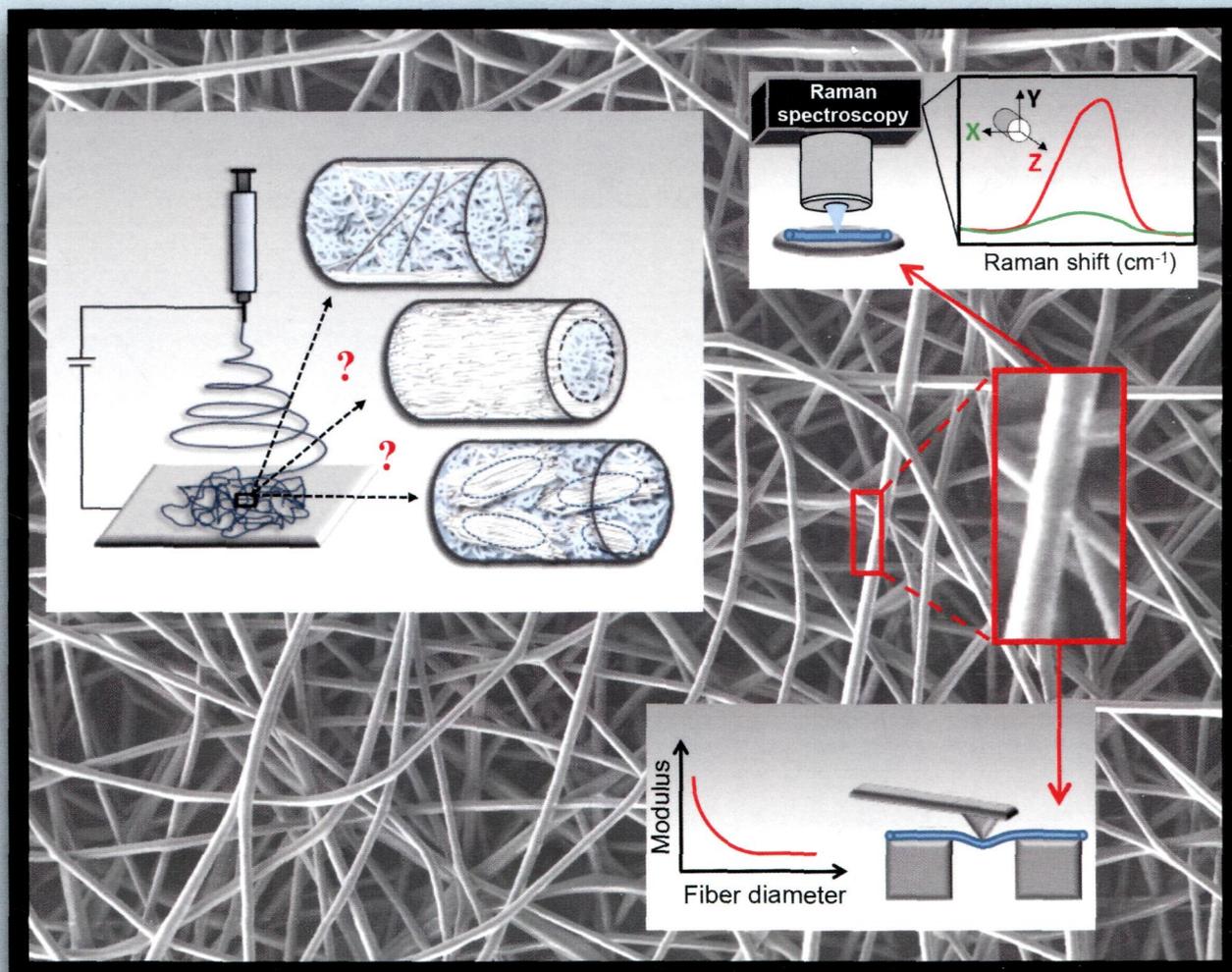


# Macromolecules

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# Macromolecules

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**ON THE COVER: Molecular Orientation in Electrospun Fibers: From Mats to Single Fibers.** Electrospinning is widely used to prepare polymer nanofibers. Single fiber AFM studies have recently transformed our vision of electrospun fibers by revealing an exponential increase of their mechanical properties with decreasing diameter. Several models suggest that molecular orientation is critical in controlling these and other properties. A main challenge is thus to characterize the structure of individual fibers, a difficult task due to their intrinsically small size. Single fiber techniques, such as Raman spectroscopy, help uncover the structural origin of the intriguing properties of electrospun fibers. See page 9473.

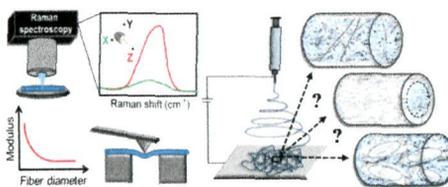
## Perspective

9473

[dx.doi.org/10.1021/ma401681m](https://doi.org/10.1021/ma401681m)

### Molecular Orientation in Electrospun Fibers: From Mats to Single Fibers

Marie Richard-Lacroix and Christian Pellerin\*



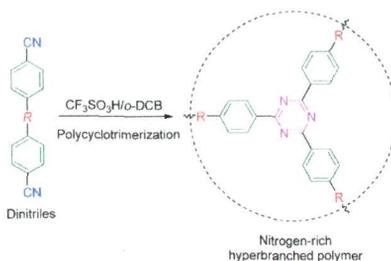
## Articles

9494

[dx.doi.org/10.1021/ma402066k](https://doi.org/10.1021/ma402066k)

### Polycyclotrimerization of Dinitriles: A New Polymerization Route for the Construction of Soluble Nitrogen-Rich Polytriazines with Hyperbranched Structures and Functional Properties

Carrie Y. K. Chan, Jacky W. Y. Lam, Cathy K. W. Jim, Herman H. Y. Sung, Ian D. Williams, and Ben Zhong Tang\*

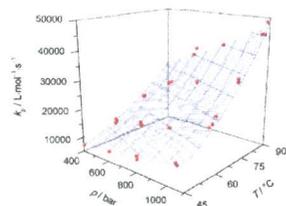


9507

## Propagation Rate Coefficients for Vinylidene Fluoride Homopolymerizations

Rebekka Siegmann, Marco Drache, and Sabine Beuermann\*

dx.doi.org/10.1021/ma401830a



9515

## Postelectrospinning "Click" Modification of Degradable Amino Acid-Based Poly(ester urea) Nanofibers

Fei Lin, Jiayi Yu, Wen Tang, Jukuan Zheng, Sibai Xie, and Matthew L. Becker\*

dx.doi.org/10.1021/ma401964e

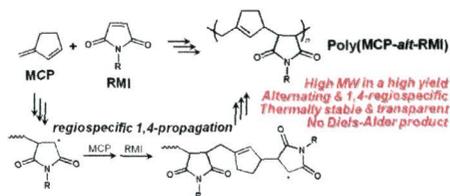


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## Controlled Radical Polymerization of 3-Methylenecyclopentene with N-Substituted Maleimides To Yield Highly Alternating and Regiospecific Copolymers

Daisuke Yamamoto and Akikazu Matsumoto\*

dx.doi.org/10.1021/ma4020092

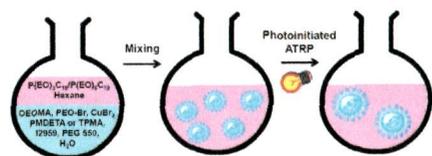


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## Photoinitiated ATRP in Inverse Microemulsion

Mustafa Ciftci, Mehmet Atilla Tasdelen, Wenwen Li, Krzysztof Matyjaszewski, and Yusuf Yagci\*

dx.doi.org/10.1021/ma402058a



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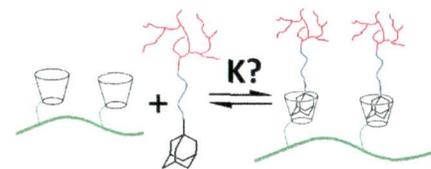
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9544

## Supramolecular Linear-g-Hyperbranched Graft Polymers: Topology and Binding Strength of Hyperbranched Side Chains

Christian Moers, Lutz Nuhn, Marcel Wissel, René Stangenberg, Mihail Mondeshki, Elena Berger-Nicoletti, Anja Thomas, David Schaeffel, Kaloian Koynov, Markus Klapper, Rudolf Zentel, and Holger Frey\*

dx.doi.org/10.1021/ma402081h

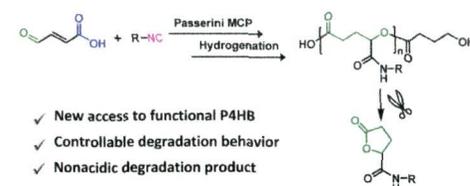


9554

## Chemical Synthesis of Functional Poly(4-hydroxybutyrate) with Controlled Degradation via Intramolecular Cyclization

Li-Jing Zhang, Xin-Xing Deng, Fu-Sheng Du, and Zi-Chen Li\*

dx.doi.org/10.1021/ma402191r

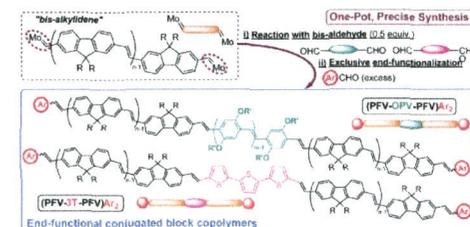


9563

## Precise One-Pot Synthesis of End-Functionalized Conjugated Multi-Block Copolymers via Combined Olefin Metathesis and Wittig-type Coupling

Kotohiro Nomura,\* Tahmina Haque, Taira Onuma, Fatin Hajjaj, Motoko S. Asano, and Akiko Inagaki

dx.doi.org/10.1021/ma4022554



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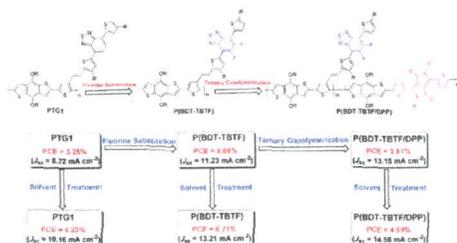
9575

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dx.doi.org/10.1021/ma401886a

### Enhancing Photovoltaic Performance of Copolymers Containing Thiophene Unit with D–A Conjugated Side Chain by Rational Molecular Design

Ping Shen, Haijun Bin, Lu Xiao, and Yongfang Li\*



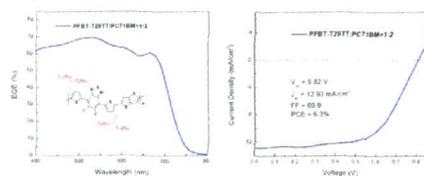
9587

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dx.doi.org/10.1021/ma401709r

### Substituent Effects on Physical and Photovoltaic Properties of 5,6-Difluorobenzo[c][1,2,5]thiadiazole-Based D–A Polymers: Toward a Donor Design for High Performance Polymer Solar Cells

Yan Wang, Xin Xin, Yong Lu, Ting Xiao, Xiaofeng Xu, Ni Zhao, Xiao Hu,\* Beng S. Ong,\* and Siu Choon Ng\*



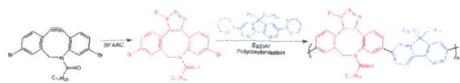
9593

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dx.doi.org/10.1021/ma4021467

### Synthesis of Conjugated Polymers Containing DIBAC-Derived Triazole Monomers

Ryan C. Chadwick, Vladimir Kardelis, Sophie Liogier, and Alex Adronov\*



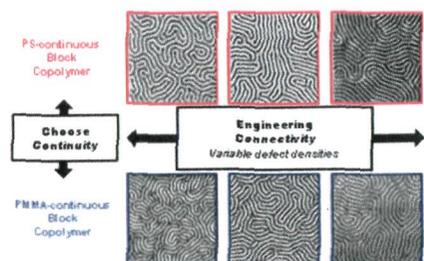
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dx.doi.org/10.1021/ma401704m

### Processing Approaches for the Defect Engineering of Lamellar-Forming Block Copolymers in Thin Films

Ian P. Campbell, Soichi Hirokawa, and Mark P. Stoykovich\*



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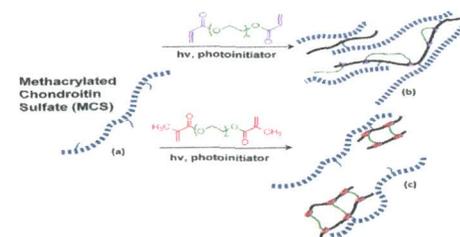
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9609

dx.doi.org/10.1021/ma401838h

### Increasing Cross-Linking Efficiency of Methacrylated Chondroitin Sulfate Hydrogels by Copolymerization with Oligo(Ethylene Glycol) Diacrylates

Anahita Khanlari, Michael S. Detamore, and Stevin H. Gehrke\*



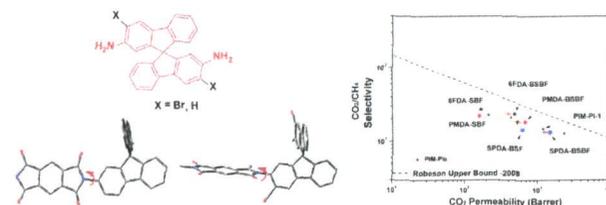
9618

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dx.doi.org/10.1021/ma402033z

### Novel Spirofluorene- and Dibromospirofluorene-Based Polyimides of Intrinsic Microporosity for Gas Separation Applications

Xiaohua Ma, Octavio Salinas, Eric Litwiller, and Ingo Pinnau\*



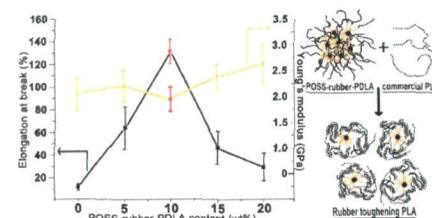
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dx.doi.org/10.1021/ma4020615

### Biodegradable “Core–Shell” Rubber Nanoparticles and Their Toughening of Poly(lactides)

Yang Sun and Chaobin He\*



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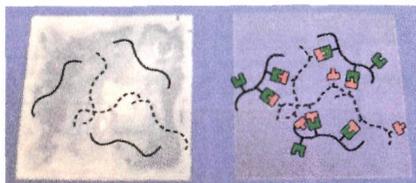
9634

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dx.doi.org/10.1021/ma402069b

## Side-Chain Supramolecular Polymers Employing Conformer Independent Triple Hydrogen Bonding Arrays

Adam Gooch, Natasha S. Murphy, Neil H. Thomson, and Andrew J. Wilson\*



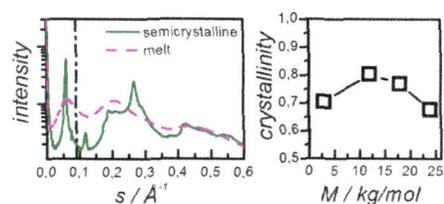
9642

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dx.doi.org/10.1021/ma401946w

## Determination of the Crystallinity of Semicrystalline Poly(3-hexylthiophene) by Means of Wide-Angle X-ray Scattering

Jens Balko, Ruth H. Lohwasser, Michael Sommer, Mukundan Thelakkat, and Thomas Thurn-Albrecht\*



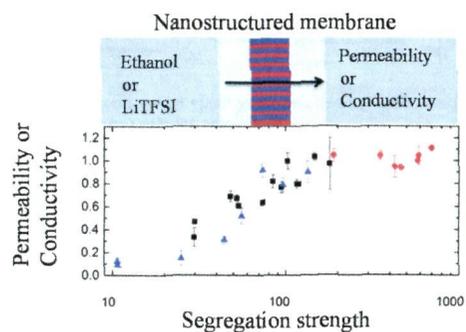
9652

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dx.doi.org/10.1021/ma401957s

## Relationship between Segregation Strength and Permeability of Ethanol/Water Mixtures through Block Copolymer Membranes

A. Evren Ozcam, Nikos Petzetakis, Skyler Silverman, Ashish K. Jha, and Nitash P. Balsara\*



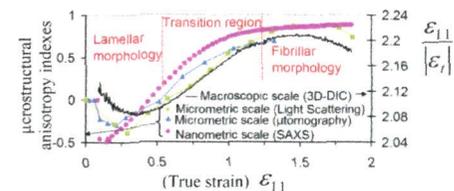
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## A Common Multiscale Feature of the Deformation Mechanisms of a Semicrystalline Polymer

L. Farge,\* S. André,\* F. Meneau, J. Dillet, and C. Cunat



dx.doi.org/10.1021/ma4019747

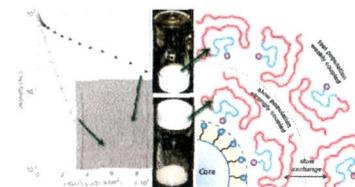
9669

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dx.doi.org/10.1021/ma402002a

## Hierarchical Canopy Dynamics of Electrolyte-Doped Nanoscale Ionic Materials

Michael L. Jespersen, Peter A. Mirau,\* Ernst D. von Meerwall, Hilmar Koerner, Richard A. Vaia, Nikhil J. Fernandes, and Emmanuel P. Giannelis



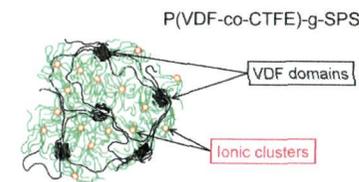
9676

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dx.doi.org/10.1021/ma402008b

## Controlling Water Content and Proton Conductivity through Copolymer Morphology

Rasoul Narimani, Ami C. C. Yang, Emily M. W. Tsang, Laurent Rubatat, Steven Holdcroft, and Barbara J. Frisken\*



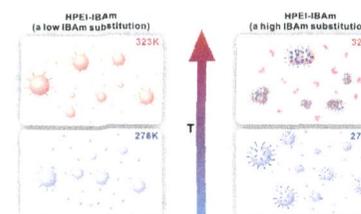
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dx.doi.org/10.1021/ma402095w

## NMR Study of Thermoresponsive Hyperbranched Polymer in Aqueous Solution with Implication on the Phase Transition

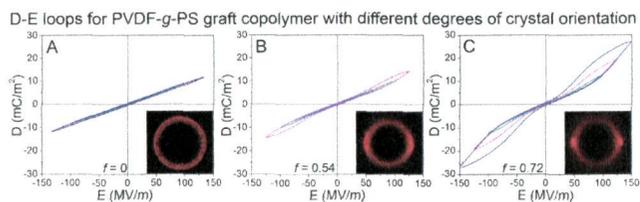
Songzi Jiang, Yefeng Yao,\* Qun Chen, and Yu Chen\*



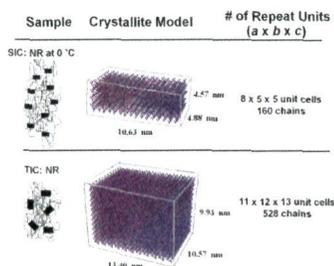
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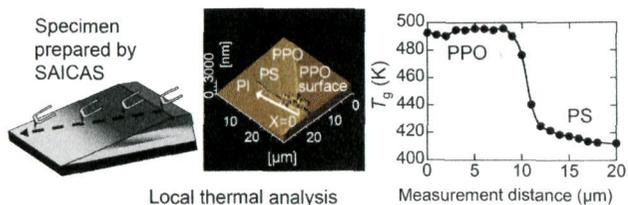
9698 **S** dx.doi.org/10.1021/ma401660k  
**Crystal Orientation and Temperature Effects on Double Hysteresis Loop Behavior in a Poly(vinylidene fluoride-co-trifluoroethylene-co-chlorotrifluoroethylene)-graft-Polystyrene Graft Copolymer**  
 Lianyun Yang, Elshad Allahyarov, Fangxiao Guan, and Lei Zhu\*



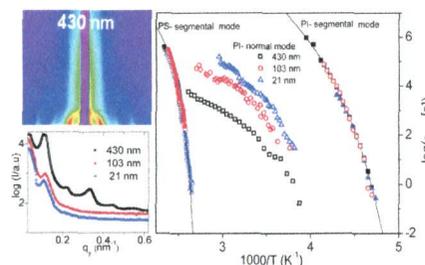
9712 dx.doi.org/10.1021/ma401812s  
**Crystal and Crystallites Structure of Natural Rubber and Peroxide-Vulcanized Natural Rubber by a Two-Dimensional Wide-Angle X-ray Diffraction Simulation Method. II. Strain-Induced Crystallization versus Temperature-Induced Crystallization**  
 Justin Che,\* Christian Burger, Shigeyuki Toki, Lixia Rong, Benjamin S. Hsiao, Sureerut Amnuaypornsi, and Jitlada Sakdapipanich



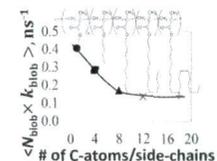
9722 **S** dx.doi.org/10.1021/ma401705v  
**Direct Measurement of Chain Diffusion at Interfaces of PPO/PS Bilayer Films by Nano-Thermal Analysis and Time-of-Flight Secondary Ion Mass Spectrometry**  
 Noriyuki Tanji, Hui Wu, Motoyasu Kobayashi, and Atsushi Takahara\*



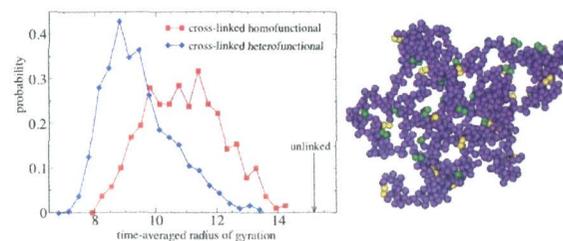
9729 dx.doi.org/10.1021/ma4019334  
**Molecular Order and Dynamics of Nanometric Thin Layers of Poly(styrene-*b*-1,4-isoprene) Diblock Copolymers**  
 Wycliffe K. Kipnusu,\* Mahdy M. Elmahdy, Martin Tress, Markus Fuchs, Emmanuel U. Mapesa, Detlef-M. Smilgies, Jianqi Zhang, Christine M. Papadakis, and Friedrich Kremer



9738 **S** dx.doi.org/10.1021/ma402093v  
**Effect of Side-Chain Length on the Polymer Chain Dynamics of Poly(alkyl methacrylate)s in Solution**  
 Shiva Farhangi, Henning Weiss, and Jean Duhamel\*

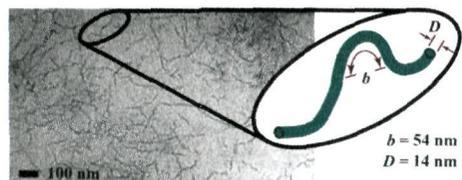


9748 dx.doi.org/10.1021/ma402139v  
**Advantages of Orthogonal Folding of Single Polymer Chains to Soft Nanoparticles**  
 Angel J. Moreno,\* Federica Lo Verso, Ana Sanchez-Sanchez, Arantxa Arbe, Juan Colmenero, and José A. Pomposo



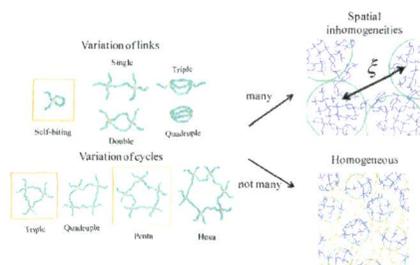
## Fibrillar Structure in Aqueous Methylcellulose Solutions and Gels

Joseph R. Lott, John W. McAllister, Matthew Wasbrough, Robert L. Sammler, Frank S. Bates,\* and Timothy P. Lodge\*



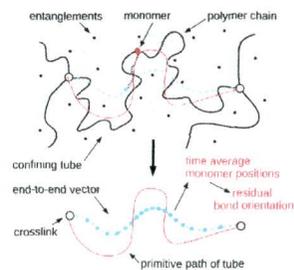
## Correlation between Local and Global Inhomogeneities of Chemical Gels

Makoto Asai,\* Takuya Katashima, Ung-il Chung, Takamasa Sakai, and Mitsuhiro Shibayama



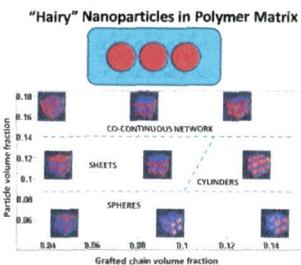
## Monomer Fluctuations and the Distribution of Residual Bond Orientations in Polymer Networks

Michael Lang\*



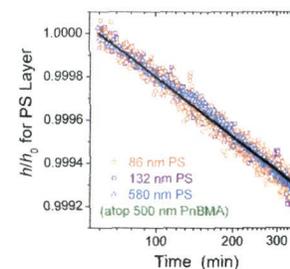
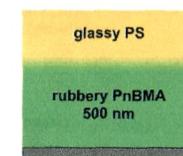
## Polymer-Grafted Nanoparticles in Polymer Melts: Modeling Using the Combined SCFT-DFT Approach

Valeriy V. Ginzburg\*



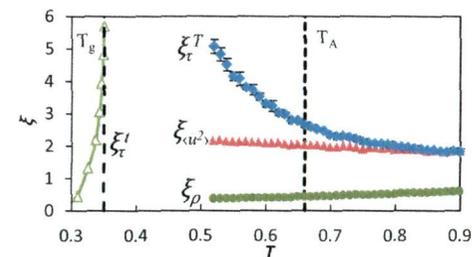
## Effect of Adjacent Rubbery Layers on the Physical Aging of Glassy Polymers

Phillip M. Rauscher, Justin E. Pye, Roman R. Baglay, and Connie B. Roth\*

Polystyrene aging rate unchanged despite  $T_g \downarrow$  of  $-25^\circ\text{C}$ 

## Interfacial Dynamic Length Scales in the Glass Transition of a Model Freestanding Polymer Film and Their Connection to Cooperative Motion

Ryan J. Lang and David S. Simmons\*

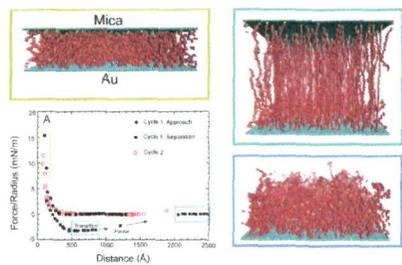


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[dx.doi.org/10.1021/ma4015356](https://doi.org/10.1021/ma4015356)

### Using Thiol–Gold Bond Formation To Bridge Surfaces with a Polymer Brush: SFA Experiments and MD Simulations

Suzanne M. Balko, Torsten Kreer,\* Dennis J. Mulder, Philip J. Costanzo, Timothy E. Patten, and Tonya L. Kuhl\*

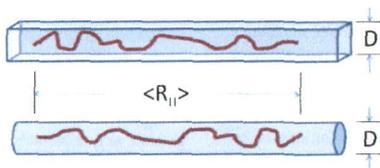


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[dx.doi.org/10.1021/ma4020824](https://doi.org/10.1021/ma4020824)

### Free Energy and Extension of a Wormlike Chain in Tube Confinement

Jeff Z. Y. Chen\*



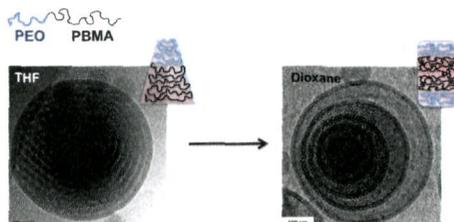
## Notes

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[dx.doi.org/10.1021/ma4019729](https://doi.org/10.1021/ma4019729)

### Bicontinuous Nanospheres from Simple Amorphous Amphiphilic Diblock Copolymers

Beulah E. McKenzie, Joël F. de Visser, Heiner Friedrich, Maarten J. M. Wirix, Paul H. H. Bomans, Gijbertus de With, Simon J. Holder, and Nico A. J. M. Sommerdijk\*



## Comments

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[dx.doi.org/10.1021/ma401183w](https://doi.org/10.1021/ma401183w)

### Comment on “New Experiments for Improved Theoretical Description of Nonlinear Rheology of Entangled Polymers”

Richard S. Graham,\* Ewan P. Henry, and Peter D. Olmsted

