(1,6-heptadiyne)-based polyacetylenes as a new class of π -conjugated polymer were designed and prepared. The cyclopolymerization of 1,6-heptadiynes having such peculiar functionalities as side-chain liquid crystalline, nonlinear optical, photoconductive, photorefractive, and self-dopable ionic groups proceeded well by the molyb-denum-based catalysts. Poly(1,6-heptadiyne) derivatives having bulky substituents revealed excellent oxidative stability in air relative to poly-acetylene and poly(1,6-heptadiyne).



Emma Thorn-Csányi, Oliver Herzog

Journal of Molecular Catalysis A: Chemical 213 (2004) 123

Synthesis of higher, *trans* configured oligomers of diisoalkyloxysubstituted divinylbenzenes (PVoligomers) via metathesis telomerization of the corresponding lower oligomers The preparation of higher, all *trans* configured oligomers of 2,5-diisoalkyloxysubstituted divinylbenzenes (PV-oligomers) via metathesis polycondensation of the corresponding trimer (telomerization) is described (Eq.).

Two highly active metathesis catalysts, a Schrock-type molybdenum complex (with the 2,6-dimethyl phenylimido ligand) and the Grubbs-ruthenium-catalyst of the second generation were used. The main concern was with the selectivity of the telomerization process.



Bart Hessen

Journal of Molecular Catalysis A: Chemical 213 (2004) 129

Intramolecular coordination of a pendant arene moiety in monocyclopentadienyl titanium catalysts can cause a dramatic switch in selectivity from ethene polymerisation to ethene trimerisation. This paper reviews the chemistry and catalytic olefin conversion properties of half-sandwich titanium catalysts with an emphasis on the role played by arene coordination to the catalytically active species.

Monocyclopentadienyl titanium catalysts: ethene polymerisation versus ethene trimerisation



Carmine Capacchione, Antonio Proto, Henner Ebeling, Rolf Mülhaupt, Klaus Möller, R. Manivannan, Thomas P. Spaniol, Jun Okuda

Journal of Molecular Catalysis A: Chemical 213 (2004) 137

Non-metallocene catalysts for the styrene polymerization: isospecific group 4 metal bis(phenolate) catalysts



Yasushi Nakayama, Hideki Bando, Yoshiho Sonobe, Terunori Fujita

Journal of Molecular Catalysis A: Chemical 213 (2004) 141

Olefin polymerization behavior of bis(phenoxy-imine) Zr, Ti, and V complexes with $MgCl_2$ -based cocatalysts

Olefin polymerization behavior of phenoxy-imine ligated Zr, Ti, and V complexes (Zr-, Ti-, and V-FI catalysts) with MgCl₂-based compounds has been studied. These methylalumoxane (MAO)-free catalyst systems are strikingly active (Zr-FI), highly active single-site (Ti-FI) or highly active, thermally robust, single-site (V-FI) catalysts. In addition, the catalyst systems behave as MgCl₂-supported catalysts and thus produce good morphology polymers.



B.B. Marvey, J.A.K. du Plessis, H.C.M. Vosloo

Journal of Molecular Catalysis A: Chemical 213 (2004) 151

The metathesis of polyunsaturated fatty esters using the homogeneous $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ catalytic systems CH_3



CH₃(CH₂)₄CH[≠] CHCH₂CH[≠] CH(CH₂)₄CH₃

$$CH_{3}(CH_{2})_{4}CH = CHCH_{2}CH = CH(CH_{2})_{7}COOMe \xrightarrow{W(OAr)_{2}Cl_{4}} CH_{3}(CH_{2})_{4}CH = CHCH_{2}CH = CH(CH_{2})_{7}COOMe \xrightarrow{+} CH_{3}(CH_{2})_{4}CH = CHCH_{2}CH = CH(CH_{2})_{7}COOMe \xrightarrow{+} MeOOC(CH_{2})_{7}CH = CH(CH_{2})_{7}COOMe \xrightarrow{+} MeOOC(CH_{2})_{7}CH = CH(CH_{2})_{7}COOMe \xrightarrow{+} CH(CH_{2})_{7}COOMe \xrightarrow{+} CHCH_{2}CH = CHCH_$$