

Macromolecular  
Symposia

H. Galina (Ed.)

**Polymer  
Networks**



**WILEY-VCH**



IUPAC

# Macromolecular Symposia

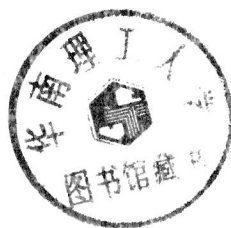
**Symposium Editor:** H. Galina

**Editor:** I. Meisel

**Associate Editors:** C.S. Kniep, S. Spiegel

**Assistant Editor:** K. Grieve

**Executive Advisory Board:** M. Antonietti, M. Ballauff, H. Höcker,  
S. Kobayashi, K. Kremer, T.P. Lodge,  
H.E.H. Meijer, R. Mülhaupt,  
A.D. Schlüter, H.W. Spiess, G. Wegner



---

**171**

pp. 1-263

June 2001

 **WILEY-VCH**



E200201077

**Macromolecular Symposia** publishes lectures given at international symposia and is issued irregularly, with normally 14 volumes published per year. For each symposium volume, an Editor is appointed. The articles are peer-reviewed. The journal is produced by photo-offset lithography directly from the authors' typescripts.

Further information for authors can be obtained from:

Editorial office "Macromolecular Symposia"

Wiley-VCH

P.O. Box 10 11 61, D-69451 Weinheim,

Germany

or for parcel and courier services: Pappelallee 3, D-69469 Weinheim,

Germany

Tel. +49 (0) 62 01/6 06-2 38 or -5 81; Fax +49 (0) 62 01/6 06-3 09 or 5 10; [macromol@wiley-vch.de](mailto:macromol@wiley-vch.de)

<http://www.wiley-vch.de/home/macrosymp>

Suggestions or proposals for conferences or symposia to be covered in this series should also be sent to the Editorial office at the address above.

### **Macromolecular Symposia:**

#### **Annual subscription rates 2001**

Germany, Austria € 1098 (DM 2147,50); Switzerland SFr 1808; other Europe € 1098; outside Europe US \$ 1328.

Macromolecular Package, including Macromolecular Chemistry & Physics (18 issues), Macromolecular Rapid Communications (18 issues), Macromolecular Theory & Simulations (9 issues) is also available. Details on request.

Packages including Macromolecular Symposia and Macromolecular Materials & Engineering are also available. Details on request.

Single issues and back copies are available. Please, inquire for prices.

**Orders** may be placed through your bookseller or directly at the publishers: WILEY-VCH Verlag GmbH, P.O. Box 10 11 61, D-69451 Weinheim, Germany, Tel.: (0 62 01) 6 06-0, Telefax (0 62 01) 60 61 17, Telex 46 55 16 vchwh d. E-mail: [subservice@wiley-vch.de](mailto:subservice@wiley-vch.de)

Macromolecular Symposia (ISSN 1022-1360) is published with 14 volumes per year by WILEY-VCH Verlag GmbH, P.O. Box 10 11 61, D-69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage pending at Jamaica, NY 11431. POSTMASTER: send address changes to Macromolecular Symposia, Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003.

WILEY-VCH Verlag GmbH grants libraries and other users registered with the Copyright Clearance Center (CCC) Transactional Reporting Service the right to photocopy items for internal or personal use, or the internal or personal use of individual clients, subject to a base fee of \$ 17.50 per copy, per article, payable to CCC, 21 Congress St., Salem, MA 01970. 1022-1360/99/\$17.50+.50.

© WILEY-VCH Verlag GmbH, D-69469 Weinheim, Germany, 2001

Printing: Strauss Offsetdruck, Mörlenbach. Binding: Wilh. Osswald, Neustadt

0631-53  
P783.8  
2000

**International Union of Pure  
and Applied Chemistry**

**15<sup>th</sup> Polymer Networks Group Meeting  
Polymer Networks'2000  
Formation–Structure–Properties**

*Rzeszów University of Technology,  
Jagiellonian University in Cracow, Poland  
17–21 July, 2000*

*Symposium Editor*

**Henryk Galina**  
Rzeszów University of Technology  
35-959 Rzeszów  
Al. Powstańców Warszawy 6  
Poland

## Author Index

Andrzejewska, Ewa . . . . .	243	Mark, James E. . . . .	1
Basser, Peter J. . . . .	201	Matějka, Libor . . . . .	181
Bokobza, Liliane . . . . .	163	Menez, Philippe . . . . .	233
Cail, J.I. . . . .	19	Meseguer Dueñas, José Maria . . . . .	151
Capaccoili, Simone . . . . .	253	Monleón Pradas, Manuel . . . . .	151
Casalini, Riccardo . . . . .	253	Morgan, Roger J. . . . .	87
Churochkina, Nataliya A. . . . .	225	Nedbal, Jan . . . . .	105
Coniglio, Antonio . . . . .	79	Patrickios, Costas S. . . . .	209
Corezzi, Silvia . . . . .	253	Pissis, Polycarpus . . . . .	151
de Arcangelis, Lucilla . . . . .	79	Pouchelon, Alain . . . . .	233
Del Gado, Emanuela . . . . .	79	Pretorius, Jannie . . . . .	45
Dukh, Oksana . . . . .	181	Pryakhina, Tatiyana I. . . . .	225
Dzhavadyan, Emma A. . . . .	87	Rogovina, Lidiya Z. . . . .	225
Eichinger, Bruce E. . . . .	45	Rolla, Pierangelo . . . . .	253
Galiatsatos, Vassilos . . . . .	97	Romiszowski, Piotr . . . . .	63
Galina, Henryk . . . . .	37	Rozenberg, Boris A. . . . .	87
Gallego Ferrer, Gloria . . . . .	151	Ryan, Anthony J. . . . .	139
Gallone, Giuseppe . . . . .	253	Sedláková, Zdenka . . . . .	105
Geissler, Erik . . . . .	171, 201	Shin, Eugene E. . . . .	87
George, Catherine . . . . .	233	Sikorski, Andrzej . . . . .	57, 63
Gómez Ribelles, José Luis . . . . .	151	Stanford, John L. . . . .	139
Gotlib, Yuli Ya. . . . .	69	Stepto, R.T.F. . . . .	19
Gurtovenko, Andrew A. . . . .	69	Subramaniam, Pazam R. . . . .	97
Hadiyannakou, Stella C. . . . .	209	Tabka, Mohamed Tahar . . . . .	123
Hecht, Anne-Marie . . . . .	171, 201	Taylor, D.J.R. . . . .	19
Horkay, Ferenc . . . . .	171, 201	te Nijenhuis, Klaas . . . . .	189
Ilavský, Michal . . . . .	105	Torres Escuriola, Débora . . . . .	151
Irzhak, Tamara F. . . . .	11	Valentová, Helena . . . . .	105
Irzhak, Vadim I. . . . .	11	Vamvakaki, Maria . . . . .	209
Janik, Helena . . . . .	115	Vasil'ev, Victor G. . . . .	225
Klein-Castner, Lisa . . . . .	97	Widmaier, Jean-Michel . . . . .	123
Korolev, Gennadii V. . . . .	11	Wimmer, Erich . . . . .	45
Kyritsis, Apostolos . . . . .	151	Yamasaki, Edna N. . . . .	209
Lechowicz, Jaromir B. . . . .	37	Yang, Ying . . . . .	139

## Preface

This volume contains selected papers presented at *Polymer Networks '2000*, the 15<sup>th</sup> *Polymer Networks Group Meeting*, held in Cracow, Poland, from 17<sup>th</sup> to 21<sup>th</sup> July, 2000. The conference was organized jointly by the Rzeszów University of Technology and the Jagellonian University, Cracow, under the sponsorship of IUPAC and the Polymer Division of the Polish Chemical Society. It was a satellite meeting of the IUPAC World Polymer Congress, held the previous week in Warsaw.

The contents of this volume reflect the main topics of the conference. In addition to theoretical papers, there are papers on the formation, structure and properties of interpenetrating polymer networks, and heterogeneous, filled and hybrid networks. The properties and characterization of hydrophilic and hydrophobic gels and swollen networks are also covered and there are contributions on calorimetric and dielectric studies of thermoset formation and on the structure of amorphous sulfur.

Our thanks are due to the authors of papers, to colleagues who helped to review them to the *Macromolecular Symposia* staff. One of us (HG) would like to express his gratitude to all members of the Advisory Board and to the Organizing Committee of the meeting for their excellent efforts before and during the conference, which resulted in it running smoothly, both scientifically and socially. We feel sure that the Cracow meeting will be remembered, not only for its scientific discussions, but also for its tours of the *Collegium Maius* and Wieliczka.

The *Polymer Networks Group* is more than 25 years old and has been associated with many events. This year we celebrate the 70<sup>th</sup> birthday of two founder members and officers: *Walther Burchard* of Freiburg and *Karel Dušek* of Prague, to whom we are pleased to dedicate this volume. Sadly, we also have to say farewell to *Manfred Gordon* of Cambridge (UK), who passed away in March 2000, and to *Toyoichi Tanaka* of Cambridge (Mass.), who passed away shortly before the conference. The volume starts with tributes to these two friends and colleagues who will always remain in our memories.

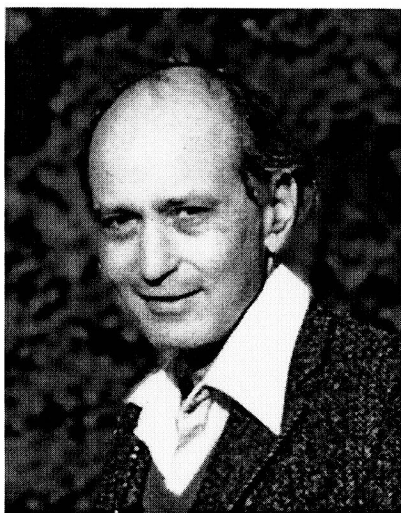
Henryk Galina  
Rzeszów

Robert Stepto  
Manchester

April 2001



## Manfred Gordon 1917-2000



Prof. Manfred Gordon, who died in Cambridge in March 2000, at the age of 82, was an inspiring scientist and teacher, a pioneer in polymer science, and one of the founders of the Polymer Networks Group. He was born in Leipzig, Germany in May 1917, and spent much of his early years in Germany, and later Switzerland. He came to England in 1938 and his career progressed via, amongst other places, the Fort Dunlop headquarters of the eponymous Rubber Company. During this time he met his future wife, and companion, Blanche. In 1950 he joined the Royal Technical College Glasgow (later Strathclyde University) as a lecturer, and then spent a short time at the University of Manchester Institute of Science and Technology, before returning to Scotland as Assistant Director of the Arthur D. Little Research Institute in Edinburgh. From 1960-4 he was a Reader in the Department of

Chemistry at Imperial College, London, moving from there to take up a position as Professor in the Department of Pure and Applied Chemistry at the University of Strathclyde, Glasgow, Scotland. He then returned to England, to the newly founded University of Essex, Colchester, England in 1967, where he stayed until retirement in 1982. Finally he moved to the Statistical Laboratory at the University of Cambridge, where he had long contacts, and was active until shortly before his final illness.

Manfred's work spanned almost the entire realms of polymer science (and much beyond) from his early published work on the glassy state (Gordon-Taylor equation) and crystallisation, through dilute solution theory, phase-behaviour and polymer gels and networks.

Amongst his most well-cited and ground-breaking work was his application of Good's branching ("cascade") theory to polymer network formation, published in 1962, which was extended to ring-formation, gelation kinetics, scattering theory and beyond. It was this approach which has been adopted subsequently by amongst others, our Chairman, Walther Burchard and ex-Chairman, Karel Dušek. His other main thrust was in the phase behaviour of polymer solutions and blends, particularly spinodal decomposition, with Ron Koningsveld, then Head of Research at DSM.

Much of Manfred's output was in conventional polymer journals, but he also published in journals of mathematics, especially his work on graph theoretical methods, chemistry and physics. At one count he had published in more than 50 such distinct journals.

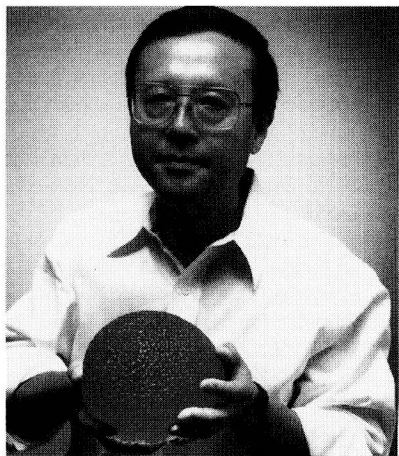
Personally he was an inspiration, endlessly patient with those of more limited intellect and breadth of vision, and always prepared to share equally work, where his input was far greater than that of his co-authors. Few, if any of those who came into contact with Manfred, as student, post-doctoral or those with already established careers, did not find him a major figure in their life and future careers. Certainly all of us who worked with him will miss his inspiration, and surprisingly to those who knew him less well, his subtle but pronounced sense of humour.

This writer for one will treasure his last communication from Manfred, a note appended to his 1999 Christmas card, wishing him a Happy New Year, and assuring him that the now present one, it would be his (Manfred's) positively last Millennium. Sadly this was almost too accurate a prediction, within a month he was taken ill, and he died only a few weeks later. We dedicate this volume to his memory.

Written by Simon B. Ross-Murphy



## Toyochi Tanaka 1946-2000



On Saturday, May 20, 2000, following his weekly routine, Toyochi Tanaka went to play tennis. He was never to come back. He died instantly on the court, of what seemed to be a heart attack followed by immediate cardiac arrest. He was only 54.

It is never easy to write obituaries. It is particularly hard when so energetic a working scientist passes away. Toyo left an actively working group, unpublished manuscripts, and many experiments in progress. He was looking forward to seeing new data and orchestrating new experiments. He had a very long lag between the actual the status of his experiments and his published results. With a characteristic soft smile, he was planning to "educate" people, to prepare them for understanding his experimental logic and the direction of his vision

and thoughts. This makes it particularly difficult to summarize his scientific achievements.

Toyochi Tanaka was born on January 4, 1946, in Nagaoka city in Japan. His father, Toyosuke, is Emeritus Professor of Chemistry at the University of Saitama. Very early in his childhood, Toyo became interested in science, mainly physics and chemistry. He graduated in 1968 and then defended his PhD in 1973 at the University of Tokyo, and he went to MIT in 1972. The MIT was to become his home for the rest of his life. He started as a postdoctoral fellow in Professor Benedek's laboratory and progressed all the way up to the rank of Professor of Physics and the Otto & Jane Morningstar Professor of Science.

Looking at Toyo Tanaka's scientific achievements, we remember many, including the first use of the Doppler technique to measure blood flow in the intact human retina. However, overall, I think, Toyo would have agreed if we were to call him Mr. Polymer Gel. At the end of the 70's, he discovered the phenomenon of polymer gel collapse, and this discovery was to become one of the most frequently cited works of the period. In the decades since then, numerous followers all over the world studied various phase transitions in gels, but it was Toyo whose comprehensive vision made the difference. In his hands, gels were to become the powerful instrument of both fundamental and applied science. To begin with, Toyo not only examined phase transitions in many different gels, but examined gel collapse transitions governed by all the fundamental molecular interactions operational in biological systems in water, such as van der Waals, Coulombic, hydrophobic interactions, and hydrogen bonding. He has achieved a systematic understanding of when gel collapse occurs discontinuously, as a first order phase transition, and when it is continuous, as a second order transition. This gave rise to industrial applications, employing gel sensitivity to heat and cold, to electric and magnetic fields, to light, acidity, and chemicals.

Toyo Tanaka was able to engineer gels with catalytic activity and, moreover, with the ability to switch the catalysis on and off depending locally on the progress of the chemical reaction. He was able to invent a gel capable of memorizing a holographic image; moreover, it was possible to destroy this image upon gel swelling and then reproduce it upon collapse, and it could be repeated many times.

Needless to say, these applications, ranging from electronics to microbiology, could have fully occupied the most sophisticated mind. They did not satisfy Toyochi Tanaka, though. In

recent years, he was working on a much more ambitious project. His idea was to realize in gels some forms of molecular self-organization which so far are known only in biological molecules, such as proteins. He wanted to prepare a gel, or better to say, a heteropolymer gel, and imprint some information in its structure in such a way that some degree of molecular self-assembly would be achieved upon gel collapse. This program remains incomplete. However, Toyo did make significant progress in this direction. He demonstrated experimentally that frustrations are operational in heteropolymer gels and he has shown that imprinting leads to the minimization of frustrations. His several works on this subject, which were to become his last, are still under various stages of processing in journals and should be published soon. It is this subject that Toyoichi Tanaka was to presents at Polymer Networks '2000. We can safely assume that his talk was to become one of the central events of the meeting. Indeed, Toyo Tanaka's papers are very simply written and they are easy to read both for chemists and physicists. Toyo was an experimenter, but he also felt at home with theory.

In many works, he supported his experimental findings by the theoretical estimates of his own. Students liked Toyo a lot; he was among the most popular teachers at MIT. Whatever he taught - mechanics, electricity & magnetism, quantum mechanics, or statistical mechanics - he showed demonstrations of the swelling and collapsing of polymer gels. Why? He was justly convinced that the demonstration of exciting modern science is more important to young minds than any artificial boundaries between subjects. And what was perhaps most valuable for the students, was the personal leadership of a scientist excited with his science. This feeling of excitement was always noticeable in Tanaka's professional talks, and we can only think of the talk at Polymer Networks'2000 that we are never to hear.

Written by Kazunori Tanaka & A. Youri Grosberg

The **tables of contents** of the published issues are displayed on the [www](http://www.wiley-vch.de/home/macrosymp).

This service as well as further information on our journals can be found at the following [www](http://www.wiley-vch.de/home/macrosymp) address:

<http://www.wiley-vch.de/home/macrosymp>

The service is free for everybody.

## Contents of Macromol. Symp. 171

### 15<sup>th</sup> Polymer Networks Group Meeting, Polymer Networks'2000 Crackow, Poland 2000

#### Preface

*H. Galina, R.T.F. Stepto*

Manfred Gordon 1917–2000

*S.B. Ross-Murphy*

Toyoichi Tanaka 1946–2000

*K. Tanaka, Y. Grosberg*

1. Some Simulations on Elastomers and Rubberlike Elasticity . . . . . 1  
*James E. Mark*
2. Critical Conversions in Chain Network Polymerization . . . . . 11  
*Vadim I. Irzhak\*, Tamara F. Irzhak, Gennadii V. Korolev*
3. Formation, Structure and Properties of Polymer Networks: Gel-Point  
Prediction in Endlinking Polymerisations. . . . . 19  
*J.I. Cail, R.T.F. Stepto\*, D.J.R. Taylor*
4. Off-Lattice Long-Range Percolation Modelling of a Network  
Polymerisation . . . . . 37  
*Henryk Galina\*, Jaromir B. Lechowicz*
5. The Structure of Amorphous Sulfur . . . . . 45  
*Bruce E. Eichinger\*, Erich Wimmer, Jannie Pretorius*
6. Motion of Star-Branched Chains in Polymer Networks:  
A Monte Carlo Study . . . . . 57  
*Andrzej Sikorski*

7. Monte Carlo Simulations of Star-Branched Polymers in a Network of Obstacles. . . . .	63
<i>Piotr Romiszowski*, Andrzej Sikorski</i>	
8. Unsolved Problems in the Theory of Dynamics in Homogeneous and Heterogeneous Polymer Networks . . . . .	69
<i>Yuli Ya. Gotlib*, Andrew A. Gurtovenko</i>	
9. Viscoelastic Properties at the Sol-Gel Transition . . . . .	79
<i>Emanuela Del Gado*, Lucilla de Arcangelis, Antonio Coniglio</i>	
10. The Polyaddition, Chain, and Polycondensation Mechanisms of Formation of Networks Based on Bismaleimides . . . . .	87
<i>Boris A. Rozenberg*, Emma A. Dzhavadyan, Roger J. Morgan, Eugene E. Shin</i>	
11. Designing Heterogeneity into Bimodal Elastomeric PDMS Networks. . . . .	97
<i>Vassilos Galiatsatos*, Pazam R. Subramaniam, Lisa Klein-Castner</i>	
12. Formation, Structure and Physical Properties of Ordered Polyurethane Networks. . . . .	105
<i>Michal Ilavský, Helena Valentová, Zdeňka Sedláková, Jan Nedbal</i>	
13. The Size of Cryofracture Figures in the Network of Segmented Polyurethane Elastomers. . . . .	115
<i>Helena Janik</i>	
14. The Role of Tin(II) Octoate – Azobisisobutyronitrile Complex in the Formation Rate of the Respective Networks in Simultaneous Interpenetrating Polymer Networks. . . . .	123
<i>Mohamed Tahar Tabka, Jean-Michel Widmaier*</i>	
15. The Formation and Properties of Acrylic-Polyurea Interpenetrating Networks Formed by Reaction Injection Moulding (RIM) . . . . .	139
<i>John L. Stanford*, Anthony J. Ryan, Ying Yang</i>	
16. Dielectric and Dynamic Mechanical Studies on Homogeneous PBA/PBMA Interpenetrating Polymer Networks. . . . .	151
<i>Polycarpus Pissis*, Apostolos Kyritsis, José Maria Meseguer Dueñas, Manuel Monleón Pradas, Débora Torres Escuriola, Gloria Gallego Ferrer, José Luis Gómez Ribelles</i>	
17. Reinforcement of Elastomeric Networks by Fillers . . . . .	163
<i>Liliane Bokobza</i>	
18. Structure of Polymer Solutions and Gels Containing Fillers . . . . .	171
<i>Erik Geissler*, Anne-Marie Hecht, Ferenc Horkay</i>	
19. Organic–Inorganic Hybrid Networks. . . . .	181
<i>Libor Matějka*, Oksana Dukh</i>	

20. Crosslink Nature in Cr(III)-Polyacrylamide Gels. . . . .	189
<i>Klaas te Nijenhuis</i>	
21. Ion-exchange Induced Change in the Structure and Osmotic Properties of Sodium Polyacrylate Hydrogels. . . . .	201
<i>Ferenc Horkay*, Peter J. Basser, Anne-Marie Hecht, Erik Geissler</i>	
22. Characterization of Hydrophilic Networks Synthesized by Group Transfer Polymerization . . . . .	209
<i>Maria Vamvakaki, Edna N. Yamasaki, Stella C. Hadiyannakou, Costas S. Patrickios*</i>	
23. Hydrophobically Associating Water-Soluble Polymers: A Dramatic Growth of Solution Viscosity and the Specificity of Physical Gel Formation . . . . .	225
<i>Lidiya Z. Rogovina*, Victor G. Vasil'ev, Nataliya A. Churochkina, Tatiyana I. Pryakhina</i>	
24. The Swelling Behaviour of Siloxane Elastomers in Relation to Their Microscopic Structure . . . . .	233
<i>Alain Pouchelon*, Catherine George, Philippe Menez</i>	
25. Calorimetric Study of Photopolymerisation of Divinyl Monomers . . . .	243
<i>Ewa Andrzejewska</i>	
26. Influence of Temperature, Pressure and Connectivity on the Dynamics of a Glass-Forming System Investigated by Dielectric Spectroscopy . . .	253
<i>Silivia Corezzi*, Simone Capaccoli, Riccardo Casalini, Pierangelo Rolla, Giuseppe Gallone</i>	

\* The asterisk indicates the name of the author to whom inquiries should be addressed

## **Some Simulations on Elastomers and Rubberlike Elasticity**

James E. Mark

Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio 45221-0172, USA

**SUMMARY:** A number of examples are given to illustrate the use of computer modeling to elucidate the structures of elastomeric polymer networks, and to provide guidance on controlling network structure to maximize mechanical properties. The first example involves simulations of the gelation process leading to the development of the network structure necessary for a material to exhibit reversible elastomeric properties. The goals here are to characterize the amounts and constituents of the sol phase, and the structure of the gel phase sufficient for prediction of its mechanical properties. Attempts are also being made to simulate the structure and properties of networks having multimodal distributions of chain lengths, for example to suggest how trimodal distributions might give additional improvements beyond those shown by bimodal networks. Network thermoelasticity can also be elucidated by simulations of the temperature dependence of the unperturbed dimensions of the network chains. Strain-induced crystallization is also being simulated to generate chains having sequence distributions that are representative of various polymerization conditions. The chains are then placed alongside one another to determine matched-sequence runs that could lead to the formation of crystallites. Finally, the long-standing problem of clarifying how fillers reinforce elastomeric materials is being approached using simulations of chains in the vicinity of impenetrable filler particles. In this way it is possible to determine how reinforcement depends on the perturbation of distributions caused by this excluded-volume effect.

### **Introduction**

The present review illustrates how computational modeling has been used in the elucidation of the structures and properties of elastomeric polymer networks, using studies with which the author has been involved. One of the main goals has been to provide guidance on how to optimize the mechanical properties of an elastomer, by control of its network structure and by the incorporation of reinforcing fillers.

### **Network Formation**

The formation of network structures has been extensively simulated by Eichinger and coworkers.<sup>1)</sup> The basic approach is to randomly end link functionally-terminated precursor chains with a multifunctional reagent, and then to examine the sol fraction with regard to

amount and types of molecules present, and the gel fraction with regard to its structure and mechanical properties. This is illustrated in Fig. 1. The systems most studied in this regard<sup>1)</sup> involve chains of poly(dimethylsiloxane) (PDMS) having end groups X that are either hydroxyl or vinyl groups, with the corresponding Y groups on the end linking agents then being OR alkoxy groups in an organosilicate, or H atoms in a multifunctional silane.<sup>2)</sup>

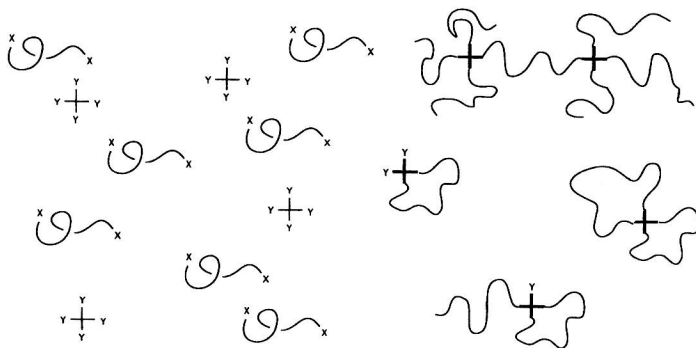


Fig. 1: End-linking reactions to form elastomeric network structures. The left portion of the figure shows the reactants, and the right portion shows some types of expected products.

The Monte Carlo method for simulating these reactions is now part of the Polymer Module in some commercial software (Molecular Simulations, Inc.), and is being used to generate additional information on the vinyl-silane end linking of PDMS.<sup>3)</sup> Some preliminary results for duplicate experiments for two PDMS molecular weights are shown in Table 1. The simulations are seen to give a very good account of gelation points, but overestimate the maximum extent of reaction attainable. The discrepancy may be due to experimental difficulties in taking a reaction close to completion within a highly viscous, entangled medium.

If cyclic molecules of PDMS are present during the end linking, they are trapped within the network if they are large enough to be penetrated by the precursor chains.<sup>2)</sup> This "incarceration" process has also been simulated successfully.<sup>2)</sup>

### Distributions of End-To-End Distances

One novel approach to obtaining non-Gaussian distribution functions utilizes the wealth of information that rotational isomeric theory provides on the spatial configurations of chain molecules. Specifically, Monte Carlo calculations based on the rotational isomeric state



approximation are used to simulate spatial configurations and thus distribution functions for the end-to-end separations.<sup>4-6)</sup> The results obtained documented the expected fact that the Gaussian distribution is generally a very poor approximation for short chains or for the high extensions that are of primary importance with regard to ultimate properties. Some typical results are shown in Fig. 2. Another example of this approach was to determine how an applied force can change the distributions for a chain that can undergo a coil-to-helix transition.<sup>7)</sup>

Table 1: Extents of reaction<sup>a)</sup> for some poly(dimethylsiloxane) end-linking reactions.<sup>3)</sup>

M <sub>n</sub> of PDMS <sup>b)</sup> (g/mol)	At gelation		At end of reaction	
	Experiments	Simulations	Experiments	Simulations
6,400	0.65	0.65	0.87	0.99
"	0.68	"	0.89	"
7,300	0.67	0.63	0.88	0.96
"	0.67	"	0.89	"

<sup>a)</sup>As gauged by Si–H consumption.

<sup>b)</sup>Number-average molecular weights.

These Monte Carlo distributions can be used in the standard three-chain model for rubberlike elasticity to generate, for example, stress-strain isotherms.<sup>2)</sup> Non-Gaussian effects can cause large increases in modulus at high elongations, because of the limited extensibilities of the network chains.<sup>8)</sup> Thus, it is very useful to identify chain structures and chain lengths giving the largest increases in stress without unacceptable decreases in extensibility. This will, of course, maximize the area under the stress-strain curve, which represents the energy for rupture or toughness of the material. One illustration of this approach is the use of multimodal distributions of network chain lengths, as described in the following Section.

### Elastomers Having Multimodal Distributions of the End-To-End Distance

One of the most interesting applications of this approach is to PDMS elastomers which have a bimodal distribution of network chain lengths<sup>9)</sup> and, correspondingly, very good mechanical properties.<sup>2)</sup> The upturns in modulus observed at high elongations are thought to be due to the

very limited extensibilities of the short chains in the bimodal structures, with the long chains increasing extensibility, and this seems to be supported by the simulated results.<sup>6,10)</sup>

Because of the improvements in properties exhibited by elastomers having bimodal distributions,<sup>2)</sup> there have been attempts to prepare and characterize "trimodal" networks.<sup>11)</sup>

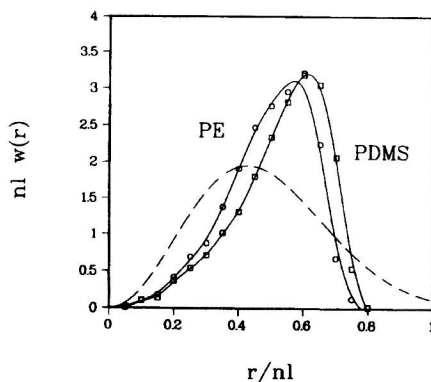


Fig. 2: Comparisons among the rotational isomeric state distributions for polyethylene and PDMS chains having only 20 skeletal bonds, and the corresponding Gaussian approximation.<sup>4)</sup>

The calculations suggest that adding a small amount of very high molecular weight polymer could further improve mechanical properties.

### Thermoelasticity

Monte Carlo simulations can also be used to interpret thermoelastic (force-temperature) results generally conducted to estimate the energetic contribution  $f_e$  to the elastic force  $f$ .<sup>8)</sup> This can be done through the relationship  $f_e/f = d \ln \langle r^2 \rangle_0 / dT$ , by carrying out calculations of the unperturbed end-to-end dimensions  $\langle r^2 \rangle_0$  as a function of temperature. An example is the calculation of  $f_e/f$  for the protein elastin,<sup>2)</sup> which showed that the usual random-network model is sufficient to explain its thermoelastic behavior, without the need to postulate more complicated structures.

### Crystallization

There is now considerable interest in using simulations for characterizing crystallization in copolymeric materials. In particular, Windle and coworkers<sup>12)</sup> have developed models capable