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Diblock copolymer healing

Nataliya A. Yufa [a], Jason Li [b], S.J. Sibener [c,*]

[a] James Franck Institute and Department of Physics, The University of Chicago, 929 E 57th Street, Chicago, IL 60637, USA
[b] Asylum Research Corporation, 6310 Hollister Ave, Santa Barbara, CA 93117, USA
[c] James Franck Institute and Department of Chemistry, The University of Chicago, 929 E 57th Street, Chicago, IL 60637, USA

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ABSTRACT

The issue of self-healing materials is of paramount importance due to its intrinsic scientific value, as well as potential applications in a wide variety of fields, such as manufacturing, medicine, and electronics. We have investigated the behavior of poly(styrene-*b*-methylmethacrylate) diblock copolymer, following deformation performed by a silicon atomic force microscopy tip. We observed the changes in the polymer as it was subsequently heated *in situ*, and found how diblock "scars" can heal. These observations give important guidance to efforts that seek to create nanostructures using these methods, while also revealing fundamental insights into the mechanisms of polymer repair on the nanoscale.

1. Introduction

Polymers and polymer–inorganic hybrids have been considered as potential self-healing materials for some time. In recent years, such self-healing materials have been made in the laboratory [1–4]. Diblock copolymers are a promising class of materials due to their ability to self-assemble into a variety of morphologies on the nanoscale. They have been studied extensively in recent years [5–7]. Diblocks have been used to create well-ordered arrays [8–10], lithographic templates [11,12] and scaffolds for magnetic hard drives [13]. Poly(styrene-*block*-methylmethacrylate) PS-*b*-PMMA is an excellent model system to study because it presents both blocks at the free surface in ultra-thin films. The behavior of PS-*b*-PMMA can therefore be imaged with atomic force microscope (AFM) *in situ*. Here we report our findings on the physical damage, including material transfer and removal, and the subsequent healing of PS-*b*-PMMA performed *in situ* at room and elevated temperatures.

Self-healing of materials is important both as a basic research issue and as a manufacturing concern. The ability of polymers to flow makes them ideal candidates for self-healing materials [14]. Thus far, there have been a number of solutions to the self-healing challenge: networks of catalyst surrounded by monomer which polymerizes on contact with the catalyst when a micro-crack is formed in the material [15], or embedding nanoparticles that flood a crack as soon as it forms [16]. There is also an extensive, complementary literature on film modification and repair in which tip-based AFM lithography and nanografting have been used to intentionally construct structures within self-assembling molecular systems [17–20].

Previous work on polymeric response to mechanical damage includes micro-indentation of various polymers [21], macro-scratches studied on the micro- and nano-level [22], and nano-scratches made using AFM [23,24]. This prior work was performed on homopolymers, unlike our work which was performed on a block copolymer. Since nanoscale morphology can be utilized to provide functionality, the healing of nanostructured block copolymers is of interest. Thus, in addition to observing the effects of nano-scratching on the topography, we can observe its effects on morphology. Another novel feature of our work was to observe *in situ* the healing of the scratches. This feature enables us not only to witness the damage, but to see the intermediate steps which result in healing.

2. Experimental procedures

Cylindrical phase syndiotactic 77,000 g/mol PS-*b*-PMMA (55 K PS-22 K PMMA) was purchased from Polymer Source, Inc. Toluene solution ($\sim$1.5% w/w) was used to spin-coat PS-*b*-PMMA films $\sim$30 nm thick at 4000 rpm onto silicon nitride substrates. The substrates had been previously cleaned using ultrasonication in toluene, acetone and methanol for a total of 30 min. Some of the samples were then pre-annealed in an ultra-pure argon atmosphere at 518 K for 12 h.

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* Corresponding author. Tel.: +1 773 702 7193; fax: +1 773 702 4180.
E-mail address: s-sibener@uchicago.edu (S.J. Sibener).

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Lithography and high-temperature *in situ* AFM imaging were performed using Asylum Research's MFP-3D and a closed cell flushed with an inert gas. We used tips with a 2 N/m spring constant to create lithographic patterns in the polymer film, and stiffer 40 N/m tips to damage the polymer by removing material, both using contact mode. To create the bull's eye pattern, we used forces of 14 nN for the outer circle, 70 nN for the middle one, and 140 nN for the inner circle. We used 40 N/m tips to image the diblock in tapping mode, without affecting the polymer, as verified by taking a large area scan and seeing no difference between repeatedly imaged areas and those imaged only once. Typical scan size was between 0.5 and 2 μm on a side. In our images, PMMA domains appeared white in topography, as in the literature [25], and black in the phase images. Although the contrast in phase imaging is not universal, by comparing the phase and height images, we can identify PMMA domains as black in phase.

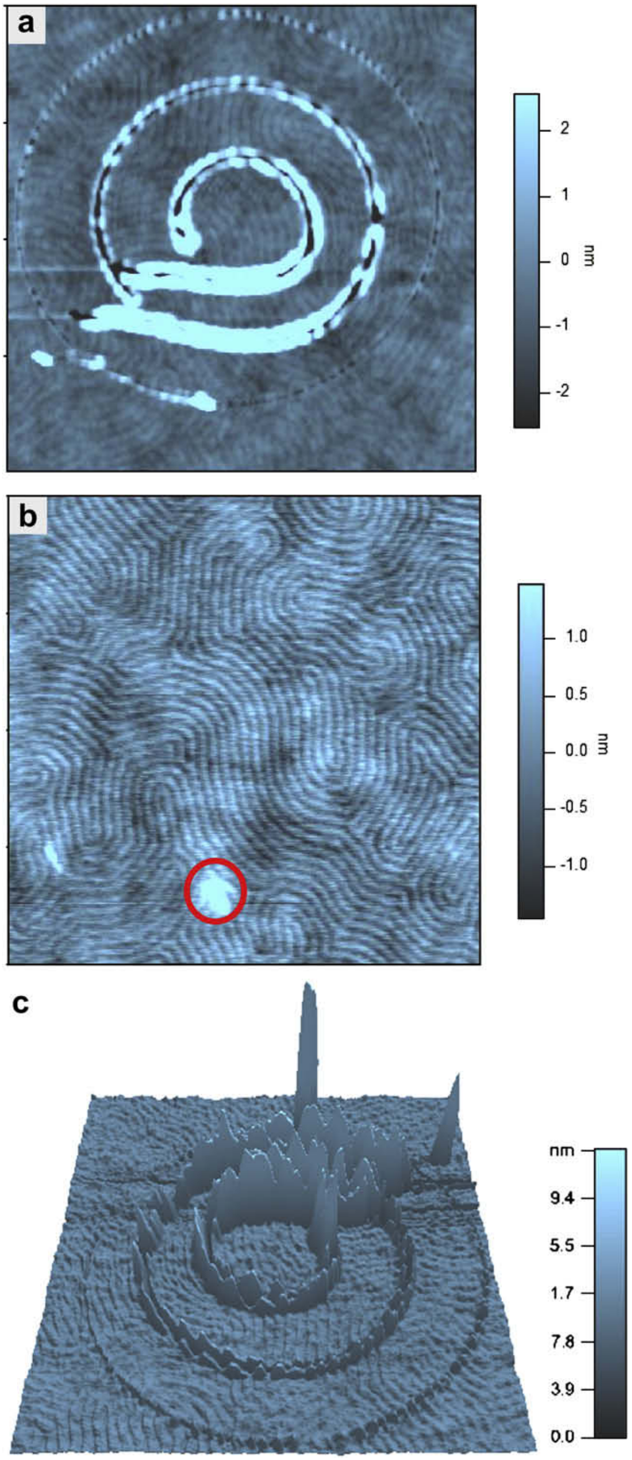

Fig. 1. Tapping height image of a $2 \times 2\ \mu m^2$ PS-*b*-PMMA before (a) and after (b) healing a scratch. The pattern was created using *MicroAngelo* software on an Asylum MFP-3D atomic force microscope. (c) 3-dimensional version of (a).

The samples were mounted directly onto the heater, in order to maximize thermal contact between the sample and the heater, as well as to minimize drift due to thermal expansion. Imaging was performed between 300 and 398 K in an environmentally controlled cell with a constant flow of argon. Differential scanning calorimetry measurements put the bulk T_g for this diblock at 383 K [26].

3. Results

3.1. Bull's eye pattern

We created a pattern of concentric circles at room temperature, using different deflection voltage values, in order to study the effect of a small deformation made across a number of domains (Fig. 1). A circle is preferred to a straight line because it offers a full range of

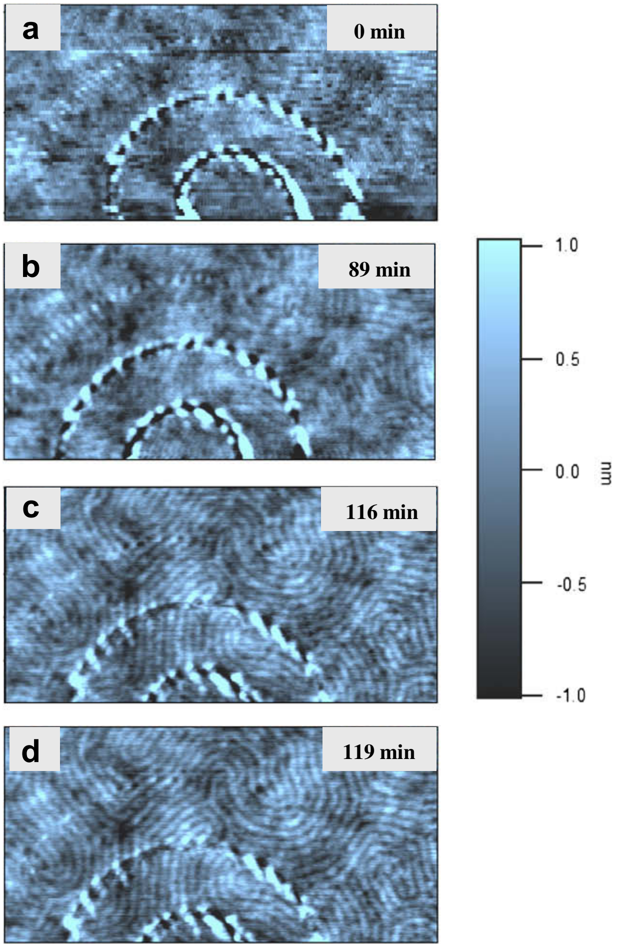

Fig. 2. A sequence of images showing the healing sequence of the bull's eye pattern. The scans are $1 \times 2\ \mu m^2$, with the height scale of 2 nm. The temperature was ramped from room temperature to 373 K between 70 and 80 min into the experiment. Notice the outer ring vanishing at this temperature.

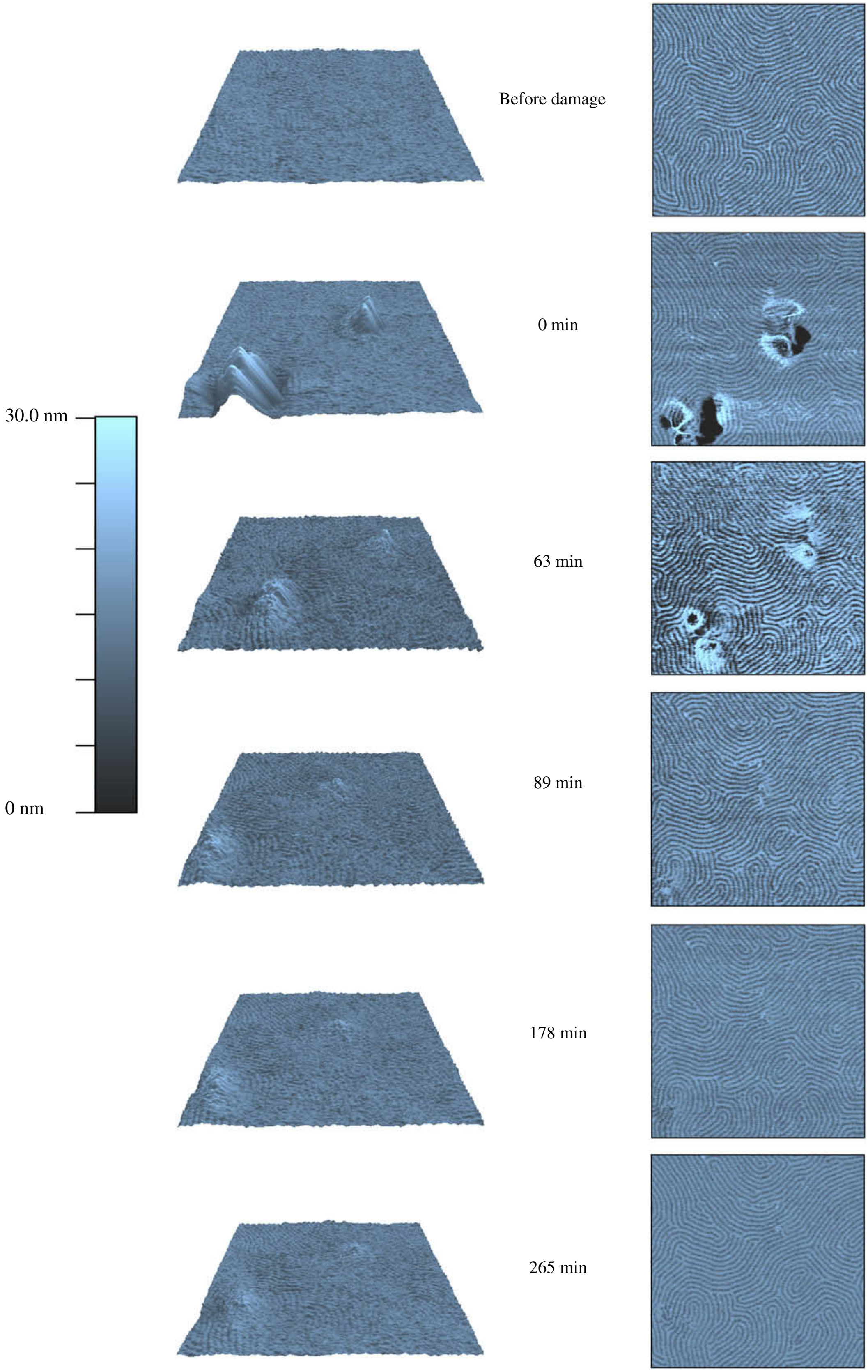

Fig. 3. AFM height (a) and corresponding phase (b) images of catastrophic polymer damage and healing, taken at 398 K. Note that the later-time phase images shows nearly-perfect recovery, while the height image shows a peak remaining. The flattening of the topographic peaks virtually stops after 90 min, just as the final fingerprint pattern is frozen in.

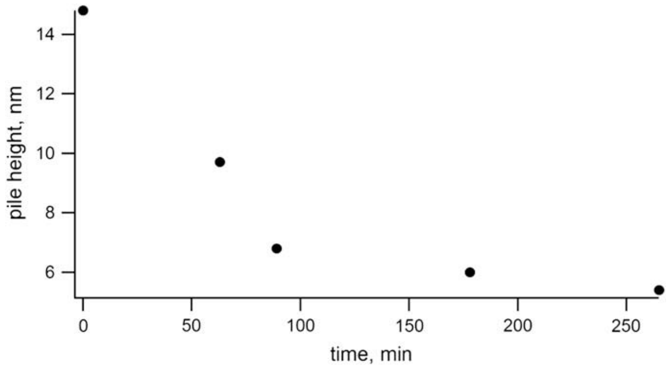

Fig. 4. The decay of the height of the tallest part of one of the peaks (the one on the right in Fig. 3) is shown as a function of time. This decay is non-linear: it proceeds more quickly at early times than at late times.

angles with respect to the direction of scanning, thereby eliminating potential dependence of healing on any transfer of material caused by the imaging process.

In the lithography software we used, the input parameter determining the force of the tip on the particular surface (in our case, diblock copolymer) was the tip's deflection. For a given circle or line, the force was constant. Since PMMA is harder than PS, deeper scratches were made into PS than PMMA domains.

A significant amount of diblock was moved over from one side of the circles to the other, due to the AFM tip not being retracted between circles. We imaged the sample at room temperature following lithography, to obtain an image of the resulting topography.

The sample was heated to 373 K *in situ* followed by repeated imaging of the area of interest. The lightest (outermost) circle virtually disappeared within minutes of the sample reaching 373 K: the pile-up around the trough associated with the outermost circle went from a height range of 1–2 nm to about 0.5 nm. Following that, maintaining the sample at 373 K for 30 min did not cause further polymer flow/healing, i.e. there was no change in the topography of the sample. We then heated the sample to 398 K, and within 30 min the pattern returned to its original state: the diblock "healed" itself. Fig. 2 shows a sequence of AFM images taken at 373 and 398 K, respectively, showing the healing of the bull's eye pattern.

Polymer flow was responsible for largely restoring the topography of the thin film following tip nano-lithography. Although not all of the material was returned to its original location, as evidenced by the small "hill" left behind (circled in Fig. 1b), most of the material was reabsorbed into the film to recreate the original fingerprint pattern. The only area which did not return to its original pattern was the area of the "hill," which showed a new point defect in the corresponding phase image.

3.2. *Catastrophic damage*

A sizable (200 nm diameter) hole was created in the polymer by using tip-based lithography at 398 K, a temperature above the diblock's glass transition of 383 K (in contrast to the bull's eye pattern discussed above which was created at room temperature). In order to observe healing the area in question was then repeatedly scanned using comparatively gentle tapping mode imaging. Fig. 3 shows the early and late time height and phase AFM images. The size of the "pile" of excess material is reduced significantly, as well as its peak height, which shrinks from 15 nm to 6 nm, as shown in Fig. 4. The phase image reveals that the original fingerprint pattern has reformed, but that the topography has been altered. Since there was a pile of residual material, the material making up the pattern in this area is not the same as it was originally.

4. Discussion and conclusions

The self-healing of diblock copolymers has been a subject of interest for many years. Here we demonstrate a first attempt at studying this healing as it unfolds *in situ*. For example, we observed the copolymer filling in a nanoscale hole we created over time, and measured the height of the pile-up as a function of time. It was also observed that the original fingerprint patterns may be reformed following damage and heating, although not all of the material returns to its original location, as evidenced by nano-hills left behind. Moreover, point defects may form following catastrophic damage, as can be seen by comparing the first and last images in Fig. 3.

Healing takes place, albeit slowly, even at 373 K. However, at this temperature after an initial filling-in, there is no significant change during 30 min of further scanning. In contrast, at 398 K, the smaller scratches healed completely within 30 min. More significant damage, where the width of the gash was 200 nm instead of 10 nm took longer to heal – approximately 5 h. While the scarring as observed in phase imaging was minimal, there was still a visible peak formed out of the material removed by the tip after 5 h. The height of the peak, as well as its area, were greatly reduced by this annealing.

In summary, we have demonstrated the ability of diblock copolymer to self-heal following damage on the nanoscale via the use of heat. From our work on this system, we find that the polymer heals itself significantly faster at elevated temperatures just above the glass transition. Moreover, the fingerprint patterns associated with microphase separation, although initially destroyed by the tip-based lithography, reformed essentially completely upon thermal annealing. These observations, when combined with studies of defect annihilation dynamics and structural fluctuations at elevated temperatures [27–30], give important guidance to efforts that seek to create nanostructures using these methods while also revealing fundamental insights into the mechanisms of polymer repair on the nanoscale.

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References

[1] White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, et al. Nature 2001;409:794–7.
[2] Brown EN, Sottos NR, White SR. Exp Mech 2002;42(4):372–9.
[3] Rule JD, Brown EN, Sottos NR, White SR, Moore JS. Adv Mater 2005;17(2): 205–8.
[4] Balazs AC, Emrick T, Russell TP. Science 2006;314:1107–10.
[5] Fredrickson GH, Bates FS. Annu Rev Mater Sci 1996;26:501–50.
[6] Hamley IW. Nanotechnology 2003;14:R39–54.
[7] Darling SB. Prog Polym Sci 2007;32:1152–204.
[8] Sundrani D, Darling SB, Sibener SJ. Nano Lett 2004;4(2):273–6.
[9] Edwards EW, Stoykovich MP, Solak HH, Nealey PF. Macromolecules 2006;39:3598–607.
[10] Kim SO, Solak HH, Stoykovich MP, Ferrier NJ, de Pablo JJ, Nealey PF. Nature 2003;424:411–4.
[11] Black CT, Ruiz R, Breyta G, Cheng JY, Coiburn ME, Guarini KW, et al. Res Dev 2007;51(5):605–33.
[12] Segalman RA. Mater Sci Eng 2005;R48:191–226.
[13] Naito K, Hieda H, Sakurai M, Kamata Y, Asakawa K. IEEE Trans Mag 2002;38:1949–51.

[14] Hull R, Osgood RM, Parisi J, Warlimont H. Self healing materials. Springer; 2007.
[15] Toohey KS, Sottos NR, Lewis JA, Moore JS, White SR. Nat Mater 2007;6(8):581–5.
[16] Zacharia NS, DeLongchamp DM, Modestino M, Hammond PT. Macromolecules 2007;40:1598–603.
[17] Liu GY, Xu S, Qian Y. Acc Chem Res 2000;33:457–66.
[18] Liu M, Amro N, Liu GY. Ann Rev Phys Chem 2008;59:367–86.
[19] Xu S, Liu GY. Langmuir 1997;12:127–9.
[20] Garno JC, Yang YY, Amro NA, Cruchon-Dupeyrat S, Chen SW, Liu GY. Nano Lett 2003;3:389–95.
[21] Liu CK, Leea S, Sung LP, Nguyen T. J Appl Phys 2006;100:033503.
[22] Dasari A, Rohrmann J, Misra RDK. Macromol Mater Eng 2002;287:889–903.
[23] Du BY, Vanlandingham MR, Zhang QL, He TB. J Mater Res 2001;16(5):1487–92.
[24] Khurshudov A, Kato K. J Vac Sci Technol B 1995;13(5):1938–44.
[25] Hahm J, Lopes WA, Jaeger HM, Sibener SJ. J Chem Phys 1998;109(23):10111–4.
[26] Polymer Source, Inc. material data sheet.
[27] Hahm J, Sibener SJ. J Chem Phys 2001;114:4730–40.
[28] Harrison C, Adamson DH, Cheng Z, Sebastian JM, Sethuraman S, Huse DA, et al. Science 2000;290:1558–60.
[29] Harrison C, Cheng Z, Sethuraman S, et al. Phys Rev E 2002;66: 011706/1-27.
[30] Yufa NA, Li J, Sibener SJ. Macromolecules 2009;42:2667–71.