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Stereoselective Cyclopolymerization of Diynes: Smart Materials for Electronics and Sensors

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Summary: A series of heptadiynes was cyclopolymerized by Schrock initiators to produce poly(ene)s exclusively based on one single repetitive unit, i.e. 1,2-cyclopent-2-enylenvinylenes. Polymers containing virtually solely 1,2-cyclopent-2-enylenvinylene units were obtained by various routes, e.g. by low-temperature-initiated cyclopolymerization of diethyldipropargyl malonate (DEDPM). A chiral poly(ene) was prepared from 4-(ethoxycarbonyl)-4-(1*S*, 2*R*, 5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (ECMHD) to determine the configuration of the double bonds and the tacticity of the poly(ene) backbone. Poly(ECMHD) consisted of >96% 5-membered rings and possessed a tactic, alternating cis-trans structure. Alternatively, poly(DEDPM) exclusively based on 1,2-(cyclopent-1-enylene)vinylene units was prepared using $MoCl_5$-*n*-Bu_4Sn-EtOH-quinuclidine (1:1:5:1) and $MoOCl_4$-*n*-Bu_4Sn-EtOH-quinuclidine (1:1:2:1). The initiator efficiency of $MoOCl_4$-*n*-Bu_4Sn-EtOH-quinuclidine (1:1:2:1) was as high as 91%, the highest value ever reported for such systems. Multistage polymerizations of DEDPM indicated for both initiator systems that the catalytic species were active for at least 6 hours in the presence of monomer yet did not fulfill the criteria of a truly living polymerization. Finally, a new modification of the Grubbs-Hoveyda catalyst, $Ru(CF_3COO)_2(CH\text{-}2\text{-}(2,4,5\text{-}(MeO)_3\text{-}C_6H_3)(SIMes)$ (SIMes=1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) allowed the first ruthenium alkylidene-catalyzed living cyclopolymerization of DEDPM. The different initiators, their properties, the resulting polymerization systems as well as the physical properties of the resulting poly(ene)s are summarized.

Keywords: conducting polymers; conjugated polymers; cyclopolymerization; metathesis; micelles

Introduction

Initiated by the discovery of the conductive properties of poly(acetylene),[1-3] conjugated polymers are widely used in organic light-emitting diodes (OLEDS), solar cells, photovoltaic

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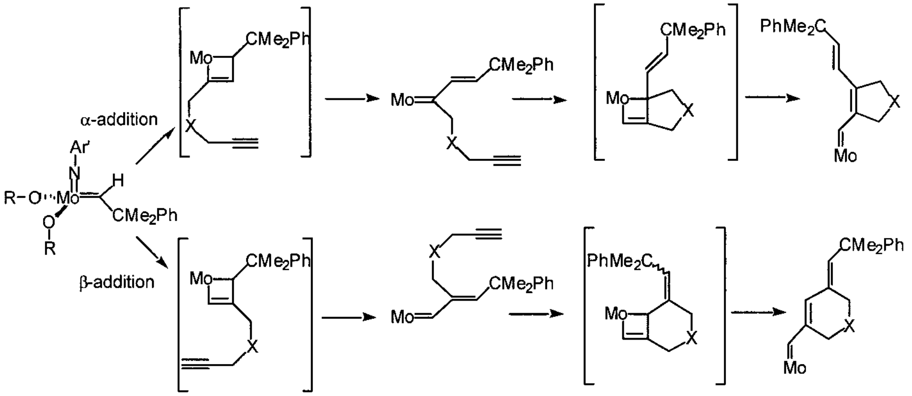
devices, field effect transistors and lasers.[1-6] Despite significant improvements, poly(acetylene)-derived materials still suffer from one or more drawbacks such as insufficient stability and processability, random composition in terms of connectivity, end groups, molecular weight or difficult synthetic accessibility. On the one hand, any successful utilization of these systems strongly depends on a high degree of definition and variability in monomer structure as well as stability and processability of the final polymeric material. On the other hand, these tasks must be accomplished via straightforward synthetic routes in order to allow commercialization. In contrast to 1-alkyne polymerization, the cyclopolymerization of 1,6-heptadiynes offers an attractive access to poly(acetylene)s with cyclic recurring units along the backbone where 1,3-interactions of the substituents, responsible for low effective conjugation lengths in poly(1-alkyne)s, are absent[7-12]. Cyclopolymerization-derived poly(acetylene)s display good solubility in common organic solvents (e.g. C_6H_6, toluene, CH_2Cl_2, $CHCl_3$), good long-term stability towards oxidation and low energy transitions between the valence and conductivity band[11-14]. They can be synthesized using Ziegler-type catalysts[15, 16], Pd-catalysts[17], anionic polymerization[18] and binary/ternary Mo- or W-based catalysts[19]. Well-defined high oxidation-state molybdenum carbenes ("Schrock catalysts") cyclopolymerize 1,6-heptadiynes in a living manner[19, 20] and can be tuned in a way that only one single repetitive unit, i.e. 1,3-(cyclopent-1-enylene)vinylens[21, 22] and 1,2-(cyclohex-1-enylene)methylidenes[13, 14], respectively, is obtained. Despite their unique catalytic properties, the strictly air- and moisture-free conditions that are required in the use of Schrock catalysts are certainly a major limitation for technically relevant applications. Therefore, keeping any potential technological use in mind, such syntheses have to be accomplished by more straightforward routes. We therefore developed a new modification of the Grubbs-Hoveyda catalyst, $Ru(CF_3COO)_2(CH\text{-}2\text{-}(2,4,5\text{-}(MeO)_3\text{-}C_6H_3)(SIMes)$ (SIMes=1,3-dimesityl-4,5-dihydroimidazol-2-ylidene). This water and air stable compound allowed the first ruthenium alkylidene-catalyzed living cyclopolymerization of DEDPM reported so far. In the following, the catalytic systems as well as the properties of the polymers will be summarized.

Results and Discussion

Cyclopolymerization of Heptadiynes using Well-Defined Schrock-Type Catalysts

Typically, molybdenum-based Schrock-type catalysts of the general formula Mo(N-2,6-R_2-C_6H_3)($CHCMe_2Ph$)(OR')$_2$ (R=Me, 2-Pr, R'=CMe_3, $CHMe_2$, $CMe(CF_3)_2$, etc.) yield poly(ene)s that contain a mixture of five- and six-membered rings (Scheme 1) [11, 20]. The formation of one particular backbone structure solely depends on the mode of insertion of the monomer. If insertion proceeds *via* α-addition, five-membered rings are formed, if β-addition dominates, six-membered rings are formed. So far, polymers exclusively consisting of six-membered rings have been prepared using the molybdenum imido alkylidene complex Mo(*N*-2-*t*-Bu-C_6H_4)(CH-*t*-Bu)(O_2CCPh_3)$_2$ [13, 14].



Scheme 1. The two possible modes of insertion-dependant pathways in the cyclopolymerization of 1,6-heptadiynes.

These polymers were prepared in a living way and were well-defined in terms of microstructure, molecular weight and molecular weight distribution, yet displayed comparably low values for N_{eff}, typically ≤ 20 (in THF). Consequently, our effort focused on the development of suitable catalysts that open access to five-membered ring-based microstructures (i. e. of poly(1,2-cyclopent-1-enylene-vinylene)s), since these should provide enhanced coplanarity and in due consequence highly conjugated materials.

The polymerization of DEDPM for the synthesis of poly(1,2-cyclopent-1-enylene-vinylene)s required some significant catalyst tuning. As a matter of fact, Schrock catalysts exclusively containing non-fluorinated alkoxides such as $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(CHCMe_2Ph)(OCH(CH_3)_2)_2$, $Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)(OC(CH_3)_3)_2$, and $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(CHCMe_2Ph)(OC(CH_3)_3)_2$ could be used for the living polymerization of DEDPM to produce poly(ene)s solely based on five-membered rings [21, 22]. Either low polymerization temperatures or the addition of quinuclidine were required to achieve this goal. Values for N_{eff} up to 52, corresponding to a λ_{max} of 592 nm ($CHCl_3$), were realized. These poly(ene)s exhibited a reversible thermochromic behavior and excellent film-building properties. Poly(DEDPM)$_{10\text{-}90}$ showed glass transition temperatures (T_g) around 26°C and was stable under air over months in the solid state as well as in solution (e.g. CH_2Cl_2). In addition, poly(DEDPM)$_{10\leq n\leq 90}$ was found to be thermally stable up to 185°C under helium [22].

In order to retrieve more accurate information about the actual configuration of the poly(ene) and the relative orientation of the repetitive units (i. e. tacticity), we performed a cyclopolymerization using the chiral monomer 4-(ethoxycarbonyl)-4-(1*S*, 2*R*, 5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (ECMHD). The use of such a chiral monomer reduces the elements of symmetry, one might detect during diade or triade interpretation (i. e. mirror plane, center of inversion, center of rotation) to one single element (i. e. center of rotation). Performing a standard triade interpretation with poly(ECMHD), an *alternating cis-trans* conformation was assigned to the polymer. Additionally, a highly tactic (presumably isotactic) base (>98%) was derived from the ^{13}C-NMR spectrum.

Cyclopolymerization of 1,6-heptadiynes by "classical" systems[23]

For reasons of simplicity and cost management, classical ternary systems have been investigated for this reason, yet were not able to compete with Schrock systems in terms of materials properties (i.e. definition, purity, etc.) so far. Nonetheless, we were still interested whether one might use classic systems in cyclopolymerization, and in particular for the synthesis of poly(ene)s solely consisting of five-membered rings. While standard ternary systems behaved as expected, yielding ill-defined polymers without any control over molecular weight, the addition of quinuclidine turned out to be a milestone in this area of research[23]. Thus, DEDPM was cyclopolymerized by $MoCl_5$-*n*-Bu_4Sn-EtOH-quinuclidine (1:1:5:1) and $MoOCl_4$-*n*-Bu_4Sn-EtOH-quinuclidine (1:1:2:1) to produce poly(DEDPM) *exclusively based on 1,2-(cyclopent-1-enylene)-vinylene units.* The catalyst efficiency of $MoOCl_4$-*n*-Bu_4Sn-EtOH-quinuclidine (1:1:2:1) was as high as 91 %, the highest value ever reported for such systems, whereas the efficiency for the corresponding $MoCl_5$-based catalyst was $\leq$ 67%. The absorption maximum λ_{max} for poly(DEDPM) was 587 nm, close to that one found for poly(DEDPM) prepared by a Schrock catalyst (592 nm). A maximum effective conjugation length N_{eff} of 49 ($CHCl_3$) was calculated therefrom. A plot of number of monomers (N) added *vs* molecular weights (M_n) as determined by light scattering showed a linear dependence for both catalysts. Multistage polymerizations of DEDPM indicated for both catalyst systems that the catalytic species were active for at least 6 hours in the presence of monomer *yet did not fulfill the criteria of a truly living polymerization*[24], which include stability of the active chain end in the *absence of monomer.* This must be regarded as one of the most significant disadvantages compared to well-defined Schrock catalysts, which in most cases provide truly living polymerizations.

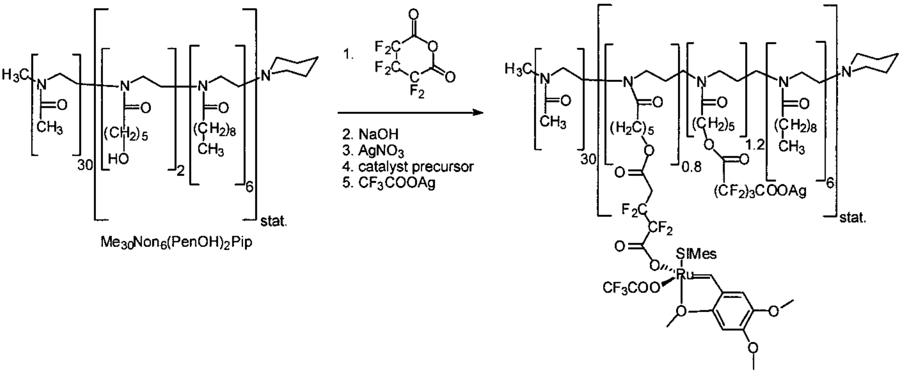
New Ruthenium-derived catalysts for cyclopolymerization

Grubbs-Herrmann (e.g. $RuCl_2$(1,3-bis(2,4,6-trimethylphenyl)4,5-dihydroimidazolin-2-ylidene)(CHPh)(PCy_3)) respectively Grubbs-Hoveyda catalysts (e.g. $RuCl_2$(=CH(2(2-PrO-C_6H_4)(1,3-bis(2,4,6-trimethylphenyl)4,5-dihydroimidazol-2-ylidene))[25] are air and moisture-stable metathesis catalysts with remarkable activity, sometimes rivaling that of highly active Schrock catalysts[26]. Nonetheless, despite their activity in ring-opening metathesis polymerization (ROMP), ring-closing, enyne and ring-opening cross metathesis reactions, none of the existing systems was capable of polymerizing alkynes or cyclopolymerizing 1,6-heptadiynes so far. The successful synthesis of a modified Grubbs-Hoveyda catalyst that can accomplish the cyclopolymerization of 1,6-heptadiynes in both a living and stereoregular way now closes the last gap between molybdenum- and ruthenium-based metathesis catalysts. $Ru(CF_3COO)_2$(=CH-(2-(2-PrO)-C_6H_4)(1,3-dimesityl-4,5-dihydroimidazl-2-ylidene) has been developed in our laboratories as a highly efficient and active catalyst for ring-closing, enyne and cross metathesis[27]. The enhanced polarization across the ruthenium-carbon double bond directly translates into an increased reactivity thus allowing the cyclopolymerization of DEDPM. Though highly active, this catalyst did not allow a living polymerization setup[24] in the polymerization of DEDPM. Irrespective of stoichiometry, molecular weights around

12,000 g/mol were obtained. Exchange of the 2-(2-propoxy)benzylidene ligand by the 2,4,5-trimethoxybenzylidene ligand[28] lead to the formation of Ru(CF_3COO)$_2$(=CH-(2,4,5-(MeO)$_3$-C_6H_4)(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene). This compound turned out to be an excellent catalyst for the cyclopolymerization of DEDPM, allowing full control over molecular weight.[29] Thus, polymerizations of DEDPM with this catalyst in methylene chloride proceeded in a class VI living manner[30]. An excellent agreement between the theoretical and experimentally determined molecular weights was observed. In fact, poly(DEDPM) was still living even after two days as shown by the stepwise addition of monomer. In terms of microstructure, poly(DEDPM) either prepared by using this catalyst consisted virtually solely (>96%) of 1,2-cyclopent-1-enylenevinylene units as shown by ^{13}C-NMR measurements[21, 22]. The polymerization mechanism certainly follows that of molybdenum-based cyclopolymerizations[11].

Using MALDI-TOF spectroscopy, 2-propoxybenzylidene was found as endgroup in all polymers prepared by the action of Ru(CF_3COO)$_2$(=CH-(2-(2-PrO)-C_6H_4)(1,3-dimesityl-4,5-dihydroimidazl-2-ylidene), indicating the absence of any chain transfer reactions. The polymerization of chiral ECMCH by this catalyst again proceeded in a stereo- and regioselective way, resulting in tactic poly(*trans*-1,2-(cyclopent-1-enylene)vinylene) with >98% stereoregularity as shown by ^{13}C-NMR spectroscopy[21, 22]. This finding is of particular interest, since polymers prepared via ring-opening metathesis polymerization (ROMP) using other Ru-based catalysts revealed a *trans*-content ≤ 90 % and low stereoregularity[26, 31].

One of the many advantages of ruthenium based catalysts is their tolerance to polar functional groups and water as a reaction medium. Consequently, we aimed on the fixation of the catalyst on micelle-forming, amphiphilic *block* copolymers. The synthetic route necessary for the realization of a polymer-bound catalyst had to fulfill two requirements. On the one hand, perfect mimics of Ru(CF_3COO)$_2$(=CH-(2,4,5-(MeO)$_3$-C_6H_4) had to be generated in order to maintain its reactivity and stereoselectivity. On the other hand and in contrast to conventional suspension/emulsion polymerization, the catalyst had to be *permanently* linked to the block copolymer amphiphile. Upon micelle formation of the functionalized block copolymer in water, the catalyst is located in the hydrophobic micellar core, where also the monomer will be dissolved. Preparation of the functionalized block copolymers was accomplished by reacting first $Me_{30}Non_6(PenOH)_2Pip$, bearing two randomly distributed hydroxyl groups in the side chain of the hydrophobic block with hexafluoroglutaric anhydride followed by deprotonation with aqueous NaOH and reaction with $AgNO_3$ to yield a polymer-bound silver carboxylate. The last steps entailed its reaction with the catalyst precursors $RuCl_2$(=CH-2-(2-PrO)-C_6H_4(1,3-bis(2,4,6-trimethylphenyl)4,5-dihydroimidazol-2-ylidene) and $RuCl_2$(=CH-2,4,5-$(OMe)_3$-C_6H_2(1,3-bis(2,4,6-trimethylphenyl)4,5-dihydroimidazol-2-ylidene)[28], respectively, followed by reaction with silver trifluoroacetate to endcap unreacted chloro groups of the catalysts. In course of this two-step chlorine exchange, the corresponding ruthenium compounds were fixed to the support to yield the poly(2-oxazoline)-immobilized catalysts $Me_{30}Non_6((PenOCO(CF_2)_3COO)(CF_3COO)Ru(=CH$-*o*-O-*i*-Pr-$C_6H_4)(SIMes)))_{0.8}(PenOCO(CF_2)_3COOAg)_{1.2}Pip$ and $Me_{30}Non_6(((PenOCO(CF_2)_3COO))((CF_3COO)Ru(=CH$-2,4,5-$(OMe)_3C_6H_2(SIMES))))_{0.8}(PenOCO(CF_2)_3COOAg)_{1.2}Pip$, respectively (Scheme 2).



Scheme 2. Immobilization of $RuCl_2$(=CH-2,4,5-$(OMe)_3$-C_6H_2(1,3-bis(2,4,6-trimethylphenyl)4,5-dihydroimidazol-2-ylidene)on a micelle-forming block-copolymer.

It is worth mentioning that such a successful immobilization required both straightforward synthetic routes and the careful design of the block sizes in the amphiphilic copolymer. Quantification of ruthenium in the block-copolymer-immobilized initiator by means of ICP-OES measurements indicated that 40 % of the polymeric silver salt had reacted with the catalyst precursor, leading to ruthenium loadings of the *block*-copolymer of 0.16 mmol/g. Poly(DEDPM) prepared with the block copolymer-immobilized system in water was characterized by lower polydispersity indices (PDIs) < 1.40 compared to poly(DEDPM) prepared by $Ru(CF_3COO)_2(CH\text{-}2\text{-}(2,4,5\text{-}(MeO)_3\text{-}C_6H_3)(SIMes)$. Due to the increased concentration of DEDPM within the micelles, reaction times required to reach complete conversion were reduced to 30 minutes compared to 2 hours with the parent catalyst indicating the catalytic effect of the micellar nanoreactors formed in aqueous medium. Stabilized by the amphiphilic structure of the *block*-copolymer the poly(acetylene) latices could be stored over two weeks without any change in terms of latex particle size, molecular weight and UV-Vis absorption maximum.

Physical Properties of Poly(DEDPM)$_n$[32]

Optical Properties

Poly(DEDPM)$_n$ as a dark colored solid is soluble in chlorinated solvents (CH_2Cl_2, $CHCl_3$) resulting in solutions with a deep violet color. Presumable due to the highly regular structure,[21, 22] polymers are insoluble in THF, benzene or toluene. The chain length has a strong influence on the fine structure of corresponding UV-VIS spectra. Already poly(DEDPM)$_5$ shows two absorption maxima, which become more pronounced in poly(DEDPM)$_n$ with a DP > 10. For $10 < n < 50$, a bathochromic shift in absorption is observed. At 25°C, the absorption maximum λ_{max} is 591 nm for DPs > 50, which is equal to a maximum effective conjugation length N_{eff} of 52. Values for N_{eff} were calculated on the base of poly(acetylene) model compounds.[33] The corresponding molar absorption coefficient ε_{50} is $1.41 \cdot 10^6$ cm^{2}mmol^{-1}. In addition, for $10 < n < 50$, the intensity of λ_{max} increases with increasing chain length. According to the literature,[34] only highly regular polymers with defined and uniform polymer architectures possess highly resolved UV-VIS spectra. The fact that poly(DEDPM)$_{70}$ possesses two well-resolved absorption maxima at 550 and 590 nm, respectively, is indicative for such a well-defined microstructure and fits structural data retrieved from ^{13}C-NMR spectroscopy, which suggested a tactic alternating *cis-trans* structure.[21, 22]

These data are in strong contrast to poly(DEDPM)$_{n \geq 50}$ consisting solely of six-membered rings. These display an absorption maximum λ_{max} of only 511 nm, corresponding to a value for N_{eff} of 20.[14] The significantly higher effective conjugation lengths of poly(DEDPM) selectively consisting of 5-membered rings are believed to be a direct consequence of the higher degree of coplanarity in poly(1,2-(cyclopent-1-enylene)-vinylene)s compared to the one that is achieved with poly(1,3-(cyclohex-1-enylene)-methylidene)s.

Interestingly, measurements of λ_{max} of poly(DEDPM)$_{50}$ solutions in chloroform within a temperature range of 20 - 50°C revealed reversible thermoresponsive properties with changes in λ_{max} of 8 nm. For all chain lengths, λ_{max} remained constant at temperatures below 20°C. Though further extensive investigations are required in order to understand and enhance this effect, this is an important finding concerning potential applications in the field of sensor technology.

Electrical Properties

If poly(ene)s consisting of >96% 5-membered rings (σ_5>95%) did in fact possess improved coplanarity due to better packing, then this effect should also result in improved conductivity. In due consequence, conductivities of various samples of poly(DEDPM) with different polymer backbone were measured. The experimental setup is shown in Figure 1.

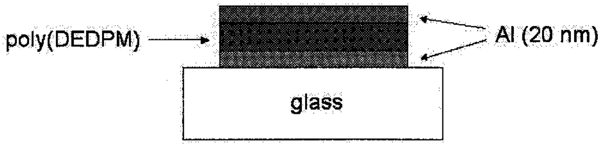


Figure 1. Conductivity measurements on poly(DEDPM) samples.

Conductivity data are shown in Figure 2. As can be deduced therefrom, undoped poly(DEDPM) consisting of virtually solely 5-membered rings shows a 600 times higher conductivity than poly(DEDPM) consisting of a mixture of 5-and 6-membered rings. Measurements concerning the conductivity of doped poly(DEDPM) with σ_5>96% are currently under way. Interestingly, none of the poly(DEDPM) samples showed any photoconductivity.

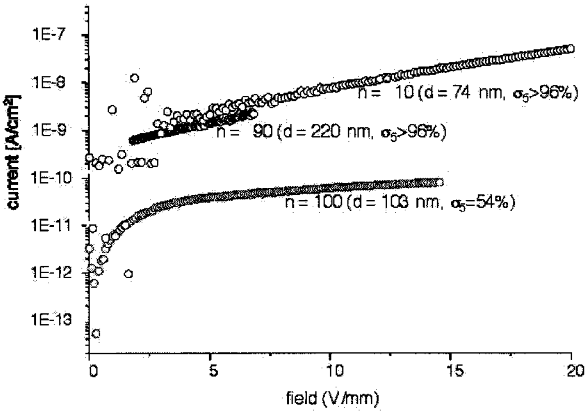


Figure 2. *I-U* characteristica for poly(DEDPM). Films were prepared by doctor blading from $CHCl_3$. E= 10 V/μm.

Thermal Properties and Long-Term Stability

DSC measurements of poly(DEDPM)$_{10}$ and poly(DEDPM)$_{90}$ revealed glass transitions between 25.8 and 26.5°C. From the constant value of λ_{max} below 20°C and these glass transition temperatures we conclude that highly regular poly(DEDPM) based on five-membered rings possesses at room temperature and below rigid structures that soften when the polymer is heated up either in solution (in $CHCl_3$) or in the solid state. Poly(DEDPM) displays an excellent long term stability in the solid state. Additionally, no thermal decomposition is observed under helium up to temperatures of 185°C. Thus, poly(DEDPM)$_{10}$ and poly(DEDPM)$_{90}$ decompose at 186.5 and 184.7°C, respectively. In solution, values for λ_{max} of freshly prepared chloroform or methylene chloride solutions remained constant over months even when exposed to air at room temperature. A decrease of λ_{max} can only be observed in chloroform, if these solutions are exposed to light. Here, values of λ_{max} for poly(DEDPM)$_{70}$ decrease from originally 590 nm to 589 and 587 nm after 6 respectively 12 days. After 18 days, λ_{max} shows a value of 583 nm. We therefore conclude that the more acidic solvent $CHCl_3$ interacts with the polymer probably *via* radical species, leading to fast deterioration.

Summary

Cyclopolymerization offers access to conjugated polymers with cyclic recurring units. The careful design of both molybdenum and ruthenium-derived catalysts allows the synthesis of stereoregular polymers in a living way. In addition, the tuning of the catalyst also accounts for dramatic changes in polymerization kinetics. In contrast to the parent poly(acetylene)s, poly(ene)s prepared by cyclopolymerization of suitable monomers are remarkable stable and are therefore expected to play a more important part in those areas that are now dominated by poly(pyrrole)s and PPVs. Fixation of the catalysts on micelle-forming block-copolymers allows the synthesis of poly(enes)s under aqueous conditions.

Acknowledgement

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