Available online at www.sciencedirect.com
ScienceDirect
Prog. Polym. Sci. 31 (2006) 1041–1067
PROGRESS IN POLYMER SCIENCE
www.elsevier.com/locate/ppolysci

Perspectives on the contributions of Michael Szwarc to living polymerization

Johannes Smid[a], Marcel Van Beylen[b], Thieo E. Hogen-Esch[c,*]

[a]*Chemistry Department, State University of New York College of Environmental Science and Forestry, Forestry Drive, Syracuse, NY 13210, USA*

[b]*Katholieke Universiteit Leuven, Department of Chemistry, Laboratory of Macromolecular & Physical Organic Chemistry, Celestijnenlaan 200F, Louvain, B-3001 Belgium*

[c]*Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, CA 90089-1661, USA*

Received 11 September 2006; received in revised form 14 September 2006; accepted 15 September 2006

Abstract

The review starts with a short historical introduction (Sections 1 and 2), followed by the famous work of Michael Szwarc on electron transfer to styrene and related monomers in THF and similar solvents (Section 3), forming the basis of most of his subsequent work. Section 4 describes his now classical work on the effects of ion pairing, ion pair solvation and triple ion formation on styrene anionic polymerization kinetics, as well as exploratory work on several related monomers and a brief description of work by others on related systems, such as the effects of LiCl and lithium alkoxides on the polymerization of styrene, and the mediation of styrene polymerizations by divalent Ba^2. Section 5 starts with a summary of solvation studies of fluorenyl ion pairs that allowed a better understanding of the role of ion pairs in styrene polymerizations. The effects of solvent and carbanion structure on ion pair solvation and dissociation and their role in initiation equilibria are discussed. Finally a study of the dynamics of ion pair dissociation and triple ion formation based on the second Wien effect is discussed. Section 6 reviews anionic copolymerization studies by Szwarc and collaborators. This is followed by subsequent work on the Hammet relationships involving the addition of 1,1-diphenylethylenes to polystyrenelithium in hydrocarbon/THF. Studies by others on the role of Li–pi donors coordination in butadiene/styrene and isoprene/styrene copolymerizations in hydrocarbon media are also reviewed in this section, as is the role of this coordination in the LiOH mediated isotactic polymerization of styrene.

Keywords: Anionic polymerization; Living polymerization; Vinyl anionic copolymerization; Ion pairs; Solvent-separated ion pairs; Radical anions

Contents

1. Introduction 1042
2. Discovery of living polymers 1043
3. Electron transfer studies 1043

*Corresponding author.
E-mail address: hogenesc@chem1.usc.edu (T.E. Hogen-Esch).

0079-6700/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.progpolymsci.2006.09.001

4. Anionic polymerization of styrene and other vinyl monomers 1045
4.1. Polymerization of styrene 1045
4.2. Other vinyl monomers 1048
4.3. Triple ion formation 1048
5. Ion pair solvation 1050
5.1. Fluorenyl anions 1050
5.2. Solvent effects 1052
5.3. Ion pairing effects in other carbanions 1052
5.4. Ion pairing effects on equilibria 1054
5.5. Dynamics of interconversion of ionic species 1055
6. Copolymerization 1057
6.1. Polar media 1057
6.2. Copolymerizations in apolar media 1059
7. Conclusions 1063
Acknowledgments 1063
References 1064

1. Introduction

The contribution by Michael Szwarc to chemistry and particularly to polymer chemistry has been far-reaching and is still evident today. This is especially the case for his discovery of living anionic polymerization of styrene and related vinyl monomers and his extensive studies on the corresponding mechanisms of initiation (electron transfer) and polymerization. These subjects were covered by Szwarc in numerous reviews [1–3] and in a number of textbooks [4–7].

Michael Szwarc was born in Poland in 1909 and received his early science education at the Warsaw Polytechnic Institute. He immigrated with his family to Israel in 1935 and earned a PhD degree in organic chemistry from Jerusalem's Hebrew University in 1942. His main interest however was physical chemistry, and his career really took off when he joined the group of Michael Polanyi, an outstanding physical chemist at the University of Manchester, England. He was awarded the prestigious Doctor of Science degree in physical chemistry in 1949 for his elegant research on bond dissociation energies. It was at Manchester University that Michael developed an interest in polymers when his pyrolysis work with *p*-xylene led him to the discovery of poly(*p*-xylylene) [8,9], a polymer commercialized in later years by Union Carbide under the name of "Parylene". In 1952 he accepted a professorship in the Chemistry Department of the State University of New York College of Forestry (presently Environmental Science and Forestry, or SUNY ESF) in Syracuse, NY. He became the first director of its newly created Polymer Research Center in 1966.

After his retirement in 1979 Michael moved to La Jolla, CA and was appointed a Senior Fellow in the Hydrocarbon Research Institute of the University of Southern California in Los Angeles, a position he held until his death in 2000. Of his more than 500 publications, over 100 were published during his 21 years of "retirement", most of them in collaboration with other researchers, including one of us (MVB). His last publication in 2002 dealt with the effect of LiCl on the anionic polymerization of styrene [10].

The scope of Michael Szwarc's research illustrates the versatility and breadth of his scientific interests. The topics on which he published include the following: bond dissociation energies; gas permeation through polymer films; radical affinities of unsaturated compounds; cage reaction of radicals; living anionic and cationic polymerization; block copolymers; electron transfer reactions in aromatic hydrocarbon; electron photon-ejection from radical anions and dianions; structure and properties of ion pairs; photolysis of carbanions; protonation of carbanions by alcohols; flexibility of polymer chains; and several other topics.

Below we will focus on the mechanistic aspects of living anionic polymerization, stemming from Michael's interests in the intricate mechanisms of these reactions. Our article is not intended as a comprehensive review of living anionic-polymerization. Many of the examples were taken from his work; others describe research, much of it our own, that was inspired by his monumental work. Thus, much excellent work on acrylate-type monomers aimed at improving the living character of their anionic polymerizations is not included. Nor does it cover the numerous synthetic applications inspired by his