# Thermally Induced Nanoimprinting of Biodegradable Polycarbonates Using Dynamic Covalent Cross-Links

Wiriya Thongsomboon,[†] Mark Sherwood, Noel Arellano, and Alshakim Nelson*

IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120, United States

S Supporting Information

ABSTRACT: The introduction of reversible covalent bonds into polymeric systems afford robust, yet dynamic, materials that can respond to external stimuli. A series of aliphatic polycarbonate polymers were synthesized via ring-opening polymerization of furanyl and maleimido-bearing cyclic carbonate monomers. These side chains undergo thermally induced Diels−Alder reactions to afford cross-linked films. Because both the diene and dienophile were incorporated into the same polymer backbone, a protected maleimido group, in the form of the furan adduct, was used. Both the forward and reverse Diels−Alder reaction are triggered thermally, which allows the deprotection of the maleimido group and the subsequent reaction with the furanyl side chains to form cross-links. Random copolymers and poly(ethylene glycol) containing block copolymers were formed using diazabicyclo[5.4.0]undec-7-ene as the catalyst and a thiourea cocatalyst. The polymers form uniform films that can be cross-linked in the bulk state. To further illustrate the dynamic nature of the covalent bonds within the cross-linked films, a patterned silicon mold was used to transfer a series of nanoscale patterns using a thermal nanoimprint process.
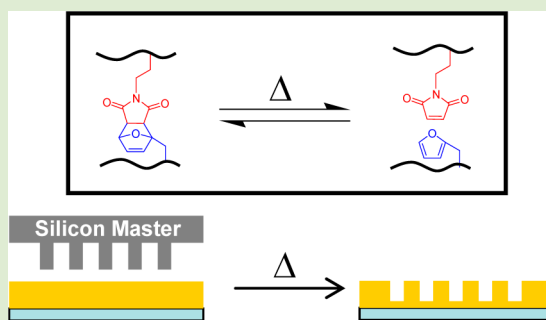
Aliphatic polycarbonates are biodegradable polymers that are of significant interest to biomedical and packaging industries.[1,2] These polymers inherently have a low T_g and, thus, are typically used as additives or in segmented polyurethanes.[3] One route to altering the mechanical properties, thermal stability, and solvent resistance of these polymeric materials is by chemical cross-linking.[4] Ideally, the polymer is first manipulated and processed freely prior to initiating the cross-linking reaction via an external stimulus such as heat or light. Many cross-linking polymeric materials are processed with additives such as small-molecule cross-linkers or catalysts, which require further purification to remove unreacted compounds after the reaction has taken place. Alternatively, a simpler system would involve a single copolymer with stimuli reactive functionalities as side chains to afford the cross-linked material. In both cases, versatile synthetic protocols are necessary to incorporate the cross-linking functionalities into aliphatic polycarbonates.

Several methodologies have been developed[5−10] to enable controlled living polymerization to afford polycarbonates that vary in physical properties and chemical functionalities. Organocatalytic approaches[10] are particularly appealing as they avoid the use of metal species that are often difficult to remove from the resulting product. Cyclic carbonate monomers[11] are typically ring-opened during the polymerization process. A particularly useful building block for carbonate monomers is 2,2-bis(methylol)propionic acid (bis-MPA), which can afford carbonate monomers with a wide range of chemical groups.[12−15] As a result, functionalized aliphatic carbonates are of interest for biomedical surface coating applications,[16,17] wherein the functional groups allow cellular interactions to be tailored or mediated.[18] In some particular cases, nanopatterned biodegradable coatings are of interest to control or mediate cell growth on a surface, as cells are known to be sensitive to the topography of the surface.[19,20]

The integration of dynamic covalent chemistry (DCC)[21−23] into polymeric systems yields an intriguing set of materials with the ability to respond to external stimuli. Reversible covalent bonds provide robust linkages that can adapt or reorganize on demand. As a result, these polymeric materials can be made to be self-healing, responsive to changes in pH, or afford a reversibly assembling micelle.[24−31] Examples of reversible covalent bonds and reactions that have been incorporated into polymeric materials include Diels−Alder adducts, imines, disulfides, and boronic acids.[21−31] These dynamic covalent bonds offer a useful platform for reversibly cross-linking polymers under relatively mild conditions. Diels−Alder reactions between a diene and dienophile have proven particularly useful for forming dynamic covalent bonds which can selectively be formed or broken in response to thermal stimuli without the aid of an additional catalyst.[32−35] For example, Chujo et al. reported the reversible cross-linking of a polymeric blend comprised of a polymer with furanyl side chains and second polymer with maleimido side chains. The forward reaction occurred at ambient temperatures that could

be reversed when the sample was heated to temperatures above 80 °C.[36]

Herein, we demonstrate the cross-linking, and subsequent imprinting, of an aliphatic polycarbonate copolymer using reversible Diels−Alder adduct formation. To develop the simplest possible polymer system, furanyl and maleimido side chains were incorporated into a single random copolymer, as this approach provides a catalyst-free method to thermally cross-link these polymers under mild conditions without the need of additives. To prevent premature Diels−Alder reactions between the polymer side chains, a maleimido group protected by furan was employed. The protecting group can be removed thermally in situ to expose the maleimide functionality[10] and allow the cross-linking reaction to proceed. We further demonstrate that the dynamic bonds of this system can be employed to thermally imprint submicrometer features onto the cross-linked film.

The monomers 1−3 were readily synthesized from bis-MPA and did not require column purification. The details for the synthesis of the bis-MPA derived monomers are provided in the Supporting Information. Random copolymerizations (Scheme 1) of the cyclic carbonates 1−3 were conducted

**Scheme 1. Synthesis of Polycarbonate Polymers**
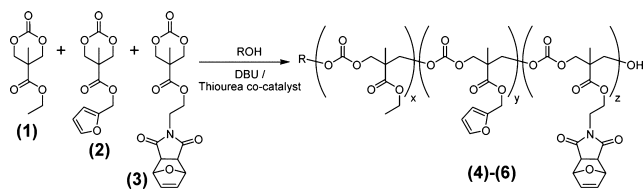
using an organocatalytic procedure with diazabicyclo[5.4.0]-undec-7-ene (DBU) as the catalyst and a thiourea cocatalyst. This versatile polymerization enables the controlled living ring-opening polymerization of cyclic carbonates initiated from alcohols. A series of polymers were synthesized via initiation from 2,2-bis(hydroxymethyl)propionic acid benzyl ester, poly-(ethylene glycol) monomethyl ether (mPEG), or poly(ethylene glycol) (PEG) and characterized using NMR spectroscopy and gel permeation chromatography (GPC). The ratios of the monomers were varied to control the number of cross-linkable sites that were introduced into the polymer. As shown in Table 1, the resulting ratios of the monomers incorporated into the polymer largely reflected the feed ratio of the reaction. The

Table 1. Results from Organocatalytic Copolymerization of Monomers 1−3

polymer	feed ratio[d] (x, y, z)	actual ratio[e] (x, y, z)	$M_n{}^e$ (kg/mol)	PDI[f]
4a[a]	80:10:10	51:6:6	13.4	1.15
4b[a]	80:10:10	68:8:8	17.8	1.26
4c[a]	80:10:10	72:7:8	12.6	1.16
4d[a]	240:30:30	235:22:25	58.5	1.19
4e[a]	50:25:25	59:21:21	23.6	1.27
4f[a]	150:75:75	52:16:17	19.7	1.22
5[b]	50:25:25	60:23:24	36.0	1.21
6[c]	80:10:10	77:7:8	32.7	1.20

[a]Copolymers initiated from diol. [b]Copolymer initiated from 5k mPEG. [c]Copolymer initiated from 6k PEG diol. [d]Molar ratio of monomer relative to 1 mol equiv of initiator. [e]Determined by ^{1}H NMR spectroscopy. [f]Determined by GPC.

polydispersity index remained low (<1.2) over a range of molecular weights as a consequence of the living nature of the polymerization. When the monomers were initated from 2,2-bis(hydroxymethyl)propionic acid benzyl ester, a linear random copolymer was formed. Initiation from mPEG or PEG afforded a diblock or triblock copolymer, respectively, comprised of a PEG block and a poly(carbonate) block (Figure 1).
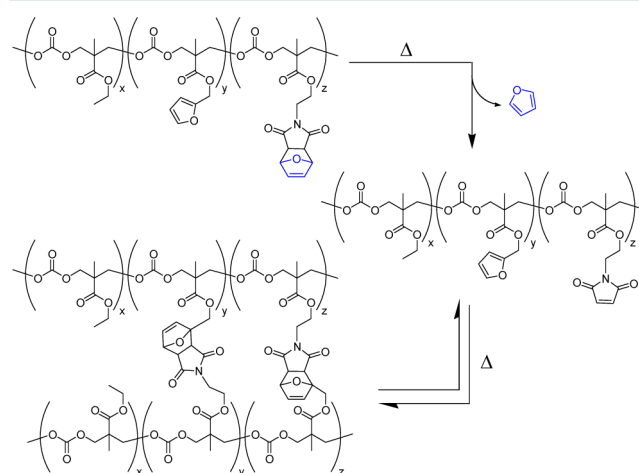
Figure 1. Reversible covalent bond formation leads to deprotection and subsequent cross-linking in the film.

We next investigated the thermally induced cross-linking of the polymers in the solid state. Solutions of the polymer were spin-coated onto silicon wafers or cast into Teflon molds to afford films. Wudl and co-workers previously reported[24] that similar systems undergo reverse Diels−Alder reaction at temperatures above 120 °C. Thus, the polymer films were baked at 130 °C for 1 h in order to initate the reverse Diels−Alder reaction to deprotect the maleimido groups of the polymer.

The films were then baked at 90 °C overnight to enable cross-linking of the film via the forward Diels−Alder reaction between the maleimido and furanyl side chains of the polymer. Polymer 4e was analyzed by ^{13}C CPMAS NMR, as shown in Figure 2. In an analysis of a model reaction in solution between furan and methylmaleimide (Supporting Information), we
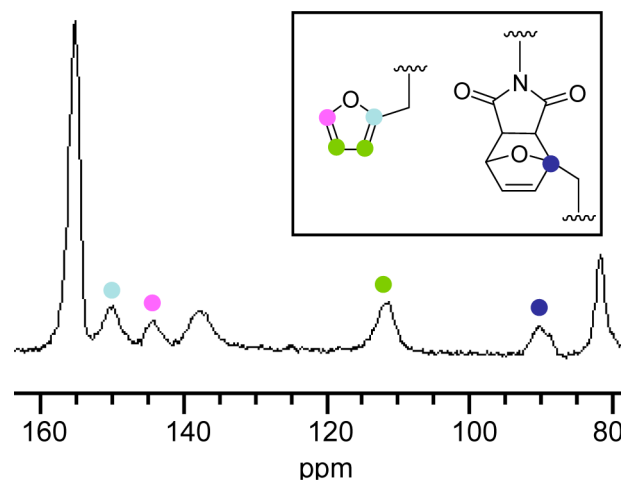
Figure 2. Partial ^{13}C CPMAS NMR spectrum of the cross-linked polymer film.

observed that a resonance at 90 ppm emerges as the adduct was formed. A similar peak was observed in the solid-state NMR spectrum of the baked polymer film which suggests that the cross-linking reaction has occurred. The NMR analysis also shows that residual unreacted furan still remains after the film was cross-linked. Free standing films were also formed using this process. In the case of polymers **5** and **6**, elastomeric films were obtained.

As shown in Figure 3, the reversible nature of the Diels–Alder reaction enables us to remold the film even after the film
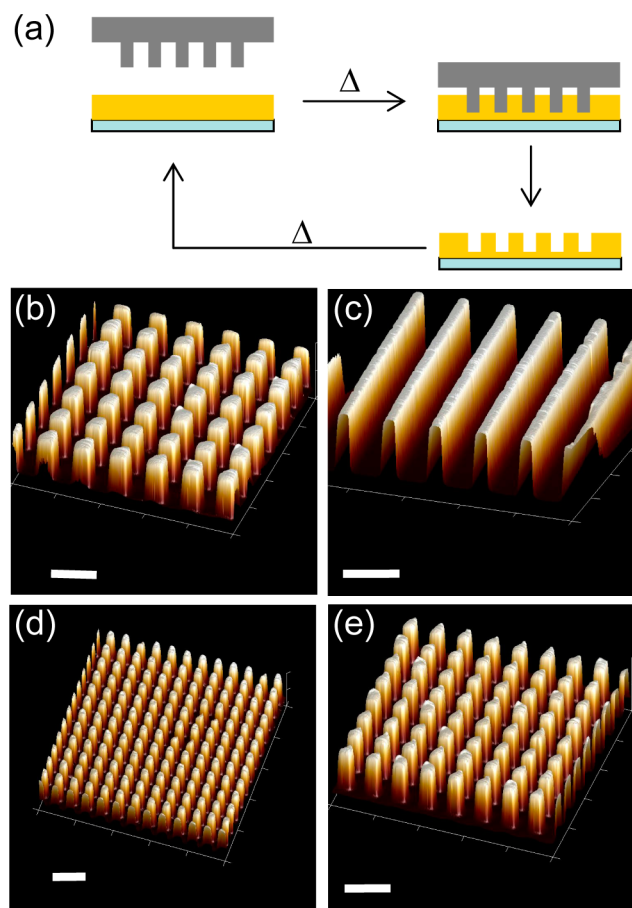
Figure 3. (a) Process for imprinting the polycarbonate film both in the presence and absence of the master template. AFM images (3D rendered) of imprinted post and line/space features formed from polymer **4e** (b–d) and polymer **6** (e). Scale bar represents 1 μm.

has been cross-linked. To demonstrate this process, polymer **4e**[37] was spin-coated onto a silicon wafer and thermally cross-linked. A silicon master was then used in a thermal nanoimprint process to transfer the pattern from the master to the cross-linked polycarbonate film. At ambient temperatures, the film can not be patterned as a consequence of the covalent cross-linking between the polymer chains. However, upon heating the film to 130 °C, the silicon master could be used to remold the film to afford a patterned substrate. As shown in Figure 3, submicrometer features were transferred in this thermal imprint process. Arrays of line/spaces and free-standing posts were formed from the random and block copolymers. Although the patterns are robust at ambient temperatures, the covalent cross-linking sites within the film are still reversible. When the patterned films were baked at 130 °C, the patterns disappeared, as the covalent bonds were broken and a featureless film was

restored. Moreover, changes to the pattern shape, either during the imprint process or afterward, were not observed unless elevated temperatures were used. Heath et al. have investigated[34] thermally labile Diels–Alder linkages to afford strippable materials for imprint lithography, but did not utilize the reversibility of the reaction to transfer a pattern from the mold to the substrate. To the best of our knowledge, this is the first time that dynamic covalent chemistry has been demonstrated for a nanoimprint process for transferring patterns into films.

In conclusion, we have successfully demonstrated the catalyst free cross-linking of a biodegradable polycarbonate film. Random copolymers and block copolymers were synthesized via living organocatalytic routes to afford aliphatic polycarbonates with furanyl and maleimido side chains. These polymers form films which undergo reversible covalent bond formation via Diels–Alder chemistry under mild thermal conditions. Both the cross-linked and un-cross-linked films were patterned using a thermal nanoimprint process. The reversibility of the Diels–Alder adducts enabled the cross-linked films to be remolded to the form of the template to afford features as small as 500 nm.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental procedures and selected ^{1}H NMR and ^{13}C spectra of monomers and copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: alshak@us.ibm.com.

Present Address
†Department of Chemistry, University of Chicago, Chicago, IL.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618–6639.
(2) Tempelaar, S.; Mespouille, L.; Coulembier, O.; Dubois, P.; Dove, A. P. *Chem. Soc. Rev.* **2012**, DOI: 10.1039/c2cs35268k.
(3) Thorat, S. D.; Phillips, P. J.; Semenov, V.; Gakh, A. *J. Appl. Polym. Sci.* **2003**, *89*, 1163–1176.
(4) Tillet, G.; Boutevin, B.; Ameduri, B. *Prog. Polym. Sci.* **2011**, *36*, 191–217.
(5) Endo, T.; Shibasaki, Y.; Sanda, F. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2190–2198.
(6) Varma, I. K.; Albertsson, A.-C.; Rajkhowa, R.; Srivastava, R. K. *Prog. Polym. Sci.* **2005**, *30*, 949–981.
(7) Matsumura, S. *Adv. Polym. Sci.* **2006**, *194*, 95–132.
(8) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* **2007**, *107*, 5813–5840.
(9) Kobayashi, S. *Macromol. Rapid Commun.* **2009**, *30*, 237–266.
(10) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43*, 2093–2107.

(11) Rokicki, G. *Prog. Polym. Sci.* **2000**, *25*, 259−342.

(12) Sanders, D. P.; Fukushima, K.; Coady, D. J.; Nelson, A.; Fujiwara, M.; Yasumoto, M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2010**, *132*, 14724−14726.

(13) Williams, R. J.; Barker, I. A.; O'Reilly, R. K.; Dove, A. P. *ACS Macro Lett.* **2012**, *1*, 1285−1290.

(14) Stevens, D. M.; Tempelaar, S.; Dove, A. P.; Harth, E. *ACS Macro Lett.* **2012**, *1*, 915−918.

(15) Pratt, R. C.; Nederberg, F.; Waymouth, R. M.; Hedrick, J. L. *Chem. Commun.* **2008**, 114−116.

(16) Ding, X.; Yang, C.; Lim, T. P.; Hsu, L. Y.; Engler, A. C.; Hedrick, J. L.; Yang, Y.-Y. *Biomaterials* **2012**, *33*, 6593−6603.

(17) Liu, S. Q.; Yang, C.; Huang, Y.; Ding, X.; Li, Y.; Fan, W. M.; Hedrick, J. L.; Yang, Y. Y. *Adv. Mater.* **2012**, DOI: 10.1002/adma.201202225

(18) Killops, K. L.; Gupta, N.; Dimitriou, M. D.; Lynd, N. A.; Jung, H.; Tran, H.; Bang, J.; Campos, L. M. *ACS Macro Lett.* **2012**, *1*, 758−763.

(19) Yim, E. K. F.; Reano, R. M.; Pang, S. W.; Yee, A. F.; Chen, C. S.; Leong, K. M. *Biomaterials* **2005**, *26*, 5405−5413.

(20) Truskett, V. N.; Watts, M. P. C. *Trends Biotechnol.* **2006**, *24*, 312−317.

(21) Lehn, J.-M. *Chem.—Eur. J.* **1999**, *5*, 2455.

(22) (a) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 898−952. (b) Kloxin, C. J.; Scott, T. F.; Adzima, B. J.; Bowman, C. N. *Macromolecules* **2010**, *43*, 2643−2653.

(23) Corbett, P. T.; Leclaire, J.; Vial, L.; West, K. R.; Wietor, J.-L.; Sanders, J. K. M.; Otto, S. *Chem. Rev.* **2006**, *106*, 3652.

(24) (a) Chen, X. X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H. B.; Nutt, S. R.; Sheran, K.; Wudl, F. *Science* **2002**, *295*, 1698. (b) Bapat, A. P.; Ray, J. G.; Savin, D. A.; Hoff, E. A.; Patton, D. L.; Sumerlin, B. S. *Polym. Chem.* **2012**, *3*, 3112−3120.

(25) Adzima, B. J.; Kloxin, C. J.; Bowman, C. N. *Adv. Mater.* **2010**, *22*, 2784−2787.

(26) Jackson, A. W.; Stakes, C.; Fulton, D. A. *Polym. Chem.* **2011**, *2*, 2500−2511.

(27) Bapat, A. P.; Roy, D.; Ray, J. G.; Savin, D. A.; Sumerlin, B. S. *J. Am. Chem. Soc.* **2011**, *133*, 19832−19838.

(28) Roy, D.; Sumerlin, B. S. *ACS Macro Lett.* **2012**, *1*, 529−532.

(29) Jackson, A. W.; Fulton, D. A. *Macromolecules* **2012**, *45*, 2699−2708.

(30) Imbesi, P. M.; Fidge, C.; Raymond, J. E.; Cauet, S. I.; Wooley, K. L. *ACS Macro Lett.* **2012**, *1*, 473−477.

(31) Deng, G.; Li, F.; Yu, H.; Liu, F.; Liu, C.; Sun, W.; Jiang, H.; Chen, Y. *ACS Macro Lett.* **2012**, *1*, 275−279.

(32) Durmaz, H.; Colakoglu, B.; Tunca, U.; Hizal, G. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1667−1675.

(33) Dispinar, T.; Sanyal, R.; Sanyal, A. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4545−4551.

(34) Heath, W. H.; Palmieri, F.; Adams, J. R.; Long, B. K.; Chute, J.; Holcombe, T. W.; Zieren, S.; Truitt, M. J.; White, J. L.; Willson, C. G. *Macromolecules* **2008**, *41*, 719−726.

(35) Onbulak, S.; Tempelaar, S.; Pounder, R. J.; Gok, O.; Sanyal, R.; Dove, A. P.; Sanyal, A. *Macromolecules* **2012**, *45*, 1715−1722.

(36) Chujo, Y.; Sada, K.; Saegusa, T. *Macromolecules* **1990**, *23*, 2636−2641.

(37) The copolymers synthesized in these experiments had glass-transition temperatures (T_g) ranging from 15 to 25 °C, as determined by differential scanning calorimetry (DSC).