



Modeling of the Free Radical Copolymerization Kinetics of Vinyl/Divinyl Monomers in the Presence of NMRP Controllers



Julio C. Hernández-Ortiz¹, Eduardo Vivaldo-Lima¹, Liliane M.F. Lona², Neil T. McManus³, and Alexander Penlidis³

¹Facultad de Química, Departamento de Ingeniería Química, Universidad Nacional Autónoma de México, 04510, México D.F., México, Phone: +(5255)5622-5256, Fax: +(5255)5622-5355, E-mail: vivaldo@unam.mx

²Universidade Estadual de Campinas, Faculdade de Engenharia Química, Departamento de Processos Químicos, CP 6066 CEP: 13083-970, Campinas, São Paulo, Brazil

³Institute for Polymer Research (IPR), Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada

1. INTRODUCTION

Crosslinked polymers (polymer networks) are very important in technology, medicine, biotechnology, agriculture, and other areas. The production of polymer networks by controlled/"living" radical copolymerization (CLRC) techniques has already been addressed in the open literature [1-7], suggesting that polymer networks obtained by this route are less heterogeneous, in comparison with its conventional counterpart.

2. MODELING

Complete Reaction Scheme (considering monoradical and "monocapped" polymer molecules)

Pseudo-kinetic rate constants method

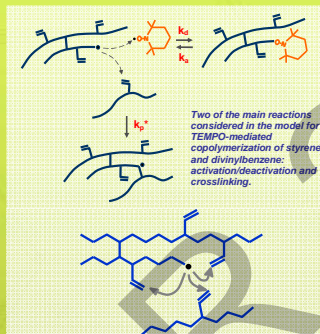
Simplified Reaction Scheme (reduced as a homopolymerization)

Diffusion-controlled effects (free volume theory)

Balance equations

Method of moments (molecular weight development during pre-gel period)

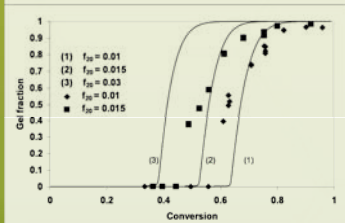
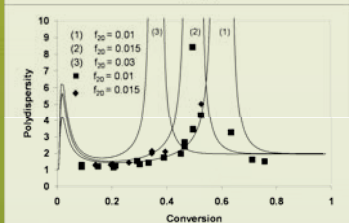
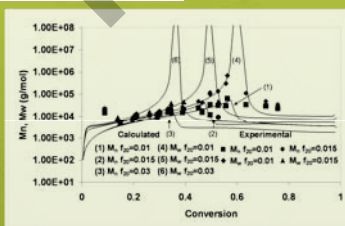
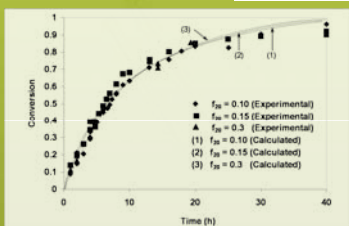
Flory-Stockmayer (molecular weight development during post-gel period and sol fraction)



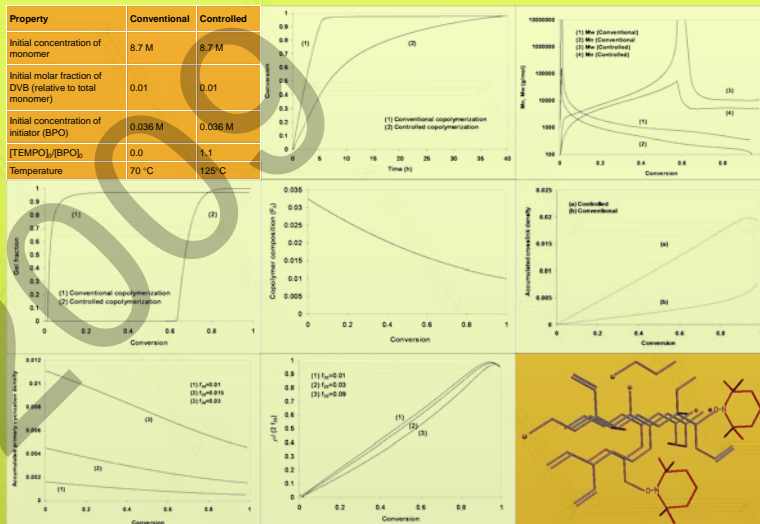
3. RESULTS

3.1. Comparison of model prediction versus experimental data

Copolymerization of STY/DVB controlled by TEMPO ¹	
Initial concentration of monomer	8.7 M
Initial fraction of DVB	0.01, 0.015 or 0.03
Initial concentration of BPO	0.03605 M
[TEMPO] ₀ /[BPO] ₀	1.1
Temperature	120 °C



3.2 Conventional vs controlled copolymerization



4. CONCLUDING REMARKS

- Diffusion-controlled effects are weak, compared with conventional copolymerization.
- Apparent reactivity of the pendant double bonds in V/D NMRP is higher than in conventional free radical copolymerization.
- The presence of an NMRP controller decreases polymerization rate, and delays the gelation point, without any appreciable effect on copolymer composition.
- Crosslink density for the CLRC is higher than that obtained in the conventional case, and it becomes close to its maximum theoretical value of $2f_{2D}$, indicating low cyclization rates.
- CLRC with crosslinking can lead to a more homogeneous polymer network. The homogeneity of the network will decrease as the initial fraction of crosslinker increases.

5. REFERENCES

- N. Ide, T. Fukuda, "Nitroxide-controlled free-radical copolymerization of vinyl and divinyl monomers. Evaluation of pendant-vinyl reactivity" *Macromolecules* **1997**, *30*, 4268-4271.
- N. Ide, T. Fukuda, "Nitroxide-controlled free-radical copolymerization of vinyl and divinyl monomers. 2. Gelation" *Macromolecules* **1999**, *32*, 95-99.
- J. H. Ward, N. A. Peppas, "Kinetic gelation modeling of controlled radical polymerization" *Macromolecules* **2000**, *33*, 5137-5142.
- C. Jiang, Y. Shen, S. Zhu, D. Hunkeler, "Gel formation in atom transfer radical polymerization of 2-(N,N-dimethylamino)ethyl methacrylate and ethylene glycol dimethacrylate" *J. Polym. Sci. Part A, Poly. Chem.* **2001**, *39*, 3780-3788.
- Q. Yu, Y. Zhu, Y. Ding, S. Zhu, "Reaction behavior and network development in RAFT radical polymerization of dimethacrylates" *Macromol. Chem. Phys.* **2008**, *209*, 551-556.
- E. Tuinman, N. T. McManus, M. Roa-Luna, E. Vivaldo-Lima, L. M. F. Lona, A. Penlidis, "TEMPO-controlled free-radical copolymerization kinetics of styrene and divinylbenzene" *J. Macromol. Sci., A: Pure Appl. Chem.* **2006**, *43*, 995-1011.
- J.C. Hernández-Ortiz, E. Vivaldo-Lima, L. M. F. Lona, N. T. McManus, A. Penlidis, "Modeling of the nitroxide-mediated radical copolymerization of styrene and divinylbenzene" *Macromol. React. Eng.* **2009**, *00*, 000. DOI:10.1002/mren.200900007 (in press)