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Controlling Volume Shrinkage in Soft Lithography through Heat-Induced Cross-Linking of Patterned Nanofibers

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S *Supporting Information*

ABSTRACT: When poly(isopropylidene diallylmalonate) rich in *threo*-disyndiotactic sequences (st_{rich}-**2**) was utilized as a cross-linkable ink for microcontact printing, the resultant submicrometer-scale patterns featuring 700 and 300 nm wide stripes were successfully insolubilized while maintaining their high dimensional integrity by heat-induced cross-linking with elimination of CO_2 and acetone. In sharp contrast, although the thermal properties and reactivities of a polymer rich in *threo*-diisotactic sequences (it_{rich}-**2**) and a polymer having low stereoregularity (**2**$_{\mathrm{low}}$) are little different from those of st_{rich}-**2**, the patterns printed with these reference polymers collapsed considerably upon heating as a result of a volume shrinkage effect. The striking difference between st_{rich}-**2** and the other two polymers most likely arises from the nanofiber-forming character of st_{rich}-**2**, where the printed stripes are porous and much less affected by the volume shrinkage of individual nanofibers.

Microcontact printing[1] is a method for developing fine patterns of organic/polymer materials on the surface of a substrate by using relief patterns on a polydimethylsiloxane (PDMS) stamp through conformal contact. Such patterned surfaces with certain periodicity and dimensions can display interesting physical properties such as high adhesivity,[2] superhydrophobicity,[3] and structural colors.[4] The importance of microcontact printing has already been recognized by its successful application to the development of electronic,[5] photonic,[6] and bio-[7] and microfluidic[8] devices. However, from a practical point of view, printed patterns, in general, are not thermally stable and can also be disrupted upon exposure to organic solvents. To overcome these essential problems, post-cross-linking of patterned materials is one promising approach. However, with some exceptions,[9] volume shrinkage upon cross-linking is usually inevitable and results in deterioration of the printed patterns. Here we report that such a negative effect of volume shrinkage can be considerably suppressed when a cross-linkable polymer that has been preorganized into nanofibers is utilized as a printing ink.

This promising strategy was first observed during an attempt to utilize poly(isopropylidene diallylmalonate) (**2**; Figure 1) as a cross-linkable polymeric ink for microcontact printing. Recently, Leibfarth et al.[10a] reported that polymers **3** and **4** (Figure 2) carrying dialkyl Meldrum's acid as side-chain pendants can be thermally cross-linked through the generation and subsequent dimerization of ketenes after elimination of acetone and CO_2. By taking advantage of this clean cross-linking chemistry, they also succeeded in fabricating an insoluble square dot pattern ~10 μm on a side by microcontact printing.[10a] Coincidentally, Aida and co-workers[11] reported the first syndiospecific cyclopolymerization of isopropylidene diallylmalonate (**1**; Figure 1). The resulting polymer (st_{rich}-**2**), which bears dialkyl Meldrum's acid pendants, is rich in *threo*-disyndiotactic sequences and adopts a barbed shape. Taking advantage of the facile nature of the above cross-linking chemistry,[10] we explored the potential utility of this stereochemically unique polymer as a cross-linkable ink for microcontact printing. Consequently, we found that printed patterns of st_{rich}-**2** with a scale of 300 nm can be successfully cross-linked while satisfactorily maintaining their dimensional integrity. Significantly, features prepared with a polymer rich in *threo*-diisotactic sequences (it_{rich}-**2**)[12] or a polymer with a low stereoregularity (**2**$_{\mathrm{low}}$),[11] in sharp contrast, displayed poor dimensional stability upon heating, although their thermal properties and reactivities were little different from those of st_{rich}-**2**.[13,14]

For the present study, st_{rich}-**2**[11] with a syndiotactic triad content ([*mm*]) of 71% (M_n = 8600, M_w/M_n = 2.09; Figure 1b), it_{rich}-**2**[12] with an isotactic triad content ([*rr*]) of 78% (M_n = 6500, M_w/M_n = 1.92; Figure 1c), and **2**$_{\mathrm{low}}$[11] with [*mm*] = 30% (M_n = 8000, M_w/M_n = 1.99) were prepared and employed, together with **3**[10a] (M_n = 27 000, M_w/M_n = 2.25) and **4**[10a] (M_n = 11 300, M_w/M_n = 1.12) [for thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) profiles of **3** and **4**, see Figures S9 and S10 in the Supporting Information].[13] At ≥150 °C, st_{rich}-**2** showed a 42% weight loss in TGA (black curve in Figure 3a), which is very close to that (45.5%) expected for complete elimination of CO_2 and acetone from the repeating units (Figure 1a). When st_{rich}-**2** was heated at 240 °C for 5 min, its IR

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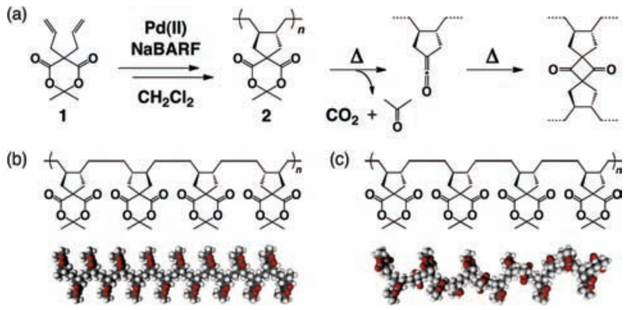

Figure 1. (a) Polymerization of diallylmalonate **1** initiated by α-diimine Pd(II) complexes[11−13] and thermal cross-linking of the resulting cycloolefin polymer (**2**). NaBARF = sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. (b, c) Structures and corresponding computer-generated CPK models of 16-mers of **1** composed exclusively of (b) *threo*-disyndiotactic (*st*) and (c) *threo*-diisotactic (*it*) sequences.

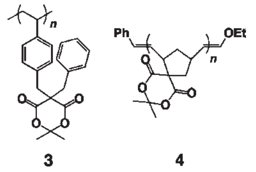

Figure 2. Structures of polymers **3** and **4**.[10a]

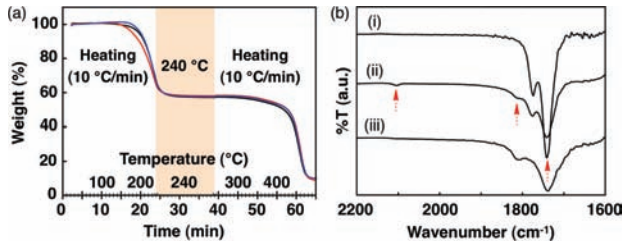

Figure 3. (a) TGA profiles of st_{rich}-**2** (black curve), it_{rich}-**2** (red curve), and $\mathbf{2}_{low}$ (blue curve) upon heating at a rate of 10 °C/min (orange-colored shaded area: held at 240 °C for 15 min). (b) IR spectra of st_{rich}-**2** held at 240 °C for (i) 0, (ii) 5, and (iii) 15 min.

spectrum showed the appearance of a new vibration at 2103 cm^{-1} assignable to a dialkyl ketene species at the expense of the C═O stretching vibration at 1741 cm^{-1} due to the dialkyl Meldrum's acid pendants [Figure 3b(ii)]. After the sample was heated for 15 min, the vibration due to the dialkyl ketene species disappeared completely, while a new vibration at 1810 cm^{-1} assignable to a four-membered cyclic diketone emerged [Figure 3b(iii)]. The IR spectral changes thus observed are essentially the same as those reported for **3** and **4** upon heating.[10a] The TGA (Figure 3a) and IR spectral features (Figure S1)[13] of the reference polymers it_{rich}-**2** and $\mathbf{2}_{low}$ upon heating under conditions identical to the above were little different from those of st_{rich}-**2**, indicating that the stereochemical features of **2** do not affect its thermal decomposition and subsequent cross-linking profiles.[14] In DSC, neither st_{rich}-**2**, it_{rich}-**2**, nor $\mathbf{2}_{low}$ underwent a phase transition below the decomposition temperature (<150 °C) (Figure S2).[13]

PDMS stamps patterned with 700 nm wide stripes on their surface were fabricated by a soft lithography technique using a compact disk (CD) as a template (Figure S3).[13,15] For microcontact printing, the PDMS stamp thus obtained was placed in conformal contact and pressed for 1 min against liquid films of polymers **2** cast from 1 wt % CH_2Cl_2 solutions (10 μL) onto silicon wafers. As a result of the capillary force generated, the relief patterns on the PDMS stamp were transferred inversely to the resulting polymer films. For example, a printed film of st_{rich}-**2**, as observed by scanning electron microscopy (SEM; Figure 4a-i) and tapping-mode atomic force microscopy (AFM; Figure S4a-i), featured 700 nm wide and 100 nm thick stripes with an interstripe distance of 1600 nm.[13] As shown in Figure 4a-ii and Figure S4a-ii, these submicrometer-scale stripes, upon heating at 240 °C under air for 15 min, were maintained with a sufficiently small decrease in height from 100 to 70 nm.[13] Next, the resulting sample was immersed in CH_2Cl_2 at 25 °C, where the dimensional aspect of the stripes was perfectly preserved even after 1 h (Figure 4a-iii and Figure S5a).[13] In contrast, without the above-mentioned thermal treatment, the stripes were washed out completely upon immersion in CH_2Cl_2 (Figure S6).[13] These observations demonstrate that the thermal cross-linking proceeds successfully and makes the stripes insoluble and tolerant against solvolysis. For comparison, we prepared analogous stripe patterns by microcontact printing using

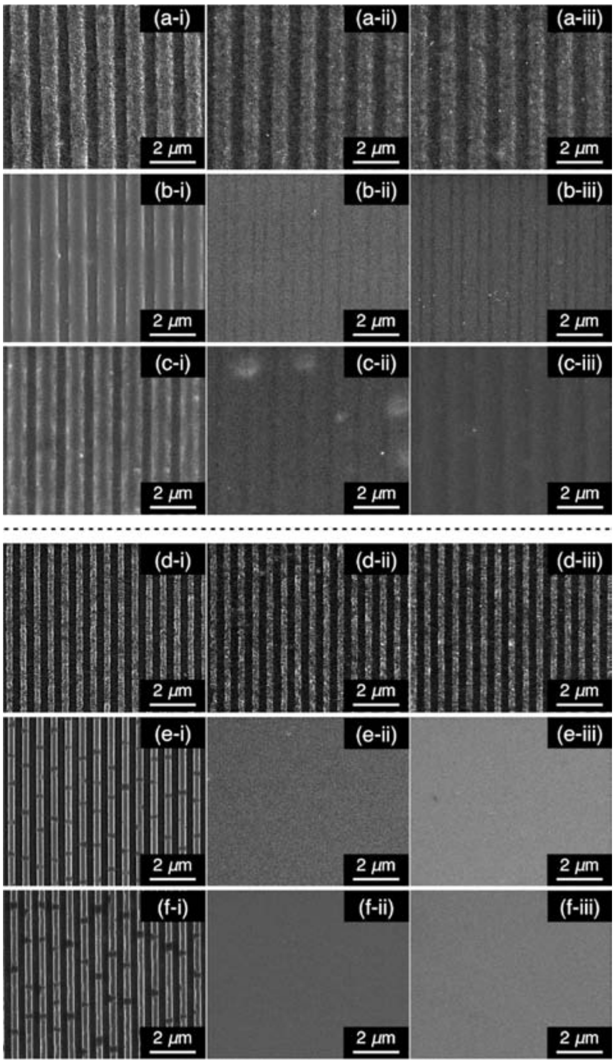

Figure 4. SEM micrographs of stripe patterns produced by microcontact printing on liquid films of (a, d) st_{rich}-**2**, (b, e) it_{rich}-**2**, and (c, f) $\mathbf{2}_{low}$: (i) as-obtained by printing; (ii) after heating at 240 °C for 15 min; (iii) after subsequent washing with CH_2Cl_2. The PDMS stamps for printing were prepared using (a−c) a CD (stripe width = 700 nm) and (d−f) a DVD (stripe width = 300 nm) as templates.

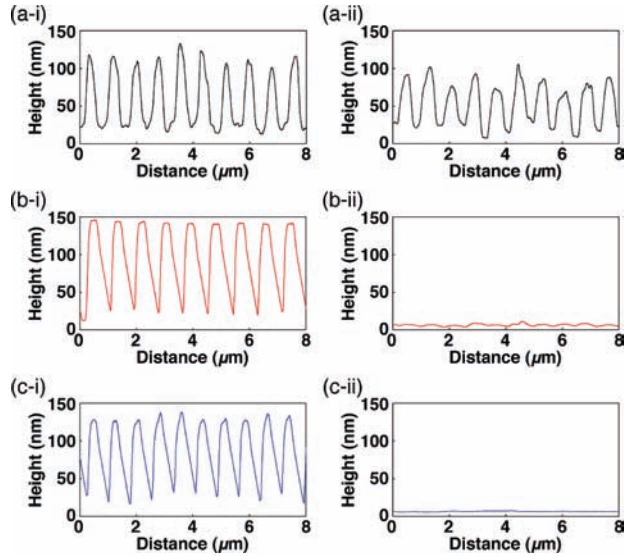

Figure 5. Cross-sectional height profiles (tapping-mode AFM) of stripe patterns produced by microcontact printing on liquid films of (a) st_{rich}-**2**, (b) it_{rich}-**2**, and (c) $\mathbf{2}_{\text{low}}$: (i) as-obtained by printing; (ii) after heating at 240 °C for 15 min. The PDMS stamps for printing were prepared using a DVD (stripe width = 300 nm) as a template.

it_{rich}-**2** (Figure 4b-i and Figure S4b-i)[13] and $\mathbf{2}_{\text{low}}$ (Figure 4c-i and Figure S4c-i)[13] instead of st_{rich}-**2** and attempted thermal cross-linking.[13] After the samples were heated at 240 °C for 15 min, these stripes collapsed considerably, resulting in an ~80% decrease in height (Figure 4b-ii and Figure S4b-ii for it_{rich}-**2** and Figure 4c-ii and Figure S4c-ii for $\mathbf{2}_{\text{low}}$),[13] although the residual stripes were likely cross-linked and maintained after immersion in CH_2Cl_2 for 1 h (Figure 4b-iii for it_{rich}-**2** and 4c-iii for $\mathbf{2}_{\text{low}}$).

The above contrasting results in dimensional stability are a powerful observation, considering that the thermal reactivities of the two reference polymers are little different from those of st_{rich}-**2**.[14] In general, cross-linking of polymeric materials is accompanied by a volume shrinkage. In the case of **2**, the effect of volume shrinkage upon thermal cross-linking is an extreme case, since decomposition of the dialkyl Meldrum's acid pendants of **2** prior to the cross-linking step is accompanied by elimination of CO_2 and acetone. For further comparison, we heated 700 nm wide stripe patterns printed with polymers **3** and **4**. Thermolysis of 700 nm wide stripes prepared with **3** (Figures S7a-i and S8a-i)[13] and **4** (Figures S7b-i and S8b-i),[13] afforded a nearly flat surface with a >95% decrease in height (Figures S7a-ii and S8a-ii for **3** and Figures S7b-ii and S8b-ii for **4**).[13] In order to address the interesting question of why the stripe patterns obtained using st_{rich}-**2** possess much better dimensional stability than the others upon heat-induced cross-linking, we should consider that this polymer adopts a barbed shape and even in dilute solution self-assembles into nanofibers with a diameter of ~10 nm by van der Waals interactions.[11] In fact, by taking a closer look at the stripes from st_{rich}-**2** (Figure 4a-i), one may recognize that they are composed solely of nanofibers and therefore porous. Such a porous architecture was maintained even after heating (Figure 4a-ii) followed by immersion in CH_2Cl_2 (Figure 4a-iii). When the sample is heated, the cross-linking reaction may occur preferentially within the individual nanofibers of st_{rich}-**2**. Consequently, while the nanofibers undergo shrinkage, this does not translate to macroscopic shrinkage because the stripes are porous and their dimensional integrity is only marginally affected by the volume shrinkage of the individual nanofibers. In sharp contrast with st_{rich}-**2**, none of the other polymers self-assembles into nanofibers, and the dense, bulk films undergo both nanoscopic as well as macroscopic shrinkage.

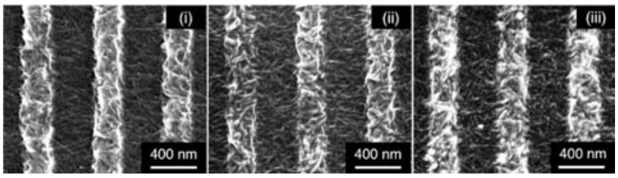

Figure 6. SEM micrographs of stripe patterns produced by microcontact printing on a liquid film of st_{rich}-**2**: (i) as-obtained by printing; (ii) after heating at 240 °C for 15 min; (iii) after subsequent washing with CH_2Cl_2. The PDMS stamp for printing was prepared using a DVD (stripe width = 300 nm) as a template.

In order to confirm the efficacy of this "nanofiber" strategy, we heated a much finer stripe pattern consisting of nanofibrous st_{rich}-**2** for thermal cross-linking. Thus, 300 nm wide stripes with a height of 90 nm and an interstripe distance of 700 nm (Figures 4d-i and 5a-i) were developed by microcontact printing with a PDMS stamp fabricated using a digital videodisk (DVD) as a template. When the pattern was heated at 240 °C for 15 min, the stripes maintained their dimensional integrity with a satisfactorily small decrease in height from 90 to 60 nm (Figures 4d-ii and 5a-ii). Furthermore, the resulting stripes neither disappeared nor deformed upon subsequent immersion in CH_2Cl_2 for 1 h (Figure 4d-iii and Figure S5b).[13] Again, the nanofibers of st_{rich}-**2** in the printed pattern (Figure 6i) were maintained after the thermal (Figure 6ii) and subsequent rinsing treatments (Figure 6iii). In sharp contrast, when 300 nm stripes were prepared with it_{rich}-**2** (Figures 4e and 5b), $\mathbf{2}_{\text{low}}$ (Figures 4f and 5c), **3** (Figures S7c and S8c),[13] or **4** (Figures S7d and S8d), they disappeared almost completely after only 15 min upon heating at 240 °C.[13]

In summary, being inspired by the clean cross-linking chemistry of Meldrum's acid derivatives,[10] we investigated the potential utilities of the cycloolefin polymers st_{rich}-**2**,[11] it_{rich}-**2**,[12] and $\mathbf{2}_{\text{low}}$[11] with different stereochemical structures as cross-linkable inks for microcontact printing. The results clearly demonstrate that nanofiber-forming st_{rich}-**2**, which is rich in *threo*-disyndiotactic sequences, is much better than the other polymers with respect to pattern stability upon thermal cross-linking. Volume shrinkage upon heat-induced cross-linking of polymers in submicrometer-scale tiny patterns is a general problem, and this issue is particularly serious when the cross-linking is accompanied by the elimination of volatile fragments. In this context, the idea of using nanofibrous cross-linkable polymer inks, which minimize the negative effects of volume shrinkage and thereby retain their structural integrity, is a powerful strategy amenable to application in lithography, membrane formation, and other fields.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** IR and DSC profiles of **2**, TGA and DSC profiles of **3** and **4**, preparation and characterization of PDMS stamps and stripe patterns developed by microcontact printing on liquid films of **2**−**4**, and complete ref 2b. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) As observed by IR spectroscopy, the ketene species thermally generated from $\mathbf{2}_{\mathrm{low}}$ was consumed slightly less smoothly than those from st_{rich}-**2** and it_{rich}-**2** (Figure S1).[13]

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