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NONIDEAL FORMATION OF NETWORK POLYMERS

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The majority of networks are formed from small monomers, typically with molecular weights less than 500, and often close to 100. In these polymerizations functional groups are close together, and hence may influence one another in a number of ways: groups on the same monomer may not be equally reactive; their reactivity may change as nearest neighbors react; and wasted cycles may form. Conversely network formation may alter the polymerization, for example through phase separation or through a glass transition leading to incomplete conversion.

Network formation from small monomers under such nonideal conditions was the focus of our research, which covered the effects of the following nonidealities: first-shell substitution effect; cyclization instep and chainwise systems; chainwise mechanisms during network formation (free-radical, anionic, and secondary site generation); diffusion; and filler and the interactions of filler with polymer.

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NONIDEAL FORMATION OF NETWORK POLYMERS

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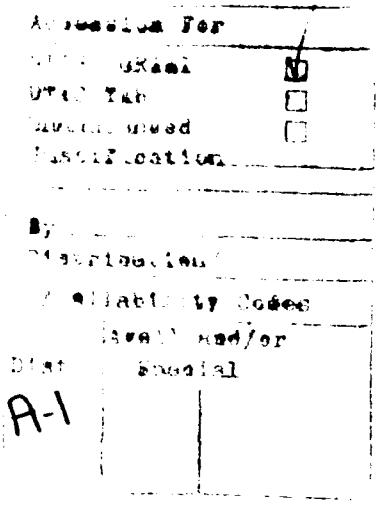

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Part I.

a. Papers submitted to refereed journals:

D.R. Miller, C. Sarmoria, "Calculation of Molecular and Network Parameters of some Branched Stepwise Polymerizations: Introduction and Review with Software."

D.R. Miller, "Branching Process Models and Analyses of Stepwise Homopolymerizations."

D.R. Miller, "Molecular Weight Relations and Network Parameters for Systems of Crosslinked Markovian Polymer Chains."

C. Sarmoria, D.R. Miller, untitled.

A.M. Gupta, C.W. Macosko, "Synthesis and Characterization of Polymers Based on the Cyanate Functional Group."

M.I. Aranguren, E. Mora, J. V. DeGroot, Jr., and C.W. Macosko, "Effect of Particulate Fillers on the Rheology of Polymer Melts" J. Rheol. to appear.

M.I. Aranguren, E. Mora, C.W. Macosko, "Rheology of Filler Rubber: Silica-Silicone."

b. Papers published in refereed journals:

N.A. Dotson, "A Statistical Derivation of the Average Degree of Polymerization in a Stirred Tank Reactor," *Macromolecules*, **22(9)**, 3690-3694 (1989).

D.R. Miller, "Calculation of Network Parameters of Crosslinked Markovian Polymer Chains," *Die Makromolekulare Chemie, Macromolecular Symposia*, **30**, 57-68 (1989).

C. Sarmoria, E.M. Vallés, D.R. Miller, "Validity of Some Approximations Used to Model Intramolecular Reaction in Irreversible Polymerization," *Macromolecules*, **23(2)**, 580-589 (1990) (other support: CONICET, prior to ARO grant).

M.I. Aranguren, C.W. Macosko, B. Thakkar, M. Tirrell, "Interfacial Interactions in Silica Reinforced Silicones," *Mat. Res. Soc. Symp. Proc.* **170**, 303-308 (1990).

A. M. Gupta, C.W. Macosko, "Modeling strategy for systems with both stepwise and chainwise chemistry: Amine-Epoxy Networks with Etherification," *J. of Polymer Sci., Physics Ed.*, **28**, 2585-2606 (1990).

C.W. Macosko, D.R. Miller, "Calculation of average structural properties during nonlinear living copolymerization," *Die Makromolekulare Chemie*, **192**, 377-404 (1991).

C. Sarmoria, D.R. Miller, "Models for First Shell Substitution Effect in Stepwise Polymerization," *Macromolecules*, **24**, 1833-1845 (1991).

A.M. Gupta, "Kinetic Solution for Cyclotrimerization of A_2: Polymers of 2,2-Bis(4-cyanatophenyl)propane," *Macromolecules*, **24**, 3459-3461 (1991).

A.M. Gupta, R.C. Hendrickson, C.W. Macosko, "Monte Carlo Description of A$_f$ Homopolymerization: Diffusional Effects," *J. Chem. Phys.*, **95**(3), 2097-2108 (1991).

c. **Books (and sections thereof) submitted for publication:** none

d. **Books (and sections thereof) published:** none

e. **Technical reports published (including ONR technical reports) and papers published in non-refereed journals:**

ONR reports submitted July 1989 and July 1991:

Technical Report #1: "Calculation of Network Parameters of Crosslinked Markovian Polymers Chains," D.R. Miller. (Paper submitted to *Makromolekular Chemie*, May 1989).

Technical Report #2: "A Statistical Derivation of the Average Degree of Polymerization in a Stirred Tank Reactor," N. Dotson. (Paper submitted to *Macromolecules*, May 1989).

Technical Report #3: "Modeling Strategy for Networks with Both Stepwise and Chainwise Mechanism: Amine-Epoxy Chemistry with Etherification," A.Gupta and C.W. Macosko. (Paper submitted to *Journal of Polymer Science*, May 1989).

Technical Report #4: "Calculation of Average Molecular Properties During Nonlinear, Living Copolymerization," C.W. Macosko, D.R. Miller. (Revised version of a paper submitted to *Die Makromolekulare Chemie*, April 1990).

Technical Report #5: "Effect of Particulate Fillers on the Rheology of Polymer Melts," M.I. Aranguren, E. Mora, J. V. DeGroot, Jr., C.W. Macosko. (Paper submitted to the *Journal of Rheology*, April 1990; other support: Dow Corning, CONICET.)

Technical Report #6: "Rheology of Filler Rubber: Silica-Silicone," M.I. Aranguren, E. Mora, C.W. Macosko. (Paper submitted to *Rubber Chemistry and Technology*; other support: Dow Corning, CONICET.)

Technical Report #7: "Validity of some Approximations Used to Model Intramolecular Reaction in Irreversible Polymerization," C. Sarmoria, E.M. Vallés, D.R. Miller. (Paper which appeared in *Macromolecules*, **23,(2)**, 580-589 (1990); other support: CONICET, prior ARO grant.)

Technical Report #8: "Interfacial Interactions in Silica Reinforced Silicones," M.L. Aranguren, C.W. Macosko, B. Thakkar, M. Tirrell. (Paper which appeared in *Mat. Res. Soc. Symp. Proc.*, **170**, 303-308 (1990).

f. **Patents filed:** none

g. **Patents granted:** none

h. **Invited presentations at topical or society conferences:** none

i. Contributed presentations at topical/technical society conferences:

A.M. Gupta, C.W. Macosko, H.M. Laun, "Effect of Random Long Chain Branching on Rheology of Polybutadiene Chains with Emphasis on Near Gel Systems", presented at SOR, Santa Fe (1990).

Network Polymers Workshop, April 4, 1992, ACS, sponsored by The Division of Polymeric Materials: Science and Engineering.

j. Honors/Awards/Prizes: none

k. Number of graduate students receiving at least 25% support on ONR grant or contract:
Total: 4
Female: 1
Minorities: 1
Asian: 1

l. Number of postdoctoral fellows receiving at least 25% support on ONR grant or contract: one

m. Other funding:

Part II.

a. Principal Investigators:

Christopher W. Macosko
Douglas R. Miller

b. Cognizant ONR scientific officer:

Dr. Joanne Milliken/Dr. Kenneth Wynne

c. Current telephone number:

Macosko: 612-625-6606
Miller: 703-993-1682

d. Brief description of project:

The majority of networks are formed from small monomers, typically with molecular weights less than 500, and often close to 100. In these polymerizations functional groups are close together, and hence may influence one another in a number of ways: groups on the same monomer may not be equally reactive; their reactivity may change as nearest neighbors react; and wasted cycles may form. Conversely network formation may alter the polymerization, for example through phase separation or through a glass transition leading to incomplete conversion.

Network formation from small monomers under such nonideal conditions was the focus of our research, which covered the effects of the following nonidealities: first-shell

substitution effect; cyclization instep and chainwise systems; chainwise mechanisms during network formation (free-radical, anionic, and secondary site generation); diffusion; and filler and the interactions of filler with polymer.

The work built on the basic foundation for structural development in highly crosslinked polymers. Major applications were for composites manufacturing models and sol-gel processing of ceramics as well as for electronics packaging, interpenetrating networks and protective coatings. To aid chemists in handling these problems, we have developed generalized computer programs. (ACS Network Polymers Workshop, April 1992)

e. Significant results during last year:

Manuscripts were completed and submitted on the following work:

1. Statistical solution of Af homopolymerization with substitution effect;
2. Statistical solution of crosslinking free-radical polymerization with substitution effect;
3. Monte Carlo Simulations of Af homopolymerization and the effects of diffusion;
4. Rheology of silica-silicone composites.

The validity of approximations for cyclization in stepwise *non* linear polymerizations were examined.

A.M. Gupta continued his work on cyanate polymerizations, investigating the disagreement between the theoretical and experimental gel points. Monofunctional compounds and the HPLC will be used. Mr. Gupta collaborated with Dr. Arthur Snow of the Naval Research Labs.

N.A. Dotson completed his thesis on nonidealities (especially cyclization and the resulting hetyerogeneities) in crosslinking free-radical polymerization on June 20, 1991. He is currently working on two manuscripts.

f. Brief summary of plans for next year's work:
Not applicable.

g. Graduate students:
Mirta Aranguren
Neil A. Dotson
Anshu M. Gupta

Postdoctoral fellow:
Claudia Sarmoria