

Edited by
J. C. Salamone and Judy S. Riffle

Contemporary Topics in
**POLYMER
SCIENCE**

**Volume 7
Advances in
New Materials**



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**Advances in
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Edited by

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University of Massachusetts
Lowell, Massachusetts

and

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Contemporary Topics in
**POLYMER
SCIENCE**

Volume 7

**Advances in
New Materials**

CONTEMPORARY TOPICS IN POLYMER SCIENCE

Sponsored by the American Chemical Society

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PREFACE

The Division of Polymer Chemistry, Inc. of the American Chemical Society held its 15th Biennial Polymer Symposium on the topic, "Advances in New Materials," November 17-21, 1990, at the Pier 66 Resort and Marina in Ft. Lauderdale, Florida. A three and one-half day program was presented by recognized leaders in major areas of new polymeric materials.

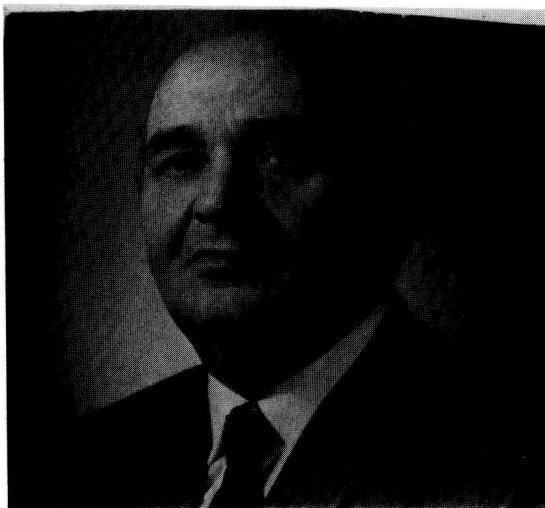
The topics of the Biennial Symposium included new high performance polymers, polymers for electronic applications, electrically conducting polymers, nonlinear optics, new polymer systems, and polymers derived from biological media. These are the subject areas of this volume of "Contemporary Topics in Polymer Science". The intent of the Symposium was to focus on recent advances in polymeric materials. The technical sessions were complemented by an initial poster session which augmented the various technical sessions.

A particular highlight of the meeting was the presentation to Professor Michael Szwarc of the 1990 Division of Polymer Chemistry Award by Dr. J. L. Benham, Chairman of the Polymer Division. During his Award address, Professor Szwarc described how he had become a polymer chemist and later developed "living polymers." Without a doubt, Professor Szwarc has made a profound contribution to the polymer field, which has yielded many new forms of living polymerization.

J. C. Salamone of the University of Massachusetts, Lowell, was Chairman of the symposium and he has been particularly grateful to his Co-Chairmen, K. J. Wynne of the Office of Naval Research and J. L. Benham of 3M Corporation, for their untiring efforts in developing the Biennial program.

The Organizing Committee was particularly grateful to the following corporations for their generous support of this Symposium: Allied Signal, American Cyanamid, Chevron Research and Technology, Ciba-Geigy, Dow Corning, Eastman Kodak, E. I. duPont de Nemours, Ethyl Corporation, General Electric, Hoechst Celanese, Inolex Chemical, Mobay, Philips Petroleum, Procter and Gamble, and Texaco.

J. C. Salamone
J. S. Riffle



PROFESSOR MICHAEL SZWARC

Winner of the 1990
Division of Polymer Chemistry Award
American Chemical Society



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PERSPECTIVES ON THE CONTRIBUTIONS OF MICHAEL SZWARC TO POLYMER SCIENCE

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Professor Michael Szwarc has published over four hundred papers, numerous reviews and three books. He has received a number of major awards, including the ACS Award in Polymer Chemistry (1969), the International Award in Plastics Science and Engineering (1972), the Gold Medal of the Benjamin Franklin Society (1978), and, at this Biennial Symposium, the 1990 Division of Polymer Chemistry Award given by the ACS Polymer Division. More recently, Professor Szwarc has been awarded the prestigious Kyoto Prize for 1991.

The research activities of Professor Michael Szwarc started in 1945, after the second World War, when he joined the research group of Professor Polanyi in Manchester, England. There he developed a pyrolytic technique (toluene carrier method) that allowed him to determine bond dissociation energies of over fifty polyatomic molecules. The work done until 1950 was summarized in a review article published in *Chem. Rev.* 47, 75, 1950 and earned him a D.Sc. in 1949.

In the course of these investigations, in 1947 Dr. Szwarc discovered a new hydrocarbon monomer, *p*-xylylene (quinomethane), that is formed in the vapor phase at high temperature ($>800^{\circ}\text{C}$) and spontaneously polymerizes upon hitting any surface kept at room temperature. The resultant polymer forms a transparent film conformally encapsulating the object on which it is deposited. The film neither melts nor decomposes until heated above 400°C . Dr. Szwarc determined the structure of this monomer and its polymer. The first publication on this work appeared in 1947 in the *Disc. Faraday Soc.* 2, 46. Subsequently, a whole class of related quinonoid monomers based on substituted *p*-xylenes, 1,4-dimethylnaphthalenes, 2,5-dimethylpyrazene, etc., was developed (*J. Polymer Sci.*, 6, 319 (1950)).

In 1952 Dr. Szwarc was appointed professor of Polymer and Physical Chemistry of SUNY in Syracuse N.Y. After coming to this country, he continued the work on various aspects of poly-*p*-xylylene in collaboration with Lou Errede of M. W. Kellogg Co. Much of the results of this later research was published in a joint review paper in *Quarterly Rev.* 12, 301 (1958). The work of Bill Gorham of Union Carbide eventually led to commercial development of poly(*p*-xylylene) marketed under the name PARYLENE.

In Syracuse, in cooperation with Vivian Stannett, Dr. Szwarc began investigating the permeability of gases and vapors through a variety of polymeric films. The most

interesting outcome of this work was reported in two papers: "The Permeability of Polymer Films to Gases, a Simple Relationship," published with Stannett in *J. Polymer Sci.* **26**, 89 (1955), and "Permeability of Gases and Vapors through Composite Membranes, Permeability Valves," published with Rogers and Stannett in *Ind. Eng. Chem.* **49**, 1933 (1957). The latter paper describes a new and interesting phenomenon, a rapid permeation in one direction and slow in the other, and quantitatively explains the theory of this behavior. Approximately twenty five other papers on this subject were published by Prof. Szwarc and his colleagues over the period of approximately six years of research.

During the same time period, Professor Szwarc also developed a versatile technique permitting determination of the relative rate constants for addition of small radicals, such as methyl, ethyl, trifluoromethyl, etc. to a large variety of aromatic, ethylenic, acetylenic, etc. compounds. This method allowed him to grade quantitatively the reactivities of various aromatic hydrocarbons, monomers, inhibitors, e.g. quinones, etc. This led to an examination of polar and steric effects in radical reactions. The theory of these additions was developed in a paper presented during the Kekule Symposium in London (1958), and published with Binks in "Theoretical Organic Chemistry" pp. 262-290, (1959), Butterworth. These studies also provided much information on cage reactions and related subjects. The investigations of radical additions continued for approximately twelve years and resulted in over one hundred publications.

In 1955 a study of the cationic polymerization of styrene initiated by trifluoroacetic acid led to discovery of a phenomenon, not appreciated at that time, which became topical in the 70's and 80's. It was found that addition of small amounts of acid (the initiator) to a large amount of styrene (the monomer) resulted in formation of low molecular weight oligomers only, whereas the addition of small amounts of styrene to a large amount of the acid rapidly produced a high molecular weight polymer (MW ~ 15000). This paradoxical result was explained by introducing the concepts of aggregation and homo-conjugation. The relevant paper was published jointly with Stannett in *J. Amer. Chem. Soc.*, **78**, 1122 (1956).

In 1956 Professor Szwarc discovered living polymers and electron transfer initiation. Simple and convincing experiments demonstrating the lack of termination and chain transfer were described in his first two papers on this subject entitled: "Polymerization Initiated by Electron Transfer to Monomer, A New Method of Preparation of Block Polymers" with Moshe Levy and Ralph Milkovich published in *J. Amer. Chem. Soc.*, **78**, 2656 (1956), and the other published in *Nature*, **178**, 5557 (1956), under the title "Living Polymers." These workers showed how such systems were capable of producing di- and ter-block polymers of predetermined composition and molecular weights. In the paper in *Nature*, the ramifications of living polymerizations were outlined. The control of molecular weight of each block and the feasibility of functionalization with any desired terminal groups was introduced. Dr. Szwarc deduced a simple relation for difunctional initiators, $DP_n = (\text{total monomer}) / (1/2 \text{ initiator})$, and the results confirming its validity were described in *J. Amer. Chem. Soc.*, **79**, 202 (1957). The first preparation of block polymers of styrene and ethylene oxide was reported in a paper with Richards, *Trans. Faraday Soc.* **55**, 1644 (1959). In the same publication, the influence of endgroups on the properties of otherwise identical polymers was described.

A variety of aspects concerned with living polymers, e.g. effect of impurities, the molecular weight distribution in living polymer systems, monomer-living polymer equilibria, etc., were treated during the years that followed. The problems of termination were reviewed in an article in *Adv. Polymer Sci.* **2**, 275 (1960), and a paper delivered during the Wiesbaden Symposium in 1959 and published in *Makromol. Chem.* **35**, 132 (1960) describes the state of art achieved in this field at that time.

In the 60's, Dr. Szwarc's studies of living polymers shifted toward kinetic problems. Much effort was placed on studying the formation and reaction of complexes of living polymers with aromatic hydrocarbons, kinetics of electron transfer processes, spontaneous isomerization of living polymers, chemistry of radical-anions, etc. Absolute rate constants of propagation were reported in a series of papers published by *J. Phys. Chem.*, **69**, 608, 612, 624 (1965). The results revealed that ion-pairs and free ions participate in

propagation, but that free ions are the main contributors to the reaction. Continuation of these studies led to a deep understanding of the reactivity of ionic species. The role of tight and loose ion-pairs, of complexation agents, of triple ions, etc. was clarified and quantified. Kinetic studies of homopolymerization were extended to anionic copolymerization. The absolute rate constants for crossover reactions were reported for a series of monomers reacting with living polystyrene, for a series of substituted, living polystyrenes reacting with styrene [J. Amer. Chem. Soc., 85, 1306 (1963)], and extended to the dienes and vinylpyridines. A most unconventional copolymerization of living poly(vinyl naphthalene) with styrene was reported in a paper published in J. Amer. Chem. Soc., 85, 3909, (1963) with Bhasteter and Johan Smid. The results accumulated in that period were published in the monograph "Carbanions, Living Polymers and Electron Transfer Processes" published by Wiley in 1968.

Studies of ionic reactions were extended to processes other than propagation of polymerization. A variety of protonation processes, electron transfers, dimerizations, cis-trans isomerizations, etc., were investigated with emphasis on the role of different types of ionic species on the course of these reactions. The results of these studies were reviewed in two volumes entitled: "Ions and Ion-Pairs in Organic Reactions" edited by Professor Szwarc, who contributed four chapters to this extensive compilation. These books were published by Wiley in 1970 (volume I) and 1972 (volume II).

Directing a research group in the University of Uppsala, Sweden for a period of four years, Professor Szwarc became acquainted with Flash Photolysis. This technique, used in Uppsala and later in Syracuse, allowed quantitative studies of numerous electron transfer reactions. For example, the determination of kinetic parameters governing the electron transfer initiation of polymerization was achieved by applying the flash photolytic technique. Flash photolysis studies were most fruitful, a number of novel and interesting results were obtained, and these were reported in a series of about twenty-five papers.

A great deal of Szwarc's studies of radical anions were performed using the ESR technique. The question of how far an electron can jump as well as the dynamics of flexible polymer chains was investigated. This work was carried out in collaboration with Shimada and published jointly in several papers, e.g., in Chem. Phys. Lett. 28, 540 (1974) and Macromolecules 5, 801 (1972).

Prof. Szwarc also contributed to the understanding of mechanisms of cationic polymerizations. In addition to the previously mentioned study of the cationic polymerization of styrene initiated by trifluoroacetic acid, he developed novel methods of initiation of cationic polymerization, e.g., the initiation of cationic polymerization by transfer of Cl^+ and NO_2^+ ions, and initiation by electron-transfer. In cooperation with deSorgo and David Pepper, he carried out the first stop-flow study of cationic polymerization that demonstrated the formation of the positive polystyryl cation and allowed its spectrum to be recorded. This work was published in J.C.S. Chem. Comm. 419, (1973). He was the first to point out that cationic polymerization induced by ionizing radiation is propagated by free cations [Makromol. Chem. 35a, 123 (1960)].

Professor Michael Szwarc is truly one of the pioneers of polymer science. The members of the ACS Division of Polymer Chemistry recognize his many creative contributions to macromolecular chemistry and his tremendous lasting impact on this field. It is with great pleasure that we honor Professor Szwarc with the Division of Polymer Chemistry award on the occasion of this 1990 Biennial Symposium.

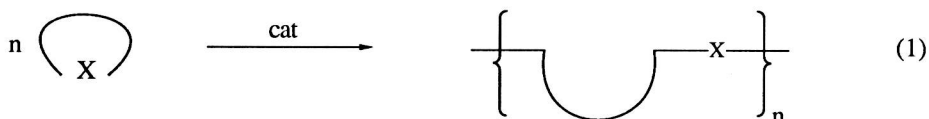
PREPARATION AND POLYMERIZATION OF MACROCYCLIC OLIGOMERS

Daniel J. Brunelle and Thomas L. Evans

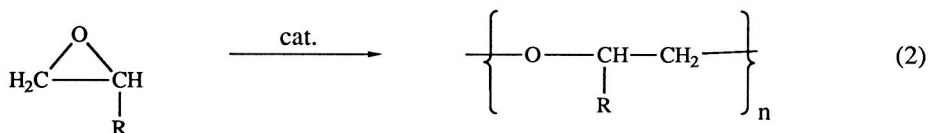
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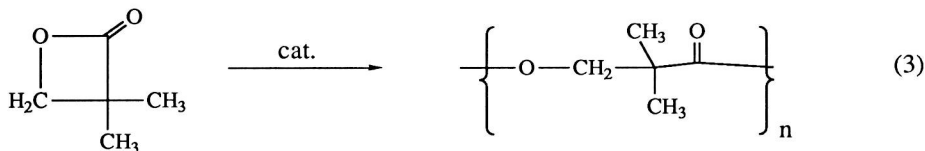
INTRODUCTION

Ring-opening polymerization reactions (Equation 1) constitute an important class of polymerization techniques. A number of commercial products are prepared via ring-opening polymerization reactions, and the preparation of monomers, studies of catalysis and mechanism, and product development of many of these materials are active areas of academic and industrial research. Ring-opening polymerization chemistry has been extensively reviewed in several monographs,¹ and in many review articles.² A wide variety of monomers have been utilized in ring-opening reactions; these polymerizations are commercially utilized for the preparation of polyamides, aliphatic polyesters, silicones, polyalkylenes (via ring-opening metathesis polymerizations), and epoxide thermosets. For this paper, discussion will be limited to three categories of ring-opening polymerization reactions: monomeric strained ring systems, which have high reaction exotherms, monomeric medium ring systems, which have moderate exotherms, and oligomeric large ring systems, which have little or no reaction exotherm.

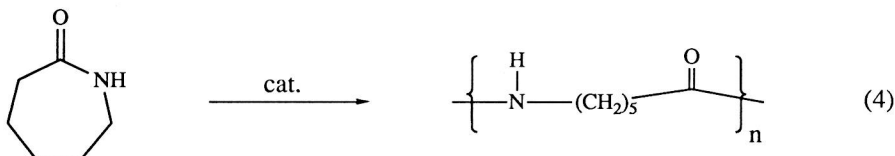


Typically, the ring size of the cyclic monomer has a controlling effect both on the preparation of the monomer, and on its inherent stability and polymerizability. The most reactive systems, those which tend to polymerize completely with little cyclic residue, usually contain strained three- or four-membered rings. Examples of these monomers are ethylene oxide, which has a strained three-membered ring, and pivalolactone, which is a four-membered lactone (equations 2 and 3). Because of the ring strain, the ring-opening polymerization of these materials are generally exothermic; for example, the epoxide opening of equation 2 has a net enthalpy of -104 kJ/mole.³ The enthalpy of reaction provides a driving force for complete reaction, but may also be a handicap in controlling the polymerization of large volumes.

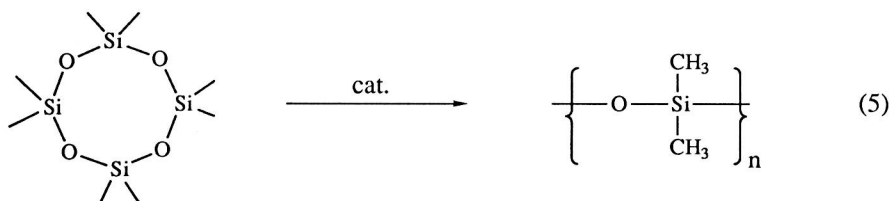




Medium-sized (5-9 members) rings generally have significantly less ring strain, and hence lower reaction exotherms during polymerization. For example, the polymerization of caprolactone (7-membered ring) has an enthalpy of -16.5 kJ/mole (Equation 4)³. In the polymerization of such monomers, an equilibrium between cyclic monomer (or oligomers) and linear polymer is achieved during the polymerization. Because the enthalpy for ring-opening is low, and the entropy decreases during polymerization (ΔS for caprolactone = -29 J/° K-mole),³ these reactions do not proceed to 100% completion, and monomer recoveries of 5-30% are typical. The removal of unreacted monomer may be a limitation if a finished part is to be formed by ring-opening polymerization. Virtually all ring-opening polymerization reactions which involve ring-chain equilibration form measurable quantities of monomeric or oligomeric cyclics.⁴

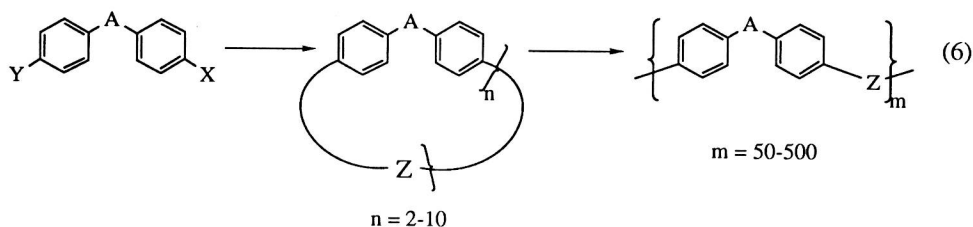


The ring-opening polymerization of the oligomeric cyclic dimethylsiloxane tetramer seems to be an unusual example, in that the entropy actually increases during polymerization.⁵ This increase in entropy is the driving force for the reaction, since the enthalpy is near zero. Nonetheless, the anionic polymerization is an equilibrium reaction, and significant amounts of cyclics remain after polymerization (18.3% for dimethylsiloxane,⁶ Equation 5).



The preparation of engineering thermoplastics with aromatic structural units via ring-opening polymerization would be commercially appealing, inasmuch as low molecular weight precursors would lead to high molecular weight polymers without formation of by-products during polymerization. Because of the size of the monomer units, and the distance of chain ends from one another, cyclic *monomeric* precursors for these materials are rare. The cyclic *oligomers* which would be precursors to engineering thermoplastics like polycarbonate or poly(ethylene terephthalate) have been known for some time. Cyclic oligomers are present in many polymers in levels of 0.25-8%,^{1,2} and a variety of extraction techniques have been published. The utility of cyclic oligomers of aromatic polyesters or polycarbonates has until now been limited chiefly by the cumbersome and low-yielding techniques for their isolation or preparation. Furthermore, in many cases the discrete oligomers are high-melting crystalline solids, a limitation affecting efficient melt processing.

By conventional thinking, the structure and large ring sizes of oligomeric cyclics in the thermoplastics class would seem to preclude efficient, high yielding cyclization. Even a cyclic carbonate dimer of bisphenol A has a ring size of 24 structural atoms, and each additional monomer unit adds 12 atoms to the ring. It is well known that formation of rings of 5, 6, and 7 structural units are most favored, medium-sized rings (8-11 members) are disfavored, due to transannular repulsions, and beyond ring sizes of 16-20 atoms, the likelihood of cyclic formation becomes minimal.^{1,2} This paper reviews work on the use of pseudo-high dilution techniques, which facilitate efficient cyclization reactions, leading to moderate to excellent yields of cyclic oligomeric aromatic carbonates, esters, ethers, amides, imides, and silicones (Equation 6).⁷ In all cases, the formation of oligomeric cyclics is selective over formation of linear oligomers, and minimal purification is necessary. The oligomeric cyclic products are mixtures of several ring sizes, and thus have melting points which are depressed relative to the pure discrete cyclic oligomers. For example, the mixture of cyclic oligomeric bisphenol carbonates have a melting range of 190-210° C, compared to melting points of 375° C and 350° C for the discrete cyclic tetramer⁸ and trimer⁹.



The oligomeric cyclics can be converted to high molecular weight polymers via ring-opening polymerization in the presence of various initiating substances. The most efficient initiators are typically anionic or nucleophilic species such as lithium phenoxide, tetramethylammonium tetraphenylborate, sodium sulfide, or lithium trifluoroethoxide. Because of the large ring size and lack of ring strain, the polymerization reactions are essentially thermoneutral. Similar to the polymerization of cyclic siloxanes, the polymerization reaction is driven by entropy, although apparently to a much greater degree. Equilibrative ring-opening polymerization leads to high molecular weight polymer with little or no detectable cyclic oligomers remaining (<1%). Apparently the ring size of the oligomeric cyclic is such that back-biting on the polymer chain is unlikely.

The technique for preparation of oligomeric cyclics relies upon kinetic reaction control for the formation of cyclics. Fast reactions are necessary for the pseudo-high dilution, intramolecular ring formation. Subsequent polymerization is thermodynamically controlled, with the ring-opening leading to high molecular weight linear polymers, with only very small amounts of cyclic present in the equilibrated mixture. Unlike many ring-opening polymerizations, the reaction has no exotherm, and complete ring-chain equilibration is achieved upon polymerization. Thus, molecular weight distributions approach 2.0.

RESULTS

Cyclic Carbonates

In the mid 1960's, Prochaska was granted several patents for the preparation of monomeric cyclic aromatic carbonates with 7- or 8-membered rings, formed from 2,2'-biphenols (Equation 7).¹⁰ The monomeric cyclic carbonates could be prepared either directly, via phosgenation, or using a vacuum distillation/depolymerization technique similar to that developed by Carothers¹¹ for the preparation of cyclic aliphatic esters and