143
Advances in Polymer Science

Springer
Berlin
Heidelberg
New York
Barcelona
Hong Kong
London
Milan
Paris
Singapore
Tokyo

Branched Polymers II

Volume Editor: J. Roovers

With contributions by
W. Burchard, J. J. Freire, A. Hult,
M. Johansson, E. Malmström,
T. C. B. McLeish, S. T. Milner

Springer

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 WWW home page: http://www.springer.de

ISSN 0065-3195
ISBN 3-540-65005-9
Springer-Verlag Berlin Heidelberg New York

Library of Congress Catalog Card Number 61642

Printed in Germany

Typesetting: Data conversion by MEDIO, Berlin
Cover: E. Kirchner, Heidelberg
SPIN: 10691413 02/3020 - 5 4 3 2 1 0 – Printed on acid-free paper

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

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 ot the melt properties of polymers by means of their long-chain branch architecture will continue to lead to new industrial applications.

Ottawa, July 1998 J. Roovers