

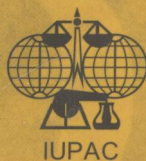
Macromolecular Symposia

J.W. Mays, R.F. Storey (Eds.)

Proceedings of the 2003 International Symposium on Ionic Polymerization and Related Processes



WILEY-VCH



0631.5-53
I64.2
2003

Macromolecular Symposia 215

**Proceedings of the 2003 International
Symposium on Ionic Polymerization
and Related Processes**



Boston, USA

June 30–July 4, 2003

Symposium Editors:

J. W. Mays, R. F. Storey, Knoxville, USA



E200501513

pp. 1–393 · August 2004
ISBN 3-527-31048-7

 **WILEY-VCH**

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 found at <http://www.ms-journal.de>

Suggestions or proposals for conferences or symposia to be covered in this series should also be sent to the Editorial office (E-mail: macro-symp@wiley-vch.de).

Editor: Ingrid Meisel

Senior Associate Editor: Stefan Spiegel

Associate Editor: Alexandra Carrick

Assistant Editors: Sandra Kalveram,
Mara Staffilani

Executive Advisory Board:

M. Antonietti (Göln), M. Ballauff (Bayreuth), S. Kobayashi (Kyoto), K. Kremer (Mainz), T. P. Lodge (Minneapolis), H. E. H. Meijer (Eindhoven), R. Mülhaupt (Freiburg), A. D. Schlüter (Zürich), J. B. P. Soares (Waterloo), H. W. Spiess (Mainz), G. Wegner (Mainz)

Macromolecular Symposia:

Annual subscription rates 2005

Macromolecular Full Package: including Macromolecular Chemistry & Physics (24 issues), Macromolecular Rapid Communications (24), Macromolecular Bioscience (12), Macromolecular Theory & Simulations (9), Macromolecular Materials and Engineering (12), Macromolecular Symposia (14):

Europe Euro 7.088 / 7.797

Switzerland Sfr 12.448 / 13.693

All other areas US\$ 8.898 / 9.788

print only **or** electronic only / print **and** electronic

Postage and handling charges included. All Wiley-VCH prices are exclusive of VAT.

Prices are subject to change.

Single issues and back copies are available. Please ask for details at: service@wiley-vch.de

Orders may be placed through your bookseller or directly at the publishers:

WILEY-VCH Verlag GmbH & Co. KGaA, P.O. Box 10 11 61, 69451 Weinheim, Germany,

Tel. +49 (0) 62 01/6 06-400, Fax +49 (0) 62 01/60 61 84, E-mail: service@wiley-vch.de

For USA and Canada: Macromolecular Symposia (ISSN 1022-1360) is published with 14 volumes per year by WILEY-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003, USA. Application to mail at Periodicals Postage rate is pending at Jamaica, NY 11431, USA. POSTMASTER please send address changes to: Macromolecular Symposia, c/o Wiley-VCH, III River Street, Hoboken, NJ 07030, USA.

Preface

This volume contains key papers presented at the International Symposium on Ionic Polymerization, held in Boston, Massachusetts on June 30–July 4, 2003 under the auspices of the International Union of Pure and Applied Chemistry (IUPAC). This meeting, held at the Tremont Hotel, featured a series of invited and contributed papers and posters, covering the areas of anionic, cationic, and related polymerization processes. The papers dealt with these polymerization systems in the broadest sense, with contributions ranging from new syntheses – to mechanistic studies – to applications. The meeting brought together most of the leading experts in this field, from academia and industry, as well as a significant number of younger scientists and students.

This meeting would not have been possible without the hard work of the chairmen and principal organizers, Professors Rudolf Faust and Roderick P. Quirk. We would like to thank them for organizing an exceptional conference in the very pleasant surroundings of Boston in the middle of summer. They were aided in this task by the Organizing Committee: Drs. J. Crivello, T. Long, J. Mays, J. Puskas, T. Shaffer, and R. Storey. This meeting could also not have taken place without the generous support of various sponsors: IUPAC; American Chemical Society – Polymer Division; The University of Akron; University of Massachusetts, Lowell; National Science Foundation DMR; American Chemical Society – Petroleum Research Fund; Asahi Kasei Corp.; BASF; Bayer Corp.; Boston Scientific Corp.; Bridgestone/Firestone; Chemetall Foote Corp.; Chevron Phillips Chem. Co.; General Electric; Kaneka Corp.; Korea Kumho Petrochemical Co., Ltd.; Kraton Polymers; Sartomer; Synthomer; John Wiley & Sons, Inc.; Wyatt Technology Corp. We are indebted to these organizations for their support.

J. W. Mays

R. F. Storey

Macromolecular Symposia

Articles published on the web will appear several weeks before the print edition. They are available through:



www.ms-journal.de

www.interscience.wiley.com

International Symposium on Ionic Polymerization Boston (USA), 2003

Preface

J. W. Mays, R. F. Storey

Anionic Polymerization

1. A New View of the Anionic Diene Polymerization Mechanism. 1
A. Z. Niu, J. Stellbrink, J. Allgaier, L. Willner, D. Richter,
B. W. Koenig, M. Gondorf, S. Willbold, L. J. Fetters, R. P. May*
2. Aluminate and Magnesiate Complexes as Propagating Species in the
Anionic Polymerization of Styrene and Dienes 17
Alain Deffieux, Larisa Shcheglova, Anna Barabanova,
Jean Marc Maréchal, Stephane Carlotti*
3. Design and Synthesis of Functionalized Styrene-Butadiene Copolymers
by Means of Living Anionic Polymerization. 29
Mayumi Hayashi
4. Synthesis of PS Star Polymers from Tetracarbanionic Initiators. 41
Arnaud Lebreton, J. K. Kallitsis, Valérie Héroguez, Yves Gnanou*
5. Fluorinated Amphiphilic Block Copolymers: Combining Anionic
Polymerization and Selective Polymer Modification 51
Marc A. Hillmyer, Nathan W. Schmuhl, Timothy P. Lodge**
6. Precise Synthesis of Star-Branched Polymers by Means of Living
Anionic Polymerization Using 1,1-Bis(3-chloromethylphenyl)ethylene. . . 57
Akira Hirao, Tomoya Higashihara*
7. Synthesis and Properties of Macrocyclic Vinylaromatic Polymers
Containing a Single 1,4-Benzylidene or 9,10-Anthracenylidene Group . . 67
*Rong Chen, Gennadi G. Nossarev, Thieo E. Hogen-Esch**

8. (Star PS)-*block*-(Linear PI)-*block*-(Star PS) Triblock Copolymers –
Thermoplastic Elastomers with Complex Branched Architectures. 81
*Tianzi Huang, Daniel M. Knauss**
9. Synthesis of Poly(1,3-cyclohexadiene) Containing Star-Shaped
Elastomers. 95
*D. T. Williamson, T. E. Long**
10. Synthesis and Structure – Property Relationships for
Regular Multigraft Copolymers. 111
Jimmy W. Mays, David Uhrig, Samuel Gido, Yuqing Zhu,
Roland Weidisch, Hermis Iatrou, Nikos Hadjichristidis, Kunlun Hong,
Frederick Beyer, Ralf Lach, Matthias Buschnakowski*
11. Triblock and Radial Star-Block Copolymers Comprised of
Poly(ethoxyethyl glycidyl ether), Polyglycidol, Poly(propylene oxide)
and Polystyrene Obtained by Anionic Polymerization Initiated by
Cs Initiators 127
*Ph. Dimitrov, St. Rangelov, A. Dworak, N. Haraguchi, A. Hirao,
Ch. B. Tsvetanov**
12. Mechanism of the Anionic Ring-Opening Oligomerization of
Propylene Carbonate Initiated by the *tert*-Butylphenol/KHCO₃ System. . 141
*Sándor Kéki, János Török, György Deák, Miklós Zsuga**

Cationic Polymerization

13. Synthesis and Self-Association of Stimuli-Responsive Diblock
Copolymers by Living Cationic Polymerization 151
Sadahito Aoshima, Shinji Sugihara, Mitsuhiro Shibayama,
Shokyoku Kanaoka*
14. Advances in the Design of Photoinitiators, Photo-Sensitizers and
Monomers for Photoinitiated Cationic Polymerization 165
J. V. Crivello, J. Ma, F. Jiang, H. Hua, J. Ahn, R. Acosta Ortiz*
15. On the Preparation and Polymerization of *p*-Methoxystyrene
Miniemulsions in the Presence of Excess Ytterbium Triflate. 179
*Séverine Cauvin, François Ganachaud**
16. Carbocationic Polymerizations for Profit and Fun 191
*Ralf M. Peetz, Joseph P. Kennedy**
17. Telechelic Polyisobutenes with Asymmetrical Reactivity 209
Arno Lange, Hans-Peter Rath, Gabriele Lang*
18. Amphiphilic Polymers Based on Poly(2-oxazoline)s –
From ABC-Triblock Copolymers to Micellar Catalysis 215
Oskar Nuyken, Ralf Weberskirch, Martin Bortenschlager,
Daniel Schönfelder*

19. Comparison of the Mechanism and Kinetics of Living Carbocationic Isobutylene and Styrene Polymerizations Based on Real-Time FTIR Monitoring	231
<i>Judit E. Puskas,* Sohel Shaikh</i>	
20. Novel Cationic Ring-Opening Polymerization of Cyclodextrin: A Uniform Macrocyclic Monomer with Unique Character	255
<i>Masato Suzuki,* Osamu Numata, Tomofumi Shimazaki</i>	
21. Wavelength Flexibility in Photoinitiated Cationic Polymerization	267
<i>Yusuf Yagci</i>	

Related Processes

22. Dual Reactivity of Magnesium Compounds as Initiators for Anionic and Cationic Polymerization	281
<i>Alexander Arest-Yakubovich,* Boris Nakhmanovich, Irina Zolotareva, Alexander Yakimansky, Natalia Pakuro</i>	
23. Templating Organosilicate Vitrification Using Unimolecular Self-Organizing Polymers Prepared from Tandem Ring Opening and Atom Transfer Radical Polymerizations	295
<i>T. Magbitang, V. Y. Lee, E. F. Connor, L. K. Sundberg, H.-C. Kim, W. Volksen, C. J. Hawker, R. D. Miller,* J. L. Hedrick*</i>	
24. Ring-Opening Polymerization of the Cyclic Ester Amide Derived from Adipic Anhydride and 1-Amino-6-hexanol in Melt and in Solution.	307
<i>Thomas Fey, Helmut Keul, Hartwig Höcker*</i>	
25. Recent Developments in the Ring-Opening Polymerization of ϵ -Caprolactone and Derivatives Initiated by Tin(IV) Alkoxides	325
<i>Ph. Lecomte, F. Stassin, R. Jérôme*</i>	
26. Functionalization of Living Polymers via Ethoxysilane Based Compounds: Synthesis and Interaction with Silica Particles	339
<i>Joël Hoffstetter, Ellen Giebeler, Rolf Peter, Pierre J. Lutz*</i>	
27. Reactivities of Carbocations and Carbanions	353
<i>Armin R. Ofial, Herbert Mayr*</i>	
28. Confinement Effects on the Crystallization Kinetics and Self-Nucleation of Double Crystalline Poly(p-dioxanone)- <i>b</i> -poly(ϵ -caprolactone) Diblock Copolymers	369
<i>Alejandro J. Müller,* Julio Albuérne, Luis M. Esteves, Leni Marquez, Jean-Marie Raquez, Philippe Degée, Philippe Dubois, Stephen Collins, Ian W. Hamley</i>	
29. Advances in the Synthesis and Characterization of Polypeptide-Based Hybrid Block Copolymers.	383
<i>Ivaylo Dimitrov, Hildegard Kukula, Helmut Cölfen, Helmut Schlaad*</i>	

Author Index

Acosta Ortiz, R.	165	Höcker, Hartwig	307
Ahn, J.	165	Hoffstetter, Joël	339
Albuérne, Julio	369	Hogen-Esch, Thieo E.	67
Allgaier, J.	1	Hong, Kunlun	111
Aoshima, Sadahito	151	Hua, H.	165
Arest-Yakubovich, Alexander	281	Huang, Tianzi	81
Barabanova, Anna	17	Iatrou, Hermis	111
Beyer, Frederick	111	Jérôme, R.	325
Bortenschlager, Martin	215	Jiang, F.	165
Buschnakowski, Matthias	111	Kallitsis, J. K.	41
Carlotti, Stephane	17	Kanaoka, Shokyoku	151
Cauvin, Séverine	179	Kéki, Sándor	141
Chen, Rong	67	Kennedy, Joseph P.	191
Cölfen, Helmut	383	Keul, Helmut	307
Collins, Stephen	369	Kim, H.-C.	295
Connor, E. F.	295	Knauss, Daniel M.	81
Crivello, J. V.	165	Koenig, B. W.	1
Deák, György	141	Kukula, Hildegard	383
Deffieux, Alain	17	Lach, Ralf	111
Degée, Philippe	369	Lang, Gabriele	209
Dimitrov, Ivaylo	383	Lange, Arno	209
Dimitrov, Ph.	127	Lebreton, Arnaud	41
Dubois, Philippe	369	Lecomte, Ph.	325
Dworak, A.	127	Lee, V. Y.	295
Esteves, Luis M.	369	Lodge, Timothy P.	51
Fetters, L. J.	1	Long, T. E.	95
Fey, Thomas	307	Lutz, Pierre J.	339
Ganachaud, François	179	Ma, J.	165
Gido, Samuel	111	Magbitang, T.	295
Giebeler, Ellen	339	Maréchal, Jean Marc	17
Gnanou, Yves	41	Marquez, Leni	369
Gondorf, M.	1	May, R. P.	1
Hadjichristidis, Nikos	111	Mayr, Herbert	353
Hamley, Ian W.	369	Mays, Jimmy W.	111
Haraguchi, N.	127	Miller, R. D.	295
Hawker, C. J.	295	Müller, Alejandro J.	369
Hayashi, Mayumi	29	Nakhmanovich, Boris	281
Hedrick, J. L.	295	Niu, A. Z.	1
Héroguez, Valérie	41	Nossarev, Gennadi G.	67
Higashihara, Tomoya	57	Numata, Osamu	255
Hillmyer, Marc A.	51	Nuyken, Oskar	215
Hirao, Akira	57, 127	Ofial, Armin R.	353

Pakuro, Natalia	281
Peetz, Ralf M.	191
Peter, Rolf	339
Puskas, Judit E.	231
Rangelov, St.	127
Raquez, Jean-Marie	369
Rath, Hans-Peter	209
Richter, D.	1
Schlaad, Helmut	383
Schmuhl, Nathan W.	51
Schönfelder, Daniel	215
Shaikh, Sohel	231
Shcheglova, Larisa	17
Shibayama, Mitsuhiro	151
Shimazaki, Tomofumi	255
Stassin, F.	325
Stellbrink, J.	1

Sugihara, Shinji	151
Sundberg, L. K.	295
Suzuki, Masato	255
Török, János	141
Tsvetanov, Ch. B.	127
Uhrig, David	111
Volksen, W.	295
Weberskirch, Ralf	215
Weidisch, Roland	111
Willbold, S.	1
Williamson, D. T.	95
Willner, L.	1
Yagci, Yusuf	267
Yakimansky, Alexander	281
Zhu, Yuqing	111
Zolotareva, Irina	281
Zsuga, Miklós	141

A New View of the Anionic Diene Polymerization Mechanism

A. Z. Niu,¹ J. Stellbrink,¹ J. Allgaier,*¹ L. Willner,¹ D. Richter,¹ B. W. Koenig,² M. Gondorf,³ S. Willbold,³ L. J. Fetters,⁴ R. P. May⁵

¹ IFF, FZ Jülich GmbH, 52425 Jülich, Germany

² IBI 2, FZ Jülich GmbH, 52425 Jülich and Institut für Physikalische Biologie, Heinrich-Heine-Univ., 40225 Düsseldorf, Germany

³ ZCH, FZ Jülich GmbH, 52425 Jülich, Germany

⁴ School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853-5201, USA

⁵ Institute Laue-Langevin, 38042 Grenoble, Cedex 9, France

Summary: We investigated the anionic polymerization of butadiene in d-heptane solvent using *tert*-butyl lithium as initiator. Two complementary techniques were used to follow the polymerization processes: ¹H NMR and small angle neutron scattering (SANS). The time resolved ¹H NMR measurements allowed us to evaluate quantitatively the kinetics of the processes involved. The initiation event commences slowly and then progressively accelerates. This indicates an autocatalytic mechanism. The microstructure of the first monomer units attached is to a high extent 1,2. The disappearance of initiator---at about 10% monomer conversion---signals the onset of the normal ~6% vinyl content of the chain. Small angle neutron scattering was used to study the aggregation behavior of the carbon lithium head groups. It is well known that the polar head groups aggregate and form micellar structures. For dienes in non-polar solvents the textbook mechanism assumes the formation of only tetramers during the propagation reaction. By combining ¹H NMR and SANS results we were able to determine quantitatively the aggregation number during all stages of the polymerization. Our measurements show the existence of large-scale structures during the initiation period. The initial degree of aggregation of more than 100 living polymer chains diminished as the polymerization progressed. In addition, even larger, giant structures with $N_{agg} \gg 1000$ and $R_g \approx 1000 \text{ \AA}$ were found.

Keywords: anionic polymerization; kinetics; neutron scattering; NMR; polybutadiene

Introduction

Organolithium compounds self-associate in organic solvents. The aggregation state depends on the solvent and the structure of the compound. It influences significantly the reactivity of organolithium reagents. In hydrocarbon solvents *sec*- and *tert*-butyl lithium form tetramers

whereas *n*-butyl lithium aggregates as hexamers.^[1,2] This behavior strongly influences the kinetics of the initiation reaction. The methods used in the past to follow the initiation kinetics were mainly UV spectroscopy^[3-5] and to some extent gas chromatographic analysis of the hydrolyzed samples taken at different times.^[6] It was found that the initiation kinetics of the butyl lithium isomers with styrene and diene monomers are complex. It is first order on monomer concentration and of fractional order in initiator concentration:

$$-d[I]/dt = k_i[\text{BuLi}]^{1/n}[\text{M}] \quad (1)$$

Depending on initiator, *n* was found to vary between 4 and 6 in benzene and was correlated with the aggregation state of the butyl lithium initiator. It was assumed that there is an equilibrium between the aggregates and the unassociated molecules, the latter ones being the only species initiating the polymerization.^[3] Most likely the initiation process is more complex and cross-associated species formed by the reaction of monomer with butyl lithium aggregates could be directly involved.^[7,8] In analogy to the short chain initiators, the living polymer chains associate due to aggregation of the carbon lithium active centers was a point of controversy. In earlier studies, the association state of diene based head-groups were a point of controversy.^[7-12] Dimers and tetramers were proposed as the association states for completely polymerized systems. The living polymer systems were investigated by concentrated solution viscosity measurements and light scattering.^[7-12] Recent publications where small angle neutron scattering (SANS) was used reveal that the aggregation behavior is more complex. All told, the diene based systems can show (depending on the conditions) association degrees ranging from 2 to >100.^[13-16]

In this work we analyze the polymerization of butadiene initiated with *tert*-butyl lithium in *n*-heptane using a combined *in situ* technique of ¹H NMR and SANS. ¹H NMR allows the simultaneous analysis of the initiation and chain propagation processes. Together, with the SANS results, it was possible to obtain a more detailed picture of the structures involved in the different processes.

Experimental

Solvent and monomer purification techniques have been described.^[1,13-16] The polymerization reactions were carried out at 8°C in sealed ¹H NMR tubes and SANS quartz cells (Fig. 1). The apparatus equipped with Young[®] stopcocks was flamed under high vacuum conditions and

transferred into the glove box (MBraun, Unilab[®], <0.1 ppm O₂ and <0.1 ppm H₂O). There the initiator solution was filled into the small reactors with a microliter syringe. The Young[®] stopcocks allowed transfer of the reactors from the glove-box to the vacuum line without contamination with air. Butadiene and d-heptane were distilled from *n*-butyl lithium solutions into small flasks equipped with Young[®] stopcocks. This allowed the weights to be precisely measured with an analytical balance. Monomer and solvent were then distilled into the reactors quantitatively and the reactors then flame sealed at liquid nitrogen temperature. This was done for the SANS cells by first filling the ingredients into the container below the stopcock (see Fig. 1). After sealing from the vacuum line the contents were warmed to dry ice temperature, poured into the SANS cell and the cell sealed off at -78°C. This procedure was necessary to prevent the cells from cracking during the warm up procedure, of the frozen content, from liquid nitrogen temperature. These procedures allowed precise assay of monomer (10-20 mg) and initiator quantities in the sub μ mol range. The monomer concentration was 0.73 mol/L for the ¹H -NMR samples and 0.69 mol/L for the SANS samples, the initiator concentration was 8.5×10^{-4} mol/L in all samples.

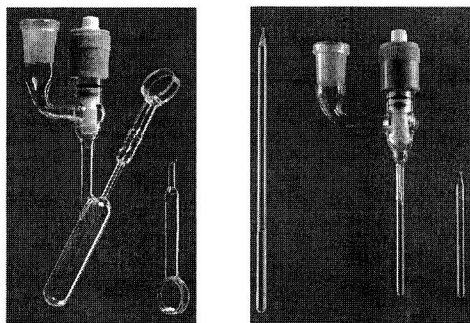


Figure 1. SANS and NMR glassware for the in situ polymerization reactions.

Polymerization reactions were carried out by warming up the samples from liquid nitrogen temperature or dry ice temperature to 8°C within 1 to 3 minutes and keeping the temperature at $8^\circ\text{C} \pm 0.7^\circ\text{C}$ for at least two weeks monitoring the polymerization reaction by ¹H NMR and SANS. Then the reactors were opened in the glove-box and terminated with degassed methanol. The solutions were filtered, the solvents evaporated and the polymers dried. The samples were

characterized via on-line GPC/light scattering in THF at 30°C. For ^1H NMR measurements the reaction mixtures were flame sealed in 4 mm outer diameter ^1H NMR tubes (Wilmad, Buena Vista, USA). For measurements in a 5 mm probe the sealed samples were placed into Wilmad 5 mm outer diameter ^1H NMR tubes.

Proton NMR spectra were recorded at a Larmor-Frequency of 600.14 MHz on a Bruker DMX600 using a 5 mm TXI probe optimized for proton observation. The free induction decay was recorded immediately after a non-selective 90° -pulse (7 μs) with a dwell time of 111 μs and 32k data points in the time domain. Four transients were added for each spectrum using the CYCLOPS phase cycle to avoid artifacts from quadrature detection. A long pre-scan delay of 300 sec was found to be necessary to ensure complete T_1 -relaxation of all signals (strict requirement for quantitative interpretation of integral peak intensity). An exponential window function was applied prior to Fourier transformation and integration of the frequency domain signals.

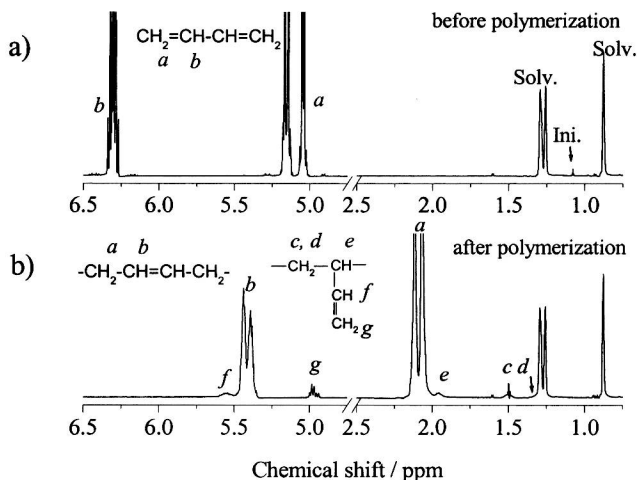


Figure 2. NMR traces of before and after polymerization.

Figures 2a and 2b show typical ^1H NMR spectra recorded before and after polymerization, respectively. Signal intensities at different reaction times were compared quantitatively via comparison with the residual proton signal of the solvent n-heptane signal at 0.88 ppm. The molarity of the solvent protons does not change during the polymerization in a sealed sample

tube. The fraction of reacted *tert*-butyl lithium at time t was calculated from the signal intensities at 1.07 ppm of the initial spectrum ($I_{1.07\text{ppm},t=0}$) and the spectrum at time t ($I_{1.07\text{ppm},t}$). Conversion as a function of time, $\text{Con.}(t)$, was calculated from the intensities of the monomer signal at ~ 6.3 ppm ($I_{6.3\text{ppm},t}$) and the polymer signals at ~ 2.1 ppm ($I_{2.1\text{ppm},t}$, 1,4 structure) and ~ 1.5 ppm ($I_{1.5\text{ppm},t}$, 1,2 structure) at time t , e.g.:

$$\text{Con.}(t) = [P(t)] / ([M(t)] + [P(t)]) = (I_{2.1\text{ppm},t}/4 + I_{1.5\text{ppm},t}) / (I_{6.3\text{ppm},t}/2 + I_{2.1\text{ppm},t}/4 + I_{1.5\text{ppm},t}). \quad (2)$$

Here, $[P(t)]$ is the polymer repeat unit concentration at time t and $[M(t)]$ is monomer concentration at time t . The polymerization degree $D_p(t)$ was calculated from the signal intensities of the polymer signals at ~ 2.1 ppm and ~ 1.5 ppm and the initiator signals at 1.07 ppm as

$$D_p(t) = [P(t)] / ([\text{Ini}(t=0)] - [\text{Ini}(t)]) = (I_{2.1\text{ppm}}/4 + I_{1.5\text{ppm}}) / ((I_{1.07\text{ppm},t=0} - I_{1.07\text{ppm},t})/9) \quad (3)$$

Here, $[\text{Ini}(t)]$ is the initiator concentration at time t and $[\text{Ini}(t=0)]$ is initial initiator concentration. Microstructures were calculated from the signal intensities of the polymer signals at ~ 2.1 ppm and ~ 1.5 ppm. In all cases the number of protons correlated with the different signals was taken into account.

SANS measurements were performed initially on the KWS2 at FZ Jülich (Germany). These were followed by a series of measurements on D22 at ILL, Grenoble (France). In general, the scattering

cross section $\frac{d\Sigma}{d\Omega}$ observed in a SANS experiment from polymers in dilute solution is given by:

$$\frac{d\Sigma}{d\Omega} = \frac{\Delta\rho^2}{N_a} \left[\frac{\phi(1-\phi)}{\frac{1}{V_w P(Q)} + 2A_2\Phi} \right] \quad (4)$$

Here, polymer concentration is given in terms of ϕ which denotes the polymer volume fraction, $P(Q)$ is the form factor of the polymer or the polymer aggregates, V_w the corresponding weight average molecular volume, A_2 the second virial coefficient, and N_a the Avogadro number. $\Delta\rho$ is the scattering contrast defined by:

$$\Delta\rho = \left[\frac{\Sigma b_s}{v_s} - \frac{\Sigma b_{mon}}{v_{mon}} \right] \quad (5)$$

The ratio $\Sigma b_s / v_s$ is the scattering length density of the solvent with b_s the scattering lengths of the

atoms forming the solvent molecule and v_s the corresponding volume. $\Sigma b_{mon}/v_{mon}$ is the corresponding quantity for the repeat unit. To achieve maximum contrast and minimum incoherent background resulting from protonated material, we investigated h-butadiene in d-heptane ($\rho_{h\text{-butadiene}}=4.12\times10^{-9}\text{cm}^{-2}$, $\rho_{d\text{-heptane}}=6.26\times10^{-10}\text{cm}^{-2}$, $\Delta\rho=5.85\times10^{-10}\text{cm}^{-2}$). Because all b_i are well defined and tabulated properties of the corresponding nucleus solely, SANS data obtained on an absolute scale can be interpreted quantitatively without any ambiguity. There is no need to determine a contrast parameter experimentally as a function of M_w (such as the (dn/dc) used in light scattering experiments).

In general all azimuthally averaged data were corrected for empty cell scattering and then normalized to absolute scattering cross section using a water standard. Contributions due to incoherent background and solvent scattering were subtracted from all data sets before analysis. A useful presentation of the theory and practice of SANS is available from Higgins and Benoit.^[18] All experiments were performed at 8°C in order to slow the propagation event. This enables us to obtain time resolved data with good statistics including those at low scattering vectors encountered in the initiation period. This is not trivial since we are starting at $t = 0$ with a monomer solution where scattering intensity is only slightly above that of the solvent.

Combined in situ ^1H NMR and SANS Technique

In our study on anionic polymerization, we choose a combination of ^1H NMR and small angle neutron scattering (SANS). Using time resolved ^1H NMR we obtain quantitative information concerning initiator, monomer, and polymer concentration and polymerisation degree of the single chains as a function of time and conversion ($[\text{Ini}(t)]$, $[\text{M}(t)]$, $[\text{P}(t)]$ and $D_p(t)$), but also structural information on a microscopic level, e.g. the 1,2-to-1,4 ratio. Time resolved SANS on the other hand provides us structural information on a mesoscopic and microscopic length scale, e.g. $R_g(t)$ ^[19] of intermediate aggregates, and quantitative information concerning their M_w . This enables us to cross check kinetics as well as structural data, which makes this combination of experimental techniques especially appealing.

The crucial parameter in a SANS experiment, which determines the spatial resolution, is the scattering vector Q , given by $4\pi\lambda^{-1} \sin(\theta/2)$, with θ the scattering angle and λ the neutron wavelength. Q has the dimensions of a reciprocal length and can therefore be regarded as an

“inverse yard stick”. For SANS experiments typically performed with different settings, i.e. different sample-to-detector distances and collimation lengths, a Q -range of nearly 2.5 orders of magnitude can be achieved, $1 \times 10^{-3} \leq Q \leq 0.2 \text{ \AA}^{-1}$. This corresponds to a spatial resolution $5 \text{ \AA} \leq D = 1/Q \leq 1000 \text{ \AA}$. Assuming that the growing chains form only star-like aggregates with a mean functionality N_{agg} , ($N_{agg} = 4$ is predicted by the textbook reaction mechanism), we can derive a quantitative relation for the scattering intensity $I(Q, t)$ observed in a SANS experiment. The scattering intensity as a function of reaction time t and scattering vector Q is then given by:

$$I(Q, t) = \left(\frac{d\Sigma}{d\Omega} \right) / \left(\frac{\Delta\rho^2}{N_a} \right) = \phi_p(t) \cdot N_{agg}(t) \cdot V_w(t) \cdot P_{star}(Q, t) \quad (6)$$

Here $P_{star}(Q, t)$ is the form factor of a Gaussian star polymer as given by Benoit^[20], which is the only Q -dependent variable in Eq. (6). For simplicity we have neglected the concentration dependence (the second virial coefficient) of $I(Q, t)$. The expected evolution of the scattering intensity calculated $I(Q, t)$ for different conversion between 1% and 100% is illustrated in Fig. 3. One clearly recognises how well suited the chosen SANS setup with respect to Q -resolution is to cover the full polymerization event.

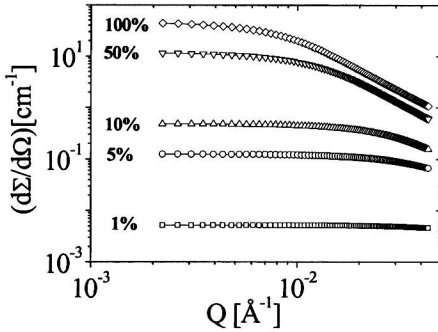


Figure 3. Expected evolution of the SANS scattering pattern with conversion assuming a time independent aggregation state of $N_{agg} = 4$.

In a previous publication,^[16] we have shown that all time dependent quantities in Eq. (6) can be reduced to only one parameter, i.e. the number density of reacted monomers $N_p(t)$, which can therefore be calculated from the observed forward scattering $I(Q = 0, t)$. However, this is only valid under two conditions: (1). the number of living chains is time independent and equal to the initiator concentration, i.e. the initiation period has already passed, and (2). all reacted monomers participate in the same type of aggregates with time independent aggregation number. In this case

SANS data alone already give direct access to the reaction kinetics. If we want to extend our studies to the initiation period or if the investigated monomer forms different types of aggregates, we need additional quantitative information to unambiguously interpret our SANS data. The needed information can be independently obtained from time resolved ^1H NMR experiments, which gives us directly $[\text{Ini}(t)]$, $[\text{M}(t)]$, and $[\text{P}(t)]$, from which we further can calculate $D_p(t)$ and $M_n(t)$. If we now use these data to analyse our SANS data, we can directly access the aggregation number as a function of time for all phases of the polymerization.

^1H NMR Measurements

Careful optimization of experimental conditions was crucial for quantitative interpretation of the ^1H NMR spectra. The design of the NMR sample cell, the filling factor of the sealed NMR tube, and the length of the relaxation period required between subsequent scans were found to be critical. ^1H NMR spectra were recorded during a first preliminary polymerization attempt with a pre-scan delay of 4 seconds, which turned out to be much too short for complete T_1 relaxation. As a result of this incorrect delay, the overall intensity of the polymer peaks after completion of the polymerization was three times higher than the overall intensity of the monomer peaks of the same sample at the beginning of the reaction. The T_1 relaxation times of the monomer peaks were determined to be (40 ± 5) sec at 8°C . Spin-lattice relaxation times are significantly shorter for the polymer peaks and decreased with the length of the polymer chain as expected for rapidly tumbling molecules in solution. The most likely explanation for the rather long T_1 values of the solute is solvent deuteration. Nuclear dipole-dipole interaction is a very important relaxation mechanism for protons and the interaction with other nearby protons is particularly efficient due to the extraordinary high gyromagnetic ratio, γ , of protons. Replacing solvent protons with low γ deuterons will increase T_1 of the solute. Paramagnetic impurities, e.g. molecular oxygen, provide another efficient source of T_1 relaxation. However, during the experiments reported here trace amounts of oxygen were carefully removed from the samples to avoid unwanted side reactions. For the quantitative NMR experiments reported in this manuscript a pre-scan delay of 300 sec was used. Further increase of the delay to 1,000 sec did not change the integral intensity of any relevant peak in the spectrum by more than 1%.