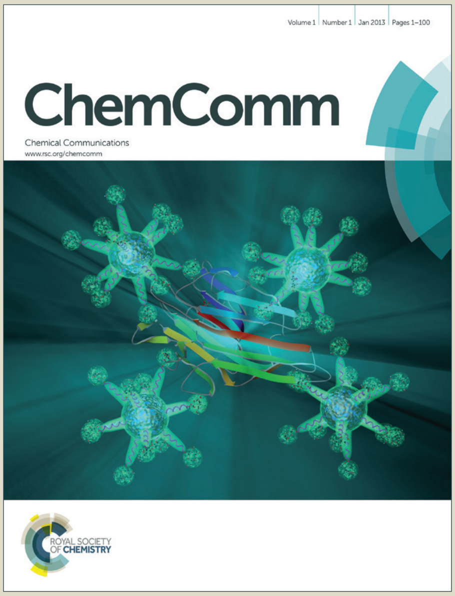
# ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

ChemComm

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

**COMMUNICATION**

# Multivalent hydrogen bonding block copolymers self-assemble into strong and tough self-healing materials

Yulin Chen[a] and Zhibin Guan*

*Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX*

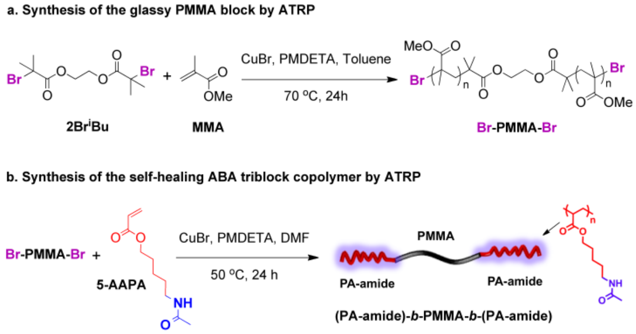
**DOI: 10.1039/b000000x**

**Triblock copolymers having glassy PMMA block and dynamic hydrogen bonding blocks were synthesized by sequential atom transfer radical polymerization (ATRP). The dynamic triblock copolymers self-assemble into nanocomposite materials exhibiting a combination of mechanical strength, toughness, and self-healing capability.**

Self-healing materials have attracted much attention recently because they can potentially improve the safety, lifetime, energy efficiency, and environmental impact of manmade materials. During the last decade, there are many exciting advances in the development of self-healing polymeric materials.[1] A number of important strategies, including encapsulation of healing agents[2] and employment of irreversible[3] and reversible[4] covalent chemistry, have been reported for self-healing polymers. Due to their inherent dynamics, various supramolecular interactions, such as hydrogen-bonding,[5] π-π stacking,[6] metal-ligand interactions,[7] and ionic interactions,[8] have been widely used to prepare novel self-healing materials.

For most supramolecular self-healing materials, there is often a trade-off between mechanical properties and dynamic healing: strong interactions result in stiff but less dynamic systems, precluding autonomous healing, while weak interactions afford dynamic healing, but yield relatively weak materials.[9] To address this conundrum, our laboratory has proposed a multiphase concept for self-healing materials design, in which the hard phase provides stiffness and strength to the material while the multivalent supramolecular interactions in the soft matrix enable autonomous self-healing.[5c] The key for our design is to program dynamic supramolecular interactions into the soft phase, preserving the dynamic nature of supramolecular interactions for autonomic healing. By applying such multiphase concept, we were able to obtain materials that are mechanically robust and truly self-healing without the need of any additives, healing agents, or external stimuli.[5c] We have demonstrated this concept in a few multiphase polymer systems including hydrogen-bonding brush copolymers,[5c] block copolymers,[5d] and core-shell nanoparticles.[10] Despite these progresses, it remains a challenge to design self-healing materials that are both stiff and tough. Here we report novel self-healing block copolymers to address this problem.

In our previously reported self-healing block copolymer design, a single quadruple hydrogen-bonding motif, 2-ureido-4-pyrimidinone (UPy), was introduced to each diblock copolymer chain end to facilitate dynamic self-healing.[5d] While the quadruple UPy:UPy interaction is relatively strong, a single supramolecular motif per chain limits the ultimate strength of the material. The synthesis of that material is also laborious. To address these issues, in this study we report a simple ABA triblock copolymer architecture by employing multivalent, pervasive hydrogen bonds in soft blocks as dynamic self-healing motif (Scheme 1). Through this design, we can achieve self-healing materials with a combination of strength, toughness, and self-healing capability.



**Scheme 1** Synthesis of self-healing ABA triblock copolymers by atom transfer radical polymerization. Self-healing block copolymers were synthesized by sequential polymerization of MMA (a) and **5-AAPA** (b) monomers. PMDETA = N, N, N', N', N''-pentamethyldiethylenetriamine, DMF = dimethylformamide.

We chose the well-established atom transfer radical polymerization (ATRP)[11] to synthesize our block copolymers. Following a literature procedure, a bifunctional initiator, ethylene glycol bis(2-bromoisobutyrate) (**2Br$^i$Bu**),[12] was used to first polymerize methyl methacrylate (MMA) to form a glassy, telechelic PMMA block (Scheme 1a). The number average molecular weight ($M_n$) of the PMMA was controlled at 49.2 kDa with a polydispersity of 1.19 as measured by GPC with PMMA standards.

Using the telechelic PMMA as macroinitiator, subsequent ATRP of our previously reported 5-acetylaminopentyl acrylate (**5-AAPA**) monomer[5c] grew two soft poly(acrylate amide) (PA-amide) end blocks to form the desired ABA triblock copolymers (Scheme 1b). Three block copolymers with different soft PA-amide block length were prepared by controlling both the feed ratio and the conversion of the **5-AAPA** monomer (Table 1 and Supporting Information). The molecular weights for the block copolymers were determined by multi-angle laser light scattering (MALLS) following size-exclusion chromatography (SEC). The number-average molecular weights ($M_n$) were in good agreement with the values estimated from the monomer conversion measured by $^1$H NMR. The molar ratio of the monomeric units in PMMA and PA-amide blocks was further confirmed by $^1$H NMR after the block copolymers were purified and dried (Supporting Information). The ratio of the total monomeric repeating units in soft PA-amide block to the hard PMMA block ranges from 1.8 (**BCP1**) to 1.1 (**BCP3**). The weight percentage of the hard PMMA component in the overall block copolymers was 22, 26 and 32% for **BCP1**, **BCP2** and **BCP3**, respectively.

**Table 1** Polymerization results of the block copolymers **BCP1-3**

| | Conversion[a] (%) | PA-amide chain length[b] | $M_n$[c] (kg/mol) | $M_n$[d] (kg/mol) | PDI[d] |
|---|---|---|---|---|---|
| **BCP1** | 35 | 430 | 220 | 214 | 1.35 |
| **BCP2** | 39 | 360 | 192 | 190 | 1.36 |
| **BCP3** | 26 | 260 | 153 | 151 | 1.35 |

[a] Monomer conversion measured by $^1$H NMR. [b] The single PA-amide block length. [c] The molecular weight estimated by monomer conversion. [d] Molecular weight data determined by SEC-MALLS.

The morphology of the block copolymers was investigated by tapping mode atomic force microscopy (AFM) on thin films. For **BCP1**, the AFM image clearly showed a microphase-separated morphology with the PMMA domain (~30 nm) dispersed in the soft matrix (Figure 1a). However, for **BCP3**, which has shorter PA-amide blocks, aggregates of spherical nanoparticles were observed (Figure S1). Presumably, during the solvent evaporation process, the hydrophobic PMMA block collapsed into the cores which were wrapped by polar PA-amide blocks to form core-shell spherical nanoparticles that further self-assemble into nanocomposite.[13] Such nanocomposite morphology is desirable for the bulk properties: the rigid, glassy PMMA core provides the stiffness to the material while the dynamic PA-amide layer on the nanoparticle surface enables self-healing. For comparison, a linear PA-amide with about 200 repeat units[10] forms smooth film without any morphological feature (Fig. 1b).

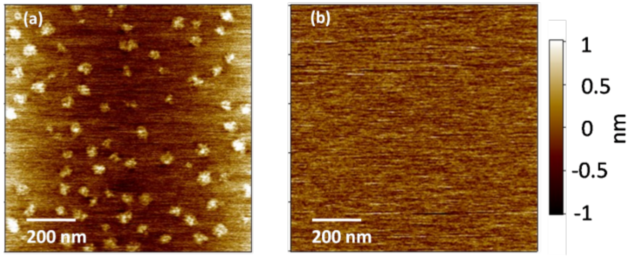


**Fig. 1** AFM images showing morphologies of thin films of the block copolymer **BCP1** (a) and the linear PA-amide with ~200 repeat units (b).

Tensile testing was carried out to evaluate the mechanical properties of the block copolymers. The stress-strain curves of the three block copolymers were plotted in Figure 2a and their key mechanical properties summarized in Table 2. By adjusting the length of the PA-amide block, the mechanical properties can be easily tuned. By increasing the PA-amide chain length and accordingly the weight fraction of the soft block in bulk, the material becomes less strong and more elastomeric (**BCP1**). On the contrary, increasing the weight fraction of PMMA by shortening the PA-amide block makes the material stronger but less elastomeric (**BCP3**). As typical for hard/soft nanocomposites, the stiffness and strength of the material increases with the weight fraction of the hard phase. For example, **BCP1** with 22 wt% of PMMA has a Young's modulus of ~26 MPa, maximal strength of ~4.38 MPa, and strain-at-break of ~750%. In contrast, **BCP3** with 32 wt% of PMMA has a Young's modulus of ~77 MPa, maximal strength of ~6 MPa, and strain-at-break of ~300%. This family of materials are significantly stronger than our previously reported self-healing brush[5c] or block[5d] copolymers (Table 2). In addition, creep and stress relaxation tests (Figure S2 and S3) showed that the block copolymers exhibit reasonable creep resistance. The high yield strength and large strain-at-break also makes the block copolymers very tough materials.

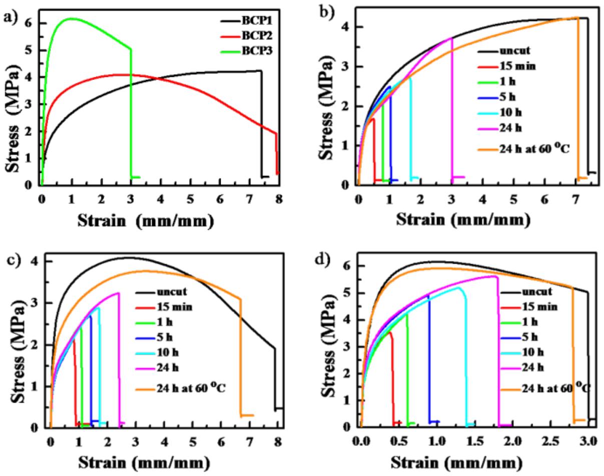


**Fig. 2** Mechanical properties of block copolymers. (a) The stress-strain curves of the pristine specimens of the block copolymers **BCP1-3**. The mechanical properties of the block copolymers were tunable by changing the relative length of between the hard and soft blocks. (b)-(d): Self-healing tests for the block copolymers **BCP1-3**. The separate halves of the specimens obtained from cutting were brought together for one minute and allowed to heal for various times at room temperature or at 60 °C as indicated in the graph: (b) for **BCP1**; (c) for **BCP2**; (d) for **BCP3**. The uniaxial pulling rate was 100 mm/min for all tests.

**Table 2** Mechanical properties of the block copolymers **BCP1-3**

| Sample name | Young's modulu (MPa) | Maximal strength[a] (MPa) | Breaking strength (MPa) | Breaking strain (mm/mm) |
|---|---|---|---|---|
| **BCP1** | 26.3±1.2 | 4.38±0.28 | 4.30±0.36 | 7.32±0.43 |
| **BCP2** | 39.2±3.3 | 4.13±0.09 | 1.70±0.34 | 8.08±0.25 |
| **BCP3** | 77.1±5.9 | 6.07±0.17 | 4.97±0.10 | 3.16±0.31 |

[a] Strength taken at maximal point along the stress-strain curves.

Thermal analysis was performed to investigate the chain mobility of the block copolymers at room temperature. The glass transition temperatures ($T_g$) observed for the soft PA-amide block in **BCP1-3** was ~ 2-4 °C, indicating that the PA-amide chains were highly mobile at room temperature. Since the PA-amide blocks carry the multivalent hydrogen bonding amide groups, the dynamics in the soft phase should facilitate self-assembly and self-healing for the block copolymers.

Following our standard protocol,[5c-d] self-healing tests were conducted by cutting sample specimens into two halves with a razor blade followed by bringing the cut surfaces into contact for one minute and then healing for a certain time. The self-healing test results were summarized in Figure 2b-d. For all samples, the healing specimens were able to regain the initiate stiffness (Young's modulus) as indicated by the good overlap of the initial region of stress-strain curves between the healed and pristine samples. As observed in previous systems,[5] the healing process takes time. Prolonging the healing time led to better recovery for both tensile strength and extensibility of the specimens. After healing at room temperature for 24 h without any treatment, the samples recovered 30-60% of their extensibility and 70-90% of their ultimate strength. The most elastomeric sample, **BCP1**, had the highest absolute value of strain recovery, ~300% (Figure 2b, purple curve). The strongest sample, **BCP3**, regained the highest value of tensile strength, ~5 MPa, after healing at room temperature for 24 h (Figure 2d, purple curve). To further improve the healing efficiency, we carried out self-healing tests with moderate heating. After healing at 60 °C for 24 hours, all three samples almost quantitatively recovered the mechanical properties (Figure 2b-d, brown curves). Understandably, the increased molecular dynamics at elevated temperature should facilitate the healing process.

In summary, we have synthesized a series of ABA block copolymers composed of a rigid PMMA middle block and two dynamic terminal blocks carrying multivalent, pervasive hydrogen bonds. The mechanical properties of the block copolymers were tunable by simply adjusting the chain length of the soft blocks. AFM imaging indicates the block copolymers self-assemble into spherical microphase-separated morphology. The hydrogen bonding block copolymers exhibit a combination of mechanical properties and self-healing capability. Compared to previously reported self-healing polymers based on hydrogen bonding interactions, the current system demonstrates significant improvement in mechanical properties. The easy synthesis and versatility also renders this approach general applicability to the design of different block copolymers carrying various supramolecular interaction motifs for further development of advanced self-healing materials.

## Acknowledgements

We acknowledge the financial support from the US National Science Foundation (award no. DMR-1217651), the US Department of Energy, Division of Materials Science (award no. DE-FG02-04ER46162), and Kuraray Co., Ltd. Y. C. acknowledges the UC Regent's Dissertation Fellowship.

## Notes and references

*Department of Chemistry, University of California, 1102 Natural Sciences 2, Irvine, CA 92697, USA. Fax: +1 9498242210; Tel: +1 9498245172; E-mail: zguan@uci.edu*
[a] *Current address: Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

† Electronic Supplementary Information (ESI): Experimental details of synthesis and characterization of block copolymers. See DOI: 10.1039/b000000x/

1 (a) S. R. White, M. M. Caruso, J. S. Moore, *MRS Bull.*, 2008, **33**, 766−769; (b) I. P. Bond, R. S. Trask, H. R. Williams, *MRS Bull.*, 2008, **33**, 770−774; (c) E. B. Murphy, F. Wudl, *Prog. Polym. Sci.*, 2010, **35**, 223−251; (d) S. Burattini, B. W. Greenland, D. Chappell, H. M. Colquhoun, W. Hayes, *Chem. Sov. Rev.*, 2010, **39**, 1973−1985; (e) N. K. Guimard, K. K. Oehlenschlaeger, J. Zhou, S. Hilf, F. G. Schmidt, C. Barner-Kowollik, *Macromol. Chem. Phys.*, 2012, **213**, 131−143.

2 (a) S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R Kessler, S. R. Sriram, E. N. Brown, S. Viswanathan, *Nature*, 2001, **409**, 794−797; (b) K. S. Toohey, N. R. Sottos, J. A. Lewis, J. S. Moore, S. R. White, *Nat. Mater.* 2007, **6**, 581−585.

3 (a) B. Ghosh, M. W. Urban, *Science*, 2009, **323**, 1458−1460; (b) B. Ghosh, K. V. Chellappan, M. W. Urban, *J. Mater. Chem.*, 2011, **21**, 14473-14486.

4 (a) X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran, F. Wudl, *Science*, 2002, **295**, 1698−1702; (b) X. Chen, F. Wudl, A. K. Mal, H. Shen, S. R. Nutt, *Macromolecules*, 2003, **36**, 1802−1807; (c) E. B. Murphy, E. Bolanos, C. Schaffner-Hamann, F. Wudl, S. R. Nutt, M. L. Auad, *Macromolecules*, 2008, **41**, 5203−5209; (d) P. Reutenauer, E. Buhler, P. J. Boul, S. J. Candau, J. -M. Lehn, *Chem. Eur. J.*, 2009, **15**, 1893−1900; (e) C. Chung, Y. Roh, S. Cho, J. Kim, *Chem. Mater.* 2004, **16**, 3982−3984; (f) J. Ling, M. Z. Rong, M. Q. Zhang, *J. Mater. Chem.*, 2011, **21**, 18373−18380; (g) J. Ling, M. Z. Rong, M. Q. Zhang, *Polymer*, 2012, **53**, 2691−2698; (h) K. Imato, M. Nishihara, T. Kanekara, Y. Amamoto, A. Takahara, H. Otsuka, *Angew. Chem. Int. Ed.*, 2012, **51**, 1138−1142; (i) C. Yuan, M. Z. Rong, M. Q. Zhang, Z. P. Zhang, Y. C. Yuan, *Chem. Mater.*, 2011, **23**, 5076−5081; (j) Y. Amamoto, J. Kamada, H. Otsuka, A. Takahara, K. Matyjaszewski, *Angew. Chem. Int. Ed.*, 2011, **50**, 1660−1663; (k) Y. Amamoto, H. Otsuka, A. Takahara, K. Matyjaszewski, *Adv. Mater.*, 2012, **24**, 3975−3980; (l) P. Zheng, T. J. McCarthy, *J. Am. Chem. Soc.*, 2012, **134**, 2024−2027; (m) Y. Lu, Z. Guan, *J. Am. Chem. Soc.*, 2012, **134**, 14226−14231; (n) H. Ying, Y. Zhang, J. Cheng, *Nat. Comm.*, 2014, **5**, 3218-3227.

5 (a) P. Cordier, F. Tournilhac, C. Soulie-Ziakoic, L. Leibler, *Nature*, 2008, **451**, 977−980; (b) F. Herbst, S. Seiffert, W. H. Binder, *Polym. Chem.*, 2012, **3**, 3084−3092; (c) Y. Chen, A. M. Kushner, G. A. Williams, Z. Guan, *Nat. Chem.,* 2012, **4**, 467−472; (d) J. Hentschel, A. M. Kushner, J. Ziller, Z. Guan, *Angew. Chem. Int. Ed.*, 2012, **51**, 10561−10565.

6 (a) S. Burattini, H. M. Colquhoun, B. W. Creenland, W. Hayes, *Faraday Discuss.*, 2009, **143**, 251−264; (b) S. Burattini, H. M. Colquhoun, F. D. Fox, D. Friedmann, B. W. Greenland, P. J. F. Harris, W. Hayes, M. E. Mackay, S. J. Rowan, *Chem. Commun.*, 2009, 6717−6719; (c) S. Burattini, B. W. Greenland, D. H. Merino, W. Weng, J. Seppala, H. M. Colquhoun, W. Hayes, M. E. Mackay, I. W. Hamley, S. J. Rowan, *J. Am. Chem. Soc.*, 2010, **132**, 12051−12058; (d) S. Burattini, B. W. Breenland, W. Hayes, M. E. Mackay, S. J. Rowan, H. M. Colquhoun, *Chem. Mater.*, 2011, **23**, 6−8; (e) J. Fox, J. J. Wie, B. W. Greenland, S. Burattini, W. Hayes, H. M. Colquhoun, M. E. Mackay, S. J. Rowan, *J. Am. Chem. Soc.*, 2012, **134**, 5362−5368.

7 (a) M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan, C. Weder, *Nature*, 2011, **472**, 334−337; (b) S. Bode, L. Zedler, F. H. Schacher; B. Dietzek; M. Schmitt, J. Popp, M. D. Hager; U. S. Schubert, *Adv. Mater.*, 2013, **25**, 1634−1638; (c) G. Hong, H. Zhang, Y. Lin, Y. Chen, Y. Xu, W. Weng, H. Xia, *Macromolecules,* 2013, **46**, 8649-8656.

8 S. J. Kalista, T. C. Ward, Z. Oyetunji, *Mech. Adv. Mater. Struc.*, 2007, **14**, 391−397.

9 R. Hoogenboom, *Angew. Chem. Int. Ed.*, 2012, **51**, 11942-11944.

10 Y. Chen, Z. Guan, *Polym. Chem.*, 2013, **4**, 4885−4889.

11 (a) J. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.*, 1995, **117**, 5614−1615; (b) K. Matyjaszewski, J. Xia, *Chem. Rev.*, 2001, **101**, 2921−2990; (c) K. Matyjaszewski, N. V. Tsarevsky, *Nat. Chem.*, 2009, **1**, 276−288.

12 K. Matyjaszewski, P. J. Miller, J. Pyun, G. Kickelbick, S. Diamanti, *Macromolecules*, 1999, **32**, 6526−6535.

13 P. Tyagi, A. Deratani, D. Bouyer, D. Cot, V. Gence, M. Barboiu, T. N. T. Phan, D. Bertin, D. Gigmes, D. Quemener, *Angew. Chem. Int. Ed.*, 2012, **51**, 7166−7170.