Carbene Polymerization

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Carbene Chemistry: Stereoregular Polymers from Diazo Compounds

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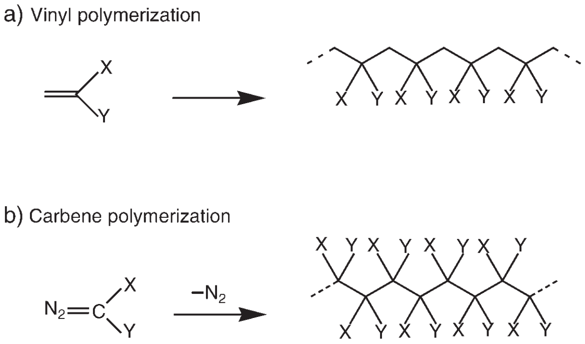
Obtaining polymers that bear a polar group on every main-chain carbon atom, while controlling their stereochemistry, remains an elusive goal. Or does it? A recent report possibly bridges the gap and paves the way for the stereoselective polymerization of carbenes.[1] What is involved is to control the construction of a polymer backbone from a one-carbon-containing monomeric unit (i.e. polymerization of substituted methylenes)—an attractive method to prepare new polymers that so far cannot be obtained by any conventional polymerization. The methodology fundamentally differs from classical vinyl polymerizations, in which the polymer chain is constructed from two-carbon-containing monomeric units (Scheme 1).


a) Vinyl polymerization

b) Carbene polymerization

Scheme 1. Comparison of substitution patterns of polymers resulting from a) two-carbon-containing and b) one-carbon-containing monomers.

Since its early days, when diazo compounds were decomposed by copper derivatives, the chemistry of "divalent carbon" has been closely linked with the development of organometallic chemistry.[2,3] First recognized as fleeting and extremely reactive reaction intermediates, carbenes nowadays also include air-stable, well-behaved species. The last two decades have witnessed the synthesis of stable, hetero-substituted singlet carbenes[4] and long-lived triplet carbenes;[5] also, additional stabilization to less-stable carbenes can be provided by confinement inside a molecular container.[6]

The dramatic development of the chemistry of metal–carbene complexes in homogeneous catalysis ranks carbene-catalyzed reactions among the most prominent strategies for the construction of carbon–carbon bonds. Among its many useful applications and in addition to olefin metathesis, the field also encompasses cycloaddition to unsaturated C=C bonds and insertion into C–H bonds.[2,7] However, carbene-transfer reactions are frequently hampered by competitive side reactions and most notably by dimerization and/or oligomerization reactions that yield respectively alkenes (carbene dimers) or ill-defined carbene oligomers or telomers. Moreover, even in cases where carbene dimerization reactions can be synthetically useful, as, for instance, for the recent synthesis of unsymmetrical *cis*-2-ene-1,4-diesters from two different diazoacetates,[8] a shortfall remains when it comes to exploiting oligomerization. The wealth of applications and mechanistic insight obtained so far from the entire area of catalyzed chemistry can still not disguise our poor understanding (and results) in the field of carbene oligomerization and polymerization from diazo compounds.

The first known route to polycarbenes was uncovered by accident in 1898 when von Pechman obtained polyethylene by thermal decomposition of diazomethane. Later, Staudinger's observation of the same reaction helped establish fundamental ideas about the formation of macromolecules (and, in a sense, macromolecular chemistry therefore appears to be a child of early diazo chemistry).[9] However, neither the early processes nor the milder catalytic versions of diazomethane or diazoalkane decomposition ever found large practical applications because none of the resulting polymers could compete with those prepared with Ziegler–Natta or metallocene catalysts.

The story, however, might be different with functionalized diazo compounds. For instance, diazoesters and diazoketones, which are reasonably stable and easy to prepare (but more difficult to polymerize), could lead to a variety of new polymers carrying a polar functionality at each main-chain carbon atom, and thus to structures that are not accessible by classical methodologies, which find their limits in their poor

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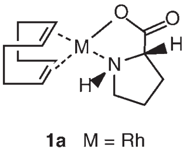
compatibility with organic functionalities. Although polymers bearing an ester group at every main-chain carbon atom can be obtained by radical polymerization of dialkyl maleate or fumarate, high-yielding synthesis were so far achieved only with bulky ester groups and with no control of the stereochemistry of the resultant polymer.[10–12]

Until now, only a few papers have reported on the polymerization of α-carbonyl-stabilized carbenes from diazocarbonyl compounds. They concern copper- and palladium-mediated formation of relatively low-molecular-weight polymers (average degree of polymerization up to about 100) from alkyl diazoacetate and some other diazocarbonyl derivatives. The resulting viscous oils all display broad NMR resonances, indicative of non-selective polymerizations.[13–15]

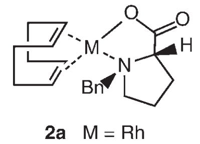
The recent report of an unprecedented stereoselective polymerization of "carbenes" from ethyl diazoacetate (EDA) to give a high-molecular-weight poly(ethyl 2-ylidene acetate) (PEA; Scheme 1 b with X = H, Y = CO_2Et) is a welcome breakthrough in the field.[1] The stereoselective synthesis of PEA was serendipitously discovered while evaluating new rhodium(I) complexes for the catalytic cyclopropanation of olefins using EDA as a carbene precursor. Whereas complex **1a** mediated the cyclopropanation of styrene in low yield, it favored the formation of carbene dimers and high-molecular-weight polycarbene. In the absence of an olefin, EDA treated with a catalytic amount of Rh^I complexes **1**–**4** (2 mol %) gave PEA as a white amorphous powder in 10–50 % isolated yields, with the rest of the diazoester being transformed into diethyl maleate and diethyl fumarate.

The molecular weights of the new polymers obtained within 14 h at 20 °C with each of the four rhodium complexes are typically in the range of 120–165 kDa. The obtained polydispersities of just over two are in agreement with a non-living polymerization process at a single-center active species. Quite remarkably, **1b**, the iridium analogue of **1a**, does not produce any PEA but yields only carbene dimers with a 9:1 ratio of maleate to fumarate. On the other hand, **2b**, which contains a weaker coordinating benzyl (Bn)-functionalized N donor, produces low-molecular-weight PEA albeit in low yield (4 %, $M_w = 12$ kDa). The scope of the reaction is not limited to EDA; for example, *n*-butyl diazoacetate gives a polymer in about 20 % yield with **1a**. Other diazo compounds as well as copolymerization reactions are under investigation.

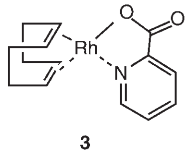
Amazingly, the nature of the catalyst has little influence on the obtained stereoregular PEA. All the new polymers obtained with catalysts **1**–**4**, including those prepared from non-chiral catalysts **3** and **4**, look quite similar. They reveal sharp NMR resonances in solution, distinctly different from those of the atactic PEA obtained by radical polymerization of diethyl fumarate. Slow evaporation of a solution of the white amorphous solid in chloroform gives a material with a high degree of crystallinity. The amorphous and crystalline polymers both decompose above 300 °C. Although additional information is needed for a definitive assignment of the configuration, NMR data, thermal analysis data, as well as molecular mechanics calculation on model compounds are consistent with syndiotactic polymers.



1a M = Rh
1b M = Ir



2a M = Rh
2b M = Ir



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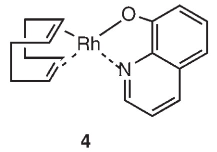

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No polymer chain-end signals were identified, even for low-molecular-weight polymers, and the mechanism of the reaction remains largely speculative. About half of the starting EDA is converted into carbene dimers, which, given the molecular weight of the polymer, indicates that only a small fraction of the added catalyst becomes really active for polymer formation. Are the dimerization and polymerization competitive processes at the same metal site, or (more likely) do they result from different catalytic species? Carbene dimerization is commonly seen as involving a nucleophilic attack of an uncomplexed diazocarbonyl compound on a metal carbene (carbenoid) to form an intermediate diazonium ion. Loss of nitrogen and regeneration of the catalyst complete the formation of a double bond. The process requires only one vacant coordination site, but other reaction pathways are conceivable for carbene dimerization.

As for polymer formation, de Bruin and co-workers suggest dissociation of the N,O ligand from the metal, formation of M–H or M–OH species, and consecutive migratory α-insertions of the metal-bound carbene into the growing chain of the polymer, with the stereoselection taking place under chain-end control. Dissociation of the quite labile cycloocta-1,5-diene ligand and carbene insertion into the carboxylic or phenolic Rh–O bond remains another plausible reaction pathway; if so, the stereocontrol of the chiral ligand (enantiomorphic site control) with catalysts **1** and **2** would be operative for only a limited number of insertions at the early stage of the polymerization.

It is expected that these new polymers, which have a unique structure, will show special material properties. What is now needed, after a definitive assignment of polymer stereochemistry, is a confirmation of the generality and usefulness of the methodology. That certainly requires an improvement of catalyst loading and yields.

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[1] D. G. H. Hetterscheid, C. Hendriksen, W. I. Dzick, J. M. M. Smits, E. R. H. van Eck, A. E. Rowan, V. Busico, M.

Vacatello, V. Van Axel Castelli, A. Segre, E. Jellema, T. G. Bloemberg, B. de Bruin, *J. Am. Chem. Soc.* **2006**, *128*, 9746.

[2] M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York, **1998**; see also p. 624 therein.

[3] G. Maas, *Top. Curr. Chem.* **1987**, *137*, 77.

[4] W. Kirmse, *Angew. Chem.* **2004**, *116*, 1799; *Angew. Chem. Int. Ed.* **2004**, *43*, 1767.

[5] W. Kirmse, *Angew. Chem.* **2003**, *115*, 2165; *Angew. Chem. Int. Ed.* **2003**, *42*, 2117.

[6] W. Kirmse, *Angew. Chem.* **2005**, *117*, 2530; *Angew. Chem. Int. Ed.* **2005**, *44*, 2476.

[7] F. Zaragoza Dörwald, *Metal Carbenes in Organic Synthesis*, Wiley-VCH, Weinheim, **1999**.

[8] D. M. Hodgson, D. Angrish, *J. Mol. Catal. A* **2006**, *254*, 93.

[9] H. Zollinger, *Diazo Chemistry II*, VCH, Weinheim, **1995**, p. 5.

[10] T. Otsu, N. Toyoda, *Polym. Bull.* **1984**, *11*, 453.

[11] T. Otsu, K. Shiraishi, A. Matsumoto, *J. Polym. Sci. Part A* **1993**, *31*, 885.

[12] T. Otsu, K. Shiraishi, *Macromolecules* **1985**, *18*, 1795.

[13] E. Ihara, N. Haida, M. Iio, K. Inoue, *Macromolecules* **2003**, *36*, 36.

[14] E. Ihara, M. Fujioka, N. Haida, T. Itoh, K. Inoue, *Macromolecules* **2005**, *38*, 2101.

[15] L. Liu, Y. Song, H. Li, *Polym. Int.* **2002**, *51*, 1047.