Progress in Polymer Science 38 (2013) 30–62

Contents lists available at SciVerse ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Synthesis of complex polymeric architectures using multilithiated carbanionic initiators—Comparison with other approaches

Rachid Matmour[a,*], Yves Gnanou[b,**]

[a] Manufacture Française des Pneumatiques Michelin, Centre de Technologie, 23 place des Carmes-Déchaux, 63040 Clermont-Ferrand, France
[b] Laboratoire de Chimie des Polymères Organiques (UMR 5629) Université Bordeaux 1/CNRS Ecole Nationale Supérieure de Chimie, de Biologie & de Physique, 16, Avenue Pey-Berland, 33607 Pessac Cedex, France

ARTICLE INFO

Article history:
Received 7 November 2011
Received in revised form 24 August 2012
Accepted 28 August 2012
Available online 11 September 2012

Keywords:
Dicarbanionic lithiated initiators
Multicarbanionic lithiated polymers
Star polymers
Dendrimer-like polymers
Miktoarm stars
Asymmetric stars

ABSTRACT

This article reviews the various methods developed to generate di- and multicarbanionic lithiated initiators, the difficulties associated with their synthesis but also their potential in macromolecular engineering. It is shown that a wealth of complex macromolecular architectures based on monomers amenable to carbanionic polymerization can now be synthesized by divergent approach from these di- and multicarbanionic lithiated initiators. A comparison is made with other types of multifunctional initiators that have been developed from other living/controlled polymerizations, generating similar complex polymeric architectures from other monomers. A comparison is also made with the structures generated by the convergent carbanionic approach.

Contents

* Corresponding author. Tel.: +33 04 73 30 43 47; fax: +33 04 73 30 40 93.
** Corresponding author. Tel.: +33 5 40 00 69 87; fax: +33 5 40 00 66 33.
E-mail addresses: rachid.matmour@fr.michelin.com (R. Matmour), gnanou@enscbp.fr (Y. Gnanou).

0079-6700/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.progpolymsci.2012.08.003

1. Introduction

Alkyllithiums such as n-butyllithium are generally obtained by mere lithiation of corresponding alkylhalides, a very convenient and straightforward reaction routinely used to prepare very strong bases in organic chemistry and initiators for polymer chemistry. To a large extent, monomers amenable to carbanionic polymerization are indeed initiated by BuLi. However, this lithiation could not be successfully applied to multialkylhalides containing more than one halogen as a means to generate well-defined multilithiated carbanionic species.

The reasons that are generally held responsible for multilithiation to be impractical—especially when the halogens to be substituted happen to be on the same carbon or on adjacent carbons—are two-fold. α-Lithium-halide eliminations and intermolecular couplings between the lithiated reagent and the halide-substituted species are indeed two important competing reactions that have long prevented polylithiation reactions from being practically considered. Another reason for the little attention given to multiple metal–halide exchanges is because polylithiated compounds exhibit low solubility in most organic solvents, forming rather insoluble aggregates of little utility. Added to the previous limitation, different requirements have to be fulfilled for such multilithiated carbanionic species to be used as multifunctional initiators in order to produce polymers with uniform arms, low molar mass distribution, and controllable molar masses: all the initiation sites must be equally reactive and have the same rate of initiation. Furthermore, the initiation rate must be higher than the propagation rate.

These are the reason for polymer chemists to have disregarded the multilithiation of alkylhalides as a means to generate multilithiated carbanionic species for initiation purpose; had it been mastered and the experimental conditions worked out multilithiation would be a viable and straightforward route to prepare multicarbanionic initiators for the subsequent synthesis of star-shaped polymers. Until the 1990s the only possibility of generating such multicarbanionic initiators was lithiation by addition to multivinyl compounds, but the very small number of reports on this strategy of synthesis indicates that it is not that convenient a route. It indeed requires the prior synthesis of multivinyl compounds that would not homopolymerize upon addition of organolithium reagents. These constraints explain why the only initiator of precise functionality (higher than 2) ever synthesized by this method is the tricarbanionic compound of Quirk and Tsai who obtained it upon addition of *sec*-butyllithium onto a molecule containing three 1,1-diphenylethylene-type unsaturations (Fig. 1) [1].

2. Multilithiated species: the different ways to generate them

The presence of two lithiums on the same or adjacent carbon atoms being long thought as leading to their destabilization and necessarily to lithium hydride elimination is a misconception that could be overturned only in the early 1970s after the work of West and Lagow [2,3]. Actually, there are four distinct methods to quantitatively convert a multifunctional compound to a polylithiated species.

2.1. By reaction with lithium

The reaction of lithium metal or vapor with different categories of molecules such as alkanes, alkenes, aromatics, or also alkyl and aryl halides was the first synthetic method discovered for the preparation of polylithium organic compounds. The use of lithium metal, notably used for the synthesis of butyllithium, was first reported in the early 1950s by West and coworkers [2,4,5] with the conversion of 1,5-dichloropentane to 1,5-dilithio compound. This strategy was later developed by the Lagow group [6–14] with the reaction at high temperature of lithium vapor with halogenated organic compounds as a general synthesis for polylithium compounds.

However, extremely low yield reactions were observed with a mixture of compounds, which prevented any purification or characterization of the pure product. This very low yield could be explained by α-lithium-halide elimination occurring from molecules having a halide and a lithium on the same or adjacent carbons producing carbenes and lithium halides. Furthermore, the reaction of lithium on the halide compound is in competition with a side reaction of intermolecular coupling between the lithiated species and the alkyl halide reagent (Wurtz coupling) [15] (Fig. 2) which has no serious consequence for a monofunctional initiator, but is detrimental for the synthesis of well-defined pluricarbanionic compounds.

2.2. By reaction of alkyllithium on multifunctional unsaturated molecules

This more recent method is based on the reaction of alkyllithium with the unsaturations of a multifunctional agent. This strategy was first applied for the synthesis of dilithiated compounds by reaction of butyllithium with difunctional unsaturated reagents such as