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Activation in anionic polymerization: Why phosphazene bases are very exciting promoters

S. Boileau*, N. Illy[1]

Institut de Chimie et des Matériaux Paris-Est (ICMPE), UMR 7182 CNRS, Université Paris- Est Créteil Val de Marne, 2 rue Henri Dunant, 94320 Thiais, France

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ABSTRACT

Recently, nitrogen–phosphorous hybrid organobases such as phosphazene bases (PBs), which possess a remarkably high basicity, have been extensively studied in organic synthesis. Their applications in the domain of anionic polymerization are reviewed. Those non-ionic superbases generate highly reactive anionic species according to two different pathways: firstly by deprotonation of weak acids in which the protonated phosphazene base forms the cation, and secondly by complexation of the lithium cation by the phosphazene base when organolithium compounds are used as initiators. They have been successfully used for the anionic ring-opening polymerization (AROP) of epoxides, cyclosiloxanes, cyclic esters, caprolactam, and very recently cyclopropane-1,1-dicarboxylates, as well as for the anionic polymerization of vinyl monomers such as methacrylates, acrylates, butadiene, and isoprene. Polymerizations with metal-free non-protonated phosphazenium counterions are also reviewed. In all cases, the rates of polymerization are much higher than those observed with metal cations, and similar to the values obtained with cryptated counterions. The use of protonated and non-protonated phosphazenium counterions leads generally to polymers with narrow molecular weight distributions, and well-controlled end groups. Advantages of PBs are discussed, and perspectives in the revisited domain of anionic activation applied to polymer chemistry are presented.

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* Corresponding author. Tel.: +33 1 49781194.
E-mail address: boileau@icmpe.cnrs.fr (S. Boileau).

[1] Present address: Department of Chemistry, University of Toronto, 80 St. George St., Toronto ON, Canada M5S 3H6.

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Nomenclature

AcH	acetic acid
ACN	acetonitrile
AROP	anionic ring-opening polymerization
n-BuLi	*n*-butyllithium
sec-BuLi	*sec*-butyllithium
[C]	living end concentration
CL	ε-caprolactone
D_3	hexamethylcyclotrisiloxane
D_3^{Et}	hexaethylcyclotrisiloxane
D_4	octamethylcyclotetrasiloxane
D_5	decamethylcyclopentasiloxane
D_6	dodecamethylcyclohexasiloxane
DMAEMA	*N,N*-dimethylaminoethyl methacrylate
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DPE	1,1-diphenylethylene
DPHLi	1,1-diphenylhexyllithium
DPMPLi	1,1-diphenyl-3-methylpentyllithium
EEGE	1-ethoxyethyl glycidyl ether
EGE	1-ethyl glycidyl ether
EO	ethylene oxide
FT-NIR	Fourier-transform near-infrared
GME	glycidyl-1-methyl ether
HMPA	hexamethyl phosphorous triamide
L-LA	L-lactide
Rac-LA	*rac*-lactide
k_p	propagation (polymerization) rate constant
MeOH	methanol
MMA	methyl methacrylate
MW	molecular weight
MWD	molecular weight distribution
*N*BS	*N*-bromosuccinimide
*N*MP	*N*-methylpyrrolidone
P_4	tetraphenyltetramethylcyclotetrasiloxane
PB	phosphazene base
PCL	poly(ε-caprolactone)
PDES	poly(diethylsiloxane)
PDMAEMA	poly(*N,N*-dimethylaminoethyl methacrylate)
PDMS	poly(dimethylsiloxane)
PEEGE	poly(1-ethoxyethyl glycidyl ether)
PEO	poly(ethylene oxide)
PMMA	poly(methyl methacrylate)
PO	propylene oxide
PPO	poly(propylene oxide)
PS	polystyrene
ROP	ring-opening polymerization
SANS	small angle neutron scattering
SEC	size exclusion chromatography
THF	tetrahydrofuran
TMC	trimethylene carbonate
TMEDA	*N,N,N′,N′*-tetramethylethylenediamine
V_4	tetravinyltetramethylcyclotetrasiloxane
VL	δ-valerolactone

1. Introduction

Anionic ring-opening polymerization (AROP) of heterocyclic monomers, namely ethylene oxide (EO), [1–3] and cyclosiloxanes [4,5] has been extensively studied using several alkali metal counterions. The propagation occurs through active centers that are generally more stable than carbanions. The polymerization rates are lower than in the case of the anionic polymerization of vinyl or dienic monomers, thus allowing convenient kinetic and conductance measurements. For EO as well as for cyclosiloxanes, the reactivity of the active chain ends increases strongly with increasing the size of the counterion. Ionic (e.g. alkoxides) active species can participate in the polymerization in a number of different physical forms: ions, ion pairs, and ionic aggregates, being in slower or faster inter exchange. Even in rather polar solvents, like THF, ion pair association causes reaction kinetics to be complex. A multistep dissociation equilibrium between inactive aggregates and active species yields a fractional order in active center concentra-