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Advances in Polymer Science

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With contributions by
W. Burchard, J. J. Freire, A. Hult,
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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.

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Volume Editor

Dr. Jacques Roovers

Institute for Chemical Process
and Environmental Technology
National Research Council Canada
Ottawa, Ontario
K1A 0R6
CANADA
E-mail: jacques.roovers@nrc.ca

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
D-79104 Freiburg i. Br., FRG
E-mail: cantow@mfz.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: office@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
D-52062 Aachen, FRG
E-mail: 100732.1557@compuserve.com

Prof. Jean-François Joanny

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

Prof. Hans-Henning Kausch

Laboratoire de Polymères
École Polytechnique Fédérale
de Lausanne, MX-D Ecublens
CH-1015 Lausanne, Switzerland
E-mail: hans-henning.kausch@lp.dmx.epfl.ch

Prof. Takashi Kobayashi

Institute for Chemical Research
Kyoto University
Uji, Kyoto 611, Japan
E-mail: kobayash@eels.kuicr.kyoto-u.ac.jp

Prof. Kwang-Sup Lee

Department of Macromolecular Science
Hannam University
Teajon 300-791, Korea
E-mail: kslee@eve.hannam.ac.kr

Prof. James E. McGrath

Polymer Materials and Interfaces Laboratories
Virginia Polytechnic and State University
2111 Hahn Hall
Blacksbourg
Virginia 24061-0344, USA
E-mail: jmcgrath@chemserver.chem.vt.edu

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 Materials Science
and Engineering
University of Illinois at Urbana-Champaign
1304 West Green Street
Urbana, IL 61801, USA
E-mail: s-stupp@uiuc.edu

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. Edwin L. Thomas

Room 13-5094
Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139, USA
E-mail. thomas@uzi.mit.edu

Prof. Gerhard Wegner

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

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

Preface

While books have been written on many topics of Polymer Science, no comprehensive treatise on long-chain branching has ever been composed. This series of reviews in Volume 142 and 143 of *Advances in Polymer Science* tries to fill this gap by highlighting active areas of research on branched polymers.

Long-chain branching is a phenomenon observed in synthetic polymers and in some natural polysaccharides. It has long been recognized as a major molecular parameter of macromolecules. Its presence was first surmised by H. Staudinger and G. V. Schulz (*Ber.* 68, 2320, 1935). Interestingly, their method of identification by means of the abnormal relation between intrinsic viscosity and molecular weight has survived to this day. Indeed, the most sophisticated method for analysis of long-chain branching uses size exclusion fractionation with the simultaneous recording of mass, molecular weight and intrinsic viscosity of the fractions.

In the 1940s and 1950s, random branching in polymers and its effect on their properties was studied by Stockmayer, Flory, Zimm and many others. Their work remains a milestone on the subject to this day. Flory dedicated several chapters of his “*Principles of Polymer Chemistry*” to non-linear polymers. Especially important at that time was the view that randomly branched polymers are intermediates to polymeric networks. Further developments in randomly branched polymers came from the introduction of percolation theory. The modern aspects of this topic are elaborated here in the chapter by W. Burchard.

As polymer science developed, greater control over the architecture of polymer molecules was obtained. In polyolefins synthesis, this was due to the introduction of new catalysts. The development of anionic living polymerization with the concomitant formation of narrow molecular weight distribution polymers and an highly reactive functional end group opened the route not only to block copolymers but also to branched polymers with highly controlled architectures such as stars, combs and graft copolymers. The model polymers allowed us to establish relations between the molecular architecture and the physical properties of the branched polymers. This development has been reviewed by e.g. G.S. Grest et al. *Adv. Chem. Phys.* 94, 65 (1996).

One chapter in this series deals with the newer use of cationic polymerization to form polymers and copolymers with controlled long-chain branched struc-

tures. Another chapter deals with the use of anionic polymerization to prepare asymmetric star polymers. The asymmetry is introduced when the arms of the polymer differ in molecular weight, chemical composition or in their topological placement. The synthesis of these polymers has led to new insights in microseparation processes of block copolymers. Anionic and cationic living polymerization has also led to macromonomers. Highlights of recent developments in poly(macromonomers) homo, comb and graft copolymers are reviewed by K. Ito. The poly(macromonomers) with their multiple densely packed small linear subchains often lead to monomolecular micelles.

Very recently, highly regular, highly controlled, dense branching has been developed. The resulting “dendrimers” often have a spherical shape with special interior and surface properties. The synthesis and properties of dendrimers has been reviewed (see e.g. G.R. Newkome et al. “Dendritic Molecules”, VCH, 1996). In this series, a chapter deals with the molecular dimensions of dendrimers and with dendrimer-polymer hybrids. One possible development of such materials may be in the fields of biochemistry and biomaterials. The less perfect “hyperbranched polymers” synthesized from A_2B -type monomers offer a real hope for large scale commercialization. A review of the present status of research on hyperbranched polymers is included.

The link between the long-chain branch structure and the properties of the polymer has to be established experimentally by means of model branched polymers. This link can also be derived theoretically or through computer modeling. As a result, a large sub-field of study has emerged. The methods and results of this theoretical work are systematically reviewed by J. Freire. Where available, comparisons with experimental results are made.

The final chapter develops the most modern insights in the relation between the rheological properties and the large scale architecture of polymers. Indeed, the largest effects of branching are encountered in their melt relaxation properties. In the absence of reptation, which dominates relaxation processes in linear polymers, a rich variety of other relaxation processes becomes apparent. The control of the melt properties of polymers by means of their long-chain branch architecture will continue to lead to new industrial applications.