

159

Advances in Polymer Science

Editorial Board:

A. Abe · A.-C. Albertsson · H.-J. Cantow

K. Dušek · S. Edwards · H. Höcker

J. F. Joanny · H.-H. Kausch · K.-S. Lee

L. Monnerie · S. I. Stupp · U. W. Suter

G. Wegner · R. J. Young

Springer

Berlin

Heidelberg

New York

Barcelona

Hong Kong

London

Milan

Paris

Tokyo

**Statistical, Gradient,
Block and Graft
Copolymers by
Controlled/Living
Radical Polymerizations**

By Kelly A. Davis, Krzysztof Matyjaszewski



Springer

Authors

Prof. Krzysztof Matyjaszewski

Dept. of Chemistry
Carnegie Mellon University
4400 Fifth Avenue
Pittsburgh, PA 15213
USA
E-mail: km3b@andrew.cmu.edu

Dr. Kelly A. Davis

Howard Hughes Medical Institute
University of Colorado-Boulder
Campus Box 424
Boulder, CO 80309
USA
E-mail: Kelly.Davis@Colorado.edu

This series presents critical reviews of the present and future trends in polymer and biopolymer science including chemistry, physical chemistry, physics and materials science. It is addressed to all scientists at universities and in industry who wish to keep abreast of advances in the topics covered.

As a rule, contributions are specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers are accepted for „Advances in Polymer Science“ in English.

In references *Advances in Polymer Science* is abbreviated *Adv Polym Sci* and is cited as a journal.

Springer APS home page: <http://link.springer.de/series/aps/> or
<http://link.springer-ny.com/series/aps/>
Springer-Verlag home page: <http://www.springer.de>

ISSN 0065-3195

ISBN 3-540-43244-2

Springer-Verlag Berlin Heidelberg New York

Library of Congress Catalog Card Number 61642

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, re-use of illustrations, recitation, broadcasting, reproduction on microfilms or in other ways, and storage in data banks. Duplication of this publication or parts thereof is only permitted under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer-Verlag. Violations are liable for prosecution under the German Copyright Law.

Springer-Verlag Berlin Heidelberg New York
a member of BertelsmannSpringer Science+Business Media GmbH
<http://www.springer.de>

© Springer-Verlag Berlin Heidelberg 2002
Printed in Germany

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting: Data conversion by MEDIO, Berlin

Cover: MEDIO, Berlin

Printed on acid-free paper SPIN: 10856712 02/3020wei - 5 4 3 2 1 0

Editorial Board

Prof. Akihiro Abe

Department of Industrial Chemistry
Tokyo Institute of Polytechnics
1583 Iiyama, Atsugi-shi 243-02, Japan
E-mail: aabe@chem.t-kougei.ac.jp

Prof. Ann-Christine Albertsson

Department of Polymer Technology
The Royal Institute of Technology
S-10044 Stockholm, Sweden
E-mail: aila@polymer.kth.se

Prof. Hans-Joachim Cantow

Freiburger Materialforschungszentrum
Stefan Meier-Str. 21
79104 Freiburg i. Br., Germany
E-mail: cantow@fmf.uni-freiburg.de

Prof. Karel Dušek

Institute of Macromolecular Chemistry, Czech
Academy of Sciences of the Czech Republic
Heyrovský Sq. 2
16206 Prague 6, Czech Republic
E-mail: dusek@imc.cas.cz

Prof. Sam Edwards

Department of Physics
Cavendish Laboratory
University of Cambridge
Madingley Road
Cambridge CB3 0HE, UK
E-mail: sfe11@phy.cam.ac.uk

Prof. Hartwig Höcker

Lehrstuhl für Textilchemie
und Makromolekulare Chemie
RWTH Aachen
Veltmanplatz 8
52062 Aachen, Germany
E-mail: hoecker@dwi.rwth-aachen.de

Prof. Jean-François Joanny

Institute Charles Sadron
6, rue Boussingault
F-67083 Strasbourg Cedex, France
E-mail: joanny@europe.u-strasbg.fr

Prof. Hans-Henning Kausch

c/o IGC I, Lab. of Polyelectrolytes
and Biomacromolecules
EPFL-Ecublens
CH-1015 Lausanne, Switzerland
E-mail: kausch.cully@bluewin.ch

Prof. Kwang-Sup Lee

Department of Polymer Science & Engineering
Hannam University
133 Ojung-Dong
Teajon 300-791, Korea
E-mail: kslee@mail.hannam.ac.kr

Prof. Lucien Monnerie

École Supérieure de Physique et de Chimie
Industrielles
Laboratoire de Physico-Chimie
Structurale et Macromoléculaire
10, rue Vauquelin
75231 Paris Cedex 05, France
E-mail: lucien.monnerie@espci.fr

Prof. Samuel I. Stupp

Department of Measurement Materials Science
and Engineering
Northwestern University
2225 North Campus Drive
Evanston, IL 60208-3113, USA
E-mail: s-stupp@nwu.edu

Prof. Gerhard Wegner

Max-Planck-Institut für Polymerforschung
Ackermannweg 10
Postfach 3148
55128 Mainz, Germany
E-mail: wegner@mpip-mainz.mpg.de

Prof. Ulrich W. Suter

Department of Materials
Institute of Polymers
ETZ,CNB E92
CH-8092 Zürich, Switzerland
E-mail: suter@ifp.mat.ethz.ch

Prof. Robert J. Young

Manchester Materials Science Centre
University of Manchester and UMIST
Grosvenor Street
Manchester M1 7HS, UK
E-mail: robert.young@umist.ac.uk

Foreword

The design and the realisation of well-defined polymer architectures has become an important goal in macromolecular science. The prerequisite for achieving this goal is the availability of controlled polymerisation reactions. Living anionic polymerisation was the first reaction fulfilling these requirements. Cationic polymerisation only came into play when it was realised that it was possible to create an equilibrium between active and dormant species with the fraction of the dormant species being far superior to that of active ones.

A corresponding principle applies to controlled radical polymerisation performed in quite a number of modes such as nitroxide-mediated polymerisation (NMP), atom transfer radical polymerisation (ATRP), reversible addition fragmentation chain transfer (RAFT) or catalytic chain transfer (CCT) reactions. All of these variants of controlled radical polymerisation lead to well-defined architectures with the particular advantage that a much larger number of monomers are suitable and the reaction conditions are much less demanding than those of living ionic polymerisation reactions.

Although in controlled radical polymerisation, termination reactions cannot be excluded completely, they are limited in their extent and consequently the molecular weight is controlled, the polydispersity index is small and functionalities can be attached to the macromolecules. These features are indicative of the realisation of well-defined polymer architectures such as block copolymers, star-shaped and comb-shaped copolymers.

The present volume is particularly concerned with the use of the different modes of controlled radical polymerisation for the preparation of copolymers such as random copolymers, linear block copolymers, as well as graft copolymers and star-shaped copolymers. It also presents the combination of controlled radical polymerisation with non-controlled radical copolymerisation, cationic and anionic polymerisation, both of vinyl monomers and cyclic monomers, and ring-opening metathesis polymerisation.

The power of controlled radical polymerisation is demonstrated convincingly and the limitations of the synthetic approaches clearly indicated.

Last but not least the volume presents some potential applications for copolymers obtained by controlled radical polymerisation. It is expected that the first commercial products will appear on the market this year, giving convincing evidence for the importance of controlled radical polymerisation methods.

Aachen, March 2002

Hartwig Höcker

Advances in Polymer Science **Available Electronically**

For all customers with a standing order for Advances in Polymer Science we offer the electronic form via LINK free of charge. Please contact your librarian who can receive a password for free access to the full articles. By registration at:

http://link.springer.de/series/aps/reg_form.htm

If you do not have a standing order you can nevertheless browse through the table of contents of the volumes and the abstracts of each article at:

<http://link.springer.de/series/aps/>
<http://link.springer-ny.com/series/aps/>

There you will find also information about the

- Editorial Board
- Aims and Scope
- Instructions for Authors
- Sample Contribution

Contents

1	Background	2
1.1	Copolymers	2
1.2	Free Radical Polymerization	3
1.3	Controlled/Living Radical Polymerization (CRP)	5
1.3.1	Stable Free Radical Polymerization and Nitroxide Mediated Polymerization (SFRP and NMP)	8
1.3.2	Atom Transfer Radical Polymerization (ATRP)	9
1.3.3	Degenerative Chain Transfer Including RAFT	10
1.4	Summary	11
2	Statistical Copolymers	14
2.1	SFRP/NMP	15
2.2	ATRP	19
2.3	Degenerative Transfer Processes	27
2.4	Comparison of Various CRP Methods Applied to Statistical Copolymers	27
3	Linear Block Copolymers	30
3.1	Linear Block Copolymers Prepared Exclusively by CRP Methods	30
3.1.1	SFRP/NMP	30
3.1.2	ATRP	44
3.1.3	Degenerative Transfer Processes	68
3.1.4	Comparison of CRP Methods for Block Copolymer Synthesis	70
3.2	Block Copolymers Prepared Through Transformation Techniques	72
3.2.1	CRP from Commercially Available Macroinitiators	72
3.2.2	Block Copolymers by Combination of Two Polymerization Techniques	79
3.2.3	Summary	103

4	Other Chain Architectures	107
4.1	Graft Copolymers	107
4.1.1	Grafting From	108
4.1.2	Grafting Through	117
4.1.3	Grafting Onto	126
4.1.4	Grafting from Surfaces	127
4.1.5	Summary	137
4.2	Star Polymers	138
4.3	Simultaneous/Dual Living Polymerizations	147
5	Overall Summary	153
5.1	General Overview	153
5.2	Critical Evaluation of CRP Methods for Materials Preparation	153
5.3	Potential Applications for Copolymers Made by CRP Methods	155
	References	157
	List of Abbreviations	166
	Author Index Volumes 101-159	171
	Subject Index	185