



## Notes from the Chair

You should be receiving this within a week of the Annual Meeting in San Francisco. Plan to attend the MESD Plenary Session (Session 368) on Wednesday at 8:00 AM. This plenary session recognizes the recipient of the Charles M. A. Stine Award of the Division, Thomas F. Kuech, and affords you an opportunity to hear talks that span the various programming groups within the Division. While you are organizing your schedules for the meeting I also ask you note the times for the area programming meetings. The different areas will all hold their meetings on Tuesday evening from 5:30 – 7:00 PM (see room information at right), where the programming chairs will discuss final plans for the 2004 Annual Meeting and preliminary plans for the 2005 Annual Meeting. It strikes me that the Materials Engineering and Science Division provides a forum for us to meet, present our work and learn about the latest advances in materials. We do this through our technical sessions at the annual meetings and your input in suggesting, organizing and chairing symposia are critical to our success and our mission. Materials operates at the interface between the more traditional disciplines and the sciences and we should be striving to define programs that embrace this interface and draw participation from a very broad audience. Come prepared to suggest sessions and most importantly come prepared to get involved in the programming of the Division.

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Inside This Issue	
1	2002 Stine Award Article
2	MESD Election Results
3	New Newsletter Editor
4	Fall Meeting Preview

You're invited to the **Area Programming Meetings** on Tuesday afternoon, Nov. 18, 5:30 – 7:00 PM in the rooms below at the Hilton. Please invite your paper presenters too. Sessions for next Fall's meeting in Austin will be prioritized at the programming meetings. Also, chairs and co-chairs are often elected.

Area 8A (Polymers), Union 15  
 Area 8B (Biomaterials), Union 16  
 Area 8D (Ceramics), Union 22  
 Area 8E (Electronic Materials), Union 23  
 Area 8F (Composites), Union 24

- *Alon McCormick*

## Election Results

The election results have been compiled by the national office for the AIChE Division 8 (MESD) Executive Committee. We are pleased to welcome the following new officers:

2 <sup>nd</sup> Vice Chair	<b>Jeffrey Koberstein</b>
Directors	<b>Christopher Bowman</b> <b>Michael Harris</b>

Congratulations to the newly-elected officers, and thank you to all of the candidates for offering their services.

## 2 Materials Engineering and Sciences Division Newsletter - November, 2003

### Controlled Crystallization in Block Copolymers

2002 Charles M.A. Stine Award Lecture

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Receiving the 2002 Stine award from the AIChE MESD has been a tremendous honor. I am also most grateful to DuPont for their continuing support of this award, which since 1979 has recognized both advances in fundamental knowledge and new directions in materials engineering. Appropriately, many of these developments over the past two decades have been based on molecular or mesoscopic materials design, a theme which I will also pursue in the paragraphs which follow, where I focus on one specific area: how polymer crystallization can be manipulated through molecular architecture.

Most polymeric materials introduced into commerce today contain multiple components or phases, with supramolecular structures ranging from nanometers to microns. Such materials offer the potential for synergistic property combinations and even entirely new applications, but their complex behavior makes tapping this potential a true challenge. A particularly versatile way to incorporate diverse functionalities into a single polymeric material is in the form of a *block copolymer*, which contains “blocks” of one monomer connected to blocks of a dissimilar monomer. Although commercial materials, used as melt-processible rubbers and adhesives [1], are based on amorphous blocks, designing crystallinity into one of the blocks could confer significant property advantages, such as vastly improved solvent resistance.

The phase behavior of noncrystallizing block copolymers is fairly well understood today [2], thanks to the strong efforts of numerous investigators over the past three decades. Microphase separation takes place when the interblock segregation strength is sufficiently high, and results in the formation of periodic structures – such as spheres, cylinders, gyroid and lamellae – depending on the relative block lengths. Spherical microdomains resemble the well-known case of surfactant micelles, and as in that case, the microdomains have sizes comparable to the molecular dimension—which for polymer molecules, given their much greater molecular weight, means tens of nanometers. So, for example, a collection of very asymmetric diblock copolymer chains (each having one short and one long block) could microphase-separate into a structure where hundreds of the short blocks aggregate to form a sphere (*ca.* 10 nm radius)

dispersed in a matrix of the long block. These spheres exhibit a narrow size distribution, and at equilibrium pack onto a regular (body-centered cubic) lattice.

When crystallizable segments are incorporated within a block copolymer, however, the structure which the material adopts is more difficult to predict a priori. These materials—semicrystalline block copolymers—possess two mechanisms that can drive phase separation: microphase separation and crystallization. The interplay between these two results in both morphological richness and kinetic complexity—the subject of this Stine Award address.

### Conventional Crystallizable Polymers

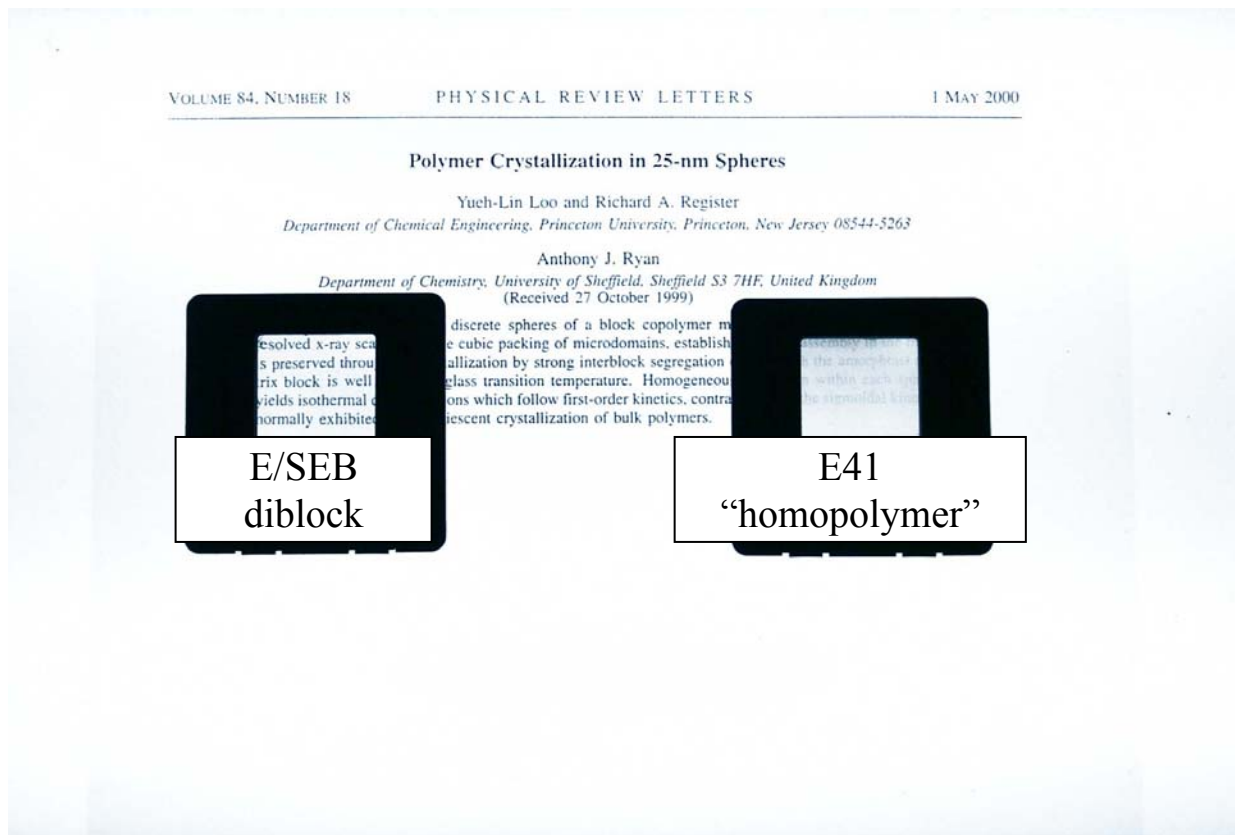
The usual growth habit for semicrystalline homopolymers (or random copolymers) is as chain-folded lamellae, with a thickness on the order of 10 nm—much shorter than the full length of the molecule, as illustrated schematically in Figure 1.



**Figure 1.** Schematic illustration of the lamellar structure of a semicrystalline homopolymer. Straight lines represent crystal stems, while curving lines represent amorphous sections of polymer chain. Crystal thickness  $t$  is typically of order 10 nm.

While the crystallites are thin, their lateral extent can be orders of magnitude greater. Indeed, when such polymers are crystallized under weak- or no-flow conditions, the laterally-growing crystals splay and branch to form spherulites—entities microns to hundreds of microns across, built up from radially-growing lamellae. This spherulitic growth is responsible for the usual haziness or opacity of semicrystalline polymers, as the spherulites are larger than the wavelength of light. The “spreading” growth habit characteristic of spherulites—where successive spherical shells (crystallized in equal time increments) have progressively greater volumes—gives rise to the characteristic Avrami-type autoaccelerating crystallization kinetics.

Simply adding a noncrystallizing block to the molecule does not change this overall picture dramatically. If the crystallizing and noncrystallizing blocks are miscible in the melt, then on cooling, lamellae of large lateral extent form, which can organize into



**Figure 2.** Comparison of optical transparency of block copolymer film (left), containing hydrogenated polybutadiene crystallized within 25 nm spheres, and hydrogenated polybutadiene homopolymer film (right), containing spherulites which scatter light strongly.

spherulites, and which crystallize according to classic Avrami-type kinetics [3,4]. Of course, the two blocks need *not* be miscible in the melt—and when interblock segregation is sufficiently large to drive the formation of a microphase-separated melt, the possibilities for structural control increase greatly. Consider first this question: can we induce one component to crystallize within the nanoscale spheres, cylinders, or lamellae formed in the melt?

**Confined Crystallization**

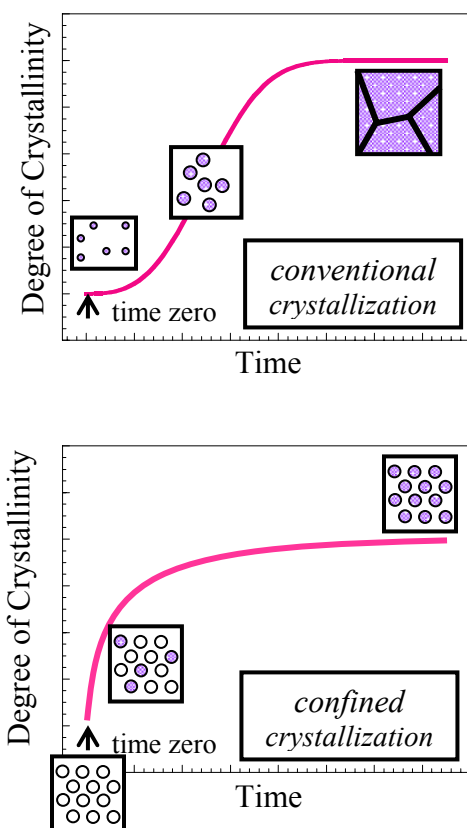
Commonly, the answer is “no”—that is, provided the noncrystallizing block is above its glass transition temperature and is thus easily deformed, crystallization usually overwhelms any morphology present in the melt and creates a new structure resembling that for crystallizable homopolymers (thin lamellae of large lateral extent, often forming spherulites) [5,6]. But we have found that if the interblock segregation strength is sufficiently high—about three times the strength needed for the blocks to barely microphase-separate—then

growing crystals are unable to break out of the spherical microdomains formed by the crystallizable blocks in the melt [7,8].

This “confined crystallization” differs profoundly from typical polymer crystallization. Since the spheres which define the crystals’ boundaries are of macromolecular size (a few tens of nm), there is no structural entity large enough to scatter light, so these materials remain completely transparent even when fully crystallized (see Figure 2).

The kinetics of crystallization within spheres also differ markedly from “ordinary” homopolymer crystallization. First, since the spheres are disconnected from each other, each must be independently nucleated. But because the spheres are so small (or conversely, their number density so large), only a trivial fraction can contain or border on the kinds of heterogeneous nuclei found in polymers (catalyst residues, dust, or typical nucleating additives). So such confined crystallization proceeds by *homogeneous* nucleation—a rarity for polymers. Since each sphere crystallizes independently, the overall crystallization rate is simply proportional to

the fraction of spheres still uncrystallized, leading to a first-order kinetic expression. (While first-order kinetics may seem wholly unremarkable to chemical engineers, this is the first time they've been found for quiescent crystallization in a polymer melt, compared with innumerable reports of Avrami-type autoaccelerating kinetics over the past several decades!) This difference is shown graphically in Figure 3.



**Figure 3.** Schematic illustration of the differences in crystallization kinetics between conventional (top) and confined (bottom) crystallization. In both cases, the pink curve illustrates the time evolution of the fractional crystallization; crystallized regions are indicated in purple. In conventional crystallization, spherulites nucleated at time zero grow at a constant linear rate, so the crystallization rate increases (autoaccelerating kinetics) until the spherulites begin to impinge. In confined crystallization (spherical microdomains illustrated here, represented by circles), each microdomain crystallizes independently, so the process obeys first-order kinetics.

The need to form a critical nucleus within each sphere means that confined crystallization requires deeper undercoolings (to proceed at a rate comparable to heterogeneously-nucleated homopolymer crystallization), and that the crystallization rate shows the steep temperature dependence characteristic of homogeneous nucleation. Indeed, we have found that the crystallization rate can be changed by an order of magnitude by shifting the crystallization temperature by only a couple degrees [8,9]. Moreover, because the sphere volume can be measured precisely by small-angle x-ray scattering, precise values for the homogeneous nucleation rate of the crystallizable block (nuclei/cm<sup>3</sup>-sec) can be measured by following the block copolymer's bulk crystallization kinetics. This approach has provided the first measurements of the nucleation rate in polyethylene at such deep undercoolings [8].

We have also examined crystallization within other block copolymer morphologies: cylinders, gyroid, and lamellae [6,8,9]. The overall trend is that as the number of "long" dimensions of the microdomain increases (from zero, to one, to two—on moving from spheres, to cylinders, to lamellae), it becomes progressively more difficult to completely confine crystallization. In strongly-segregated melts, while the crystals prefer to grow in the microdomain's "long" direction where their growth is relatively unhindered, even rare "breakthrough" events—where a growing crystal penetrates through the domains formed by the noncrystallizing block to crystallize the material in an adjacent crystallizable microdomain—are sufficient to crystallize many microdomains from a single nucleus. This "spreading" growth habit imparts conventional Avrami-type crystallization kinetics to the materials as well. Yet the general alignment of the crystals with the microdomain axes which occurs in this case, which we have termed "templated crystallization," can produce a highly-oriented crystal texture by pre-orienting the microdomains.

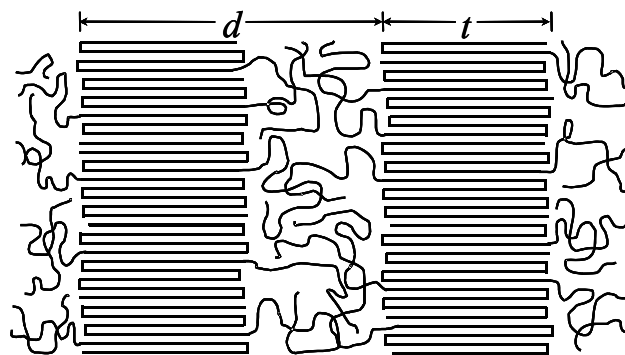
### Crystal Thickness Control

One might well ask how confinement of the crystals influences their melting point—a cardinal property for any crystallizable polymer, as it sets the upper temperature at which the material can be used. The Gibbs-Thomson equation tells us that the magnitude of the melting point depression will be proportional to the surface-to-volume ratio of the crystal, with the proportionality constant involving the crystal-melt interfacial energy—so we might anticipate a large melting point depression for crystals confined within, for example, spheres of 25 nm diameter.

But in fact, no significant melting point depression is observed in the cases described above. This is because our prior work employed hydrogenated polybutadiene (a sort of linear low-density polyethylene) as the crystallizing block—which contains a significant density of defects along the chain (ethyl branches from 1,2-type addition in the precursor polybutadiene). These defects are excluded from the crystals and limit the average crystal thickness to approximately 5 nm even in hydrogenated polybutadiene homopolymer, though crystals in the homopolymer can still have a very large lateral extent. Confining such crystals within, say, 25 nm diameter spheres will reduce their lateral extent but need not change their thickness. And for a lamellar (plate-like) crystal, the surface-to-volume ratio is essentially inversely proportional to the crystal thickness—so the confined crystals melt at essentially the same temperature that the unconfined crystals do, and well below the temperature of the thick crystals formed by a defect-free polyethylene [9].

Consequently, our present work in this area involves the synthesis and characterization of polymers containing defect-free crystallizable blocks. In such materials, we would expect to be able to alter the melting point substantially, even in the *absence* of confined crystallization, for the following reason. For crystallizable homopolymers, the extent of chain folding (hence lamellar thickness) is normally kinetically controlled, though the equilibrium structure is anticipated to be an extended-chain crystal for near-monodisperse polymers of high crystallinity. However, attaching an amorphous chain to the crystalline homopolymer must induce an *equilibrium* degree of chain folding, since the amorphous (random coil) and crystalline (folded-chain) blocks must occupy equal areas on opposite sides of the lamellar interface, as shown schematically in Figure 4. Thus, crystal thickness (and hence melting point) can be controlled thermodynamically rather than kinetically, through block copolymer composition and molecular weight.

We have developed a synthetic route to crystalline-amorphous block copolymers based on ring-opening metathesis polymerization, where the amorphous block is a saturated rubber and the crystalline block is either linear polyethylene or hydrogenated polynorbornene (hPN), both highly crystalline and free from chain defects which limit the crystal thickness [10]. Since both blocks are saturated hydrocarbons, the interblock segmental interaction parameter is modest, and single-phase melts are obtained even at relatively high molecular weights. Thus, the solid-state structure is driven entirely by crystallization of one block, without the complexity imparted by melt microphase separation.



**Figure 4.** Schematic of the equilibrium lamellar structure of a crystalline-amorphous diblock copolymer, crystallized from a single-phase melt. Since both the amorphous block (curved line) and the crystalline block (straight segments) must occupy equal areas across the interface between the crystalline and amorphous domains, the crystalline block is thermodynamically induced to fold. Crystal thickness  $t$  and spacing  $d$  indicated.

Our work on these materials is continuing, but we have already confirmed several of the key ideas put forth above. First, these block copolymers exhibit identical crystal thicknesses when crystallized over a wide range of conditions, supporting the notion of an equilibrium (*vs.* kinetically-controlled) crystal thickness in such materials. Second, the thickness is substantially lower than that for the “unattached” crystallizable block, and decreases monotonically with the length of the amorphous block, confirming that the presence of the amorphous block is driving the crystallizable block to fold. Indeed, the thickness of the crystals is in good agreement with longstanding theoretical scaling laws. Finally, the melting point can be tuned continuously over at least a 30°C range by changing the length of the amorphous block. Currently, we are investigating these materials as candidate thermoplastic elastomers, as well as thermoplastic elastomer gels which could find potential use as the active material in high-displacement actuators (“artificial muscle”) [11].

- *Continued*

## 6 Materials Engineering and Sciences Division Newsletter - November, 2003

### Acknowledgments

Financial support for this work has been generously provided by the Polymers Program (Division of Materials Research) of the National Science Foundation. I have been fortunate to work on this project with a number of outstanding Princeton Ph.D. students: Pratima Rangarajan (now at General Electric CR&D), Daniel Quiram (now at Procter & Gamble), Yueh-Lin Loo (now at the University of Texas-Austin), and Li-Bong Lee (now at ExxonMobil). In particular, the work illustrated above comprised portions of the Ph.D. theses of Drs. Loo and Lee. I have also benefited enormously from a continuing collaboration with Professor Tony Ryan (University of Sheffield), especially in the application of synchrotron x-ray scattering to study the crystallization process. Finally, let me close by again thanking the MESD, DuPont, and my supporters for this honor.

### **2003 Stine Award Lecture**

Thomas Kuech, recipient of the 2003 Charles M.A. Stine Award (see the August, 2003 edition of the newsletter), will deliver his award lecture at the MESD Plenary Session on Wednesday, November 19 in the Continental Ballroom of the Hilton Hotel in San Francisco. Other plenary speakers include C. Grant Willson, Michael Tsapatsis, Lawrence T. Drzal, and Antonios G. Mikos.

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- [3] P. Rangarajan, R.A. Register, and L.J. Fetters, *Macromolecules*, **26**, 4640 (1993).
- [4] P. Rangarajan, R.A. Register, D.H. Adamson, L.J. Fetters, W. Bras, S. Naylor, and A.J. Ryan, *Macromolecules*, **28**, 1422 (1995).
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- [8] Y.-L. Loo, R.A. Register, and A.J. Ryan, *Macromolecules*, **35**, 2365 (2002).
- [9] Y.-L. Loo, R.A. Register, A.J. Ryan, and G.T. Dee, *Macromolecules*, **34**, 8968 (2001).
- [10] S.T. Trzaska, L.-B. W. Lee, and R.A. Register, *Macromolecules*, **33**, 25, 9215 (2000).
- [11] R. Pelrine, R. Kornbluh, Q.B. Pei, and J. Joseph, *Science*, **287**, 836 (2000).

### **Materials Engineering and Sciences Division Membership Application Form**

Not a member of the MESD? Are you a member, but have a colleague who might be interested? Come join one of the most active programming divisions in AIChE. Just fill out the form below, cut it out and return it with a \$7 check made out to AIChE to:

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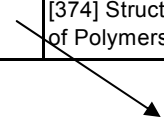
AIChE Member Number \_\_\_\_\_

## 2003 Annual Meeting MESD Events

The following is a list of MESD sponsored and co-sponsored sessions.

Please see the conference technical grid for location, list of speakers and topics.

	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
<b>8:00 AM</b>	[193] Adv. in Biosensors & Biomedical Sensors I [242] Biomolecules at Interfaces I [129] Nanotechnology Public Forum [507] Novel Catalytic Materials I [175] Plenary: Advanced Microelectronic Processing [86] Polymer Processing & Rheology I [393] Self-Assembly & Templating of Inorg. Mat's I	[179] Plasma Processing I [92] Polymer Processing: Molding and Extrusion [91] Polymerization Kinetics, Catalysis and Reaction Engineering II [180] Polymers for Photonics & Microelectronic Applications [68] Prog. on Adsorbent & Nanoporous Membranes	<b>[368] Plenary Session: Stine Award</b> [77] Diffusion in Polymers & Membranes I [327] Metallo-Organic Adsorption Materials [559] Molecular Simulation of Materials Processes [134] Nanoelectronics: Materials & Processing [185] Reaction Kinetics in Electronic Materials Processing	[385] Biomembranes & Biosensors [97] Mixing, Reactions, & Mass Transfer in Polymer Systems [370] Nanoscale Structure in Polymers I: Self-Organization of Polymers at Surfaces & Interfaces I [231] Thermodynamics of Polymers I	[387] Biomaterials II [388] Biomimetics I [377] Nanoscale Structure in Polymers IV: Nanostructured Polymeric Materials II [102] Structural Development in Polymer Processing [236] Structure & Properties of Polymers II
<b>12:30 PM</b>	[194] Advances in Biosensors and Biomedical Sensors II [246] Biomolecules at Interfaces II [402] Composites I [176] Control of Materials Manufacturing Processes [511] Novel Catalytic Materials II [88] Polymer Processing and Rheology II [394] Self-Assembly & Templating of Inorg. Mat's III [383] Tissue Engineering I	[396] Advanced Materials for Environmental Remediation [94] Numerical Methods for Polymer Systems [255] Electrokinetics I [182] Transport Phenomena in Electronic Materials Processing [93] Polymerization Kinetics, Catalysis and Reaction Engineering III [181] Plasma Processing II	[78] Advances in Ceramic & Nanocomposite Membranes [79] Diffusion in Polymers & Membranes II [186] Film Growth of Electronic Materials [398] Nanostructured Materials & Particles I	[373] Nanoscale Structure in Polymers II: Self-Organization of Polymers at Surf./Interf. II [372] Polymer Thin Films & Interfaces I [138] Nanostr. Biomaterials [400] Advances in Ceramic Thin Films [472] Bioinspired & Biomimetic Polymeric Materials I [55] Liquid Phase Synthesis of Nanomaterials & Particles [98] Polymers & Materials from Renewable Resources I [371] Thermo. of Polymers II	[63] Nanoparticle Formation for Electronic & Optical Applications [103] Polymer Processing of Composites [390] Biomimetics II [380] Polymer Thin Films & Interfaces III [389] Self-Assembled Biomaterials II [379] Nanoscale Struct. in Polymers V: Polymer Nanocomposites I [378] Struct./Prop. of Pol. III: Dynamics in Glass Formers & Confined Spaces
<b>3:15 PM</b>	[249] Biomolecules at Interfaces III [177] Chemical Vapor Deposition [403] Composites II [178] Computational & Exp. Aspects of Org. Electronics [395] Hybrid Organic-Inorganic Materials [515] Novel Catalytic Materials III [90] Polymer Processing: Extrusion [384] Tissue Engineering II [89] Polymerization Kinetics, Catalysis & Reaction Eng. I	[397] Advances in Characterization of Inorganic Materials for Energy and Environmental Applications [184] Atomic Layer Deposition [326] Nanostructured Adsorbent Materials [183] Plasma Processing III	[399] Nanostructured Materials and Particles II [187] Semiconductor Surface Chemistry [188] Synthesis of Inorganic Nanowires & Nanotubes <b>Thursday Evening Poster Sessions (7:00 p.m.):</b> [369] Materials Engineering and Science Division [101] Polymer Processing [100] Polymerization	[376] Nanoscale Structure in Polymers III: Nanostructured Polymeric Materials I [386] Biomaterials I [473] Bioinspired & Biomimetic Polymeric Materials II [375] Polymer Thin Films & Interfaces II [99] Polymers & Materials from Renewable Resources II [401] High Temperature Synthesis & Processing of Ceramics [374] Structure & Properties of Polymers I	[392] Biomimetics III [382] Nanoscale Structure in Polymers VI: Polymer Nanocomposites II [381] Polymer Thin Films & Interfaces IV [391] Self-Assembled Biomaterials II [239] Structure & Properties of Polymers IV



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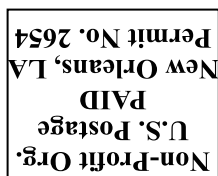
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