DOI: 10.1002/anie.201204840

Materials Science

Self-Healing Supramolecular Block Copolymers**

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The ability to spontaneously heal injury is a key feature of biological materials that increases the survivability and lifetime of plants and animals. In contrast, synthetic materials generally fail after damage or fracture. Inspired by nature, several self-healing polymer systems have been developed through the incorporation into polymers of mechanically[1] or photo-activated[2,3] healing agents, reversible covalent bonds,[4–7] metal-ligand complexes,[8] and dynamic non-covalent bonding.[9–14] Nevertheless, progress towards generally applicable and mechanically robust self-healing polymers has been hampered by a fundamental dilemma: the mechanical stiffness/strength and rapid macromolecular dynamics (required for spontaneous healing) usually have an inverse dependent relationship.[15,16] Thus the use of strong reversible interactions in polymers with high glass transition temperature (T_g) results in stiff but less dynamic materials,[4,8] while weak interactions in low T_g polymers afford more dynamic healing, but yield soft materials.[9,17]

To address this dilemma, our laboratory has been exploring a multiphase design of polymers that combine high modulus and toughness with spontaneous healing capability.[18] Recently, we reported a hydrogen-bonding brush polymer that self-assembles into a hard/soft two-phase system, combining the stiff and tough mechanical properties of the hard phase with the self-healing capacity of dynamic supramolecular assemblies in the soft matrix.[18] Unlike brush polymers, block copolymers are important commodity materials exhibiting well-defined multiphase morphologies and tunable mechanical properties through the control of block composition and length. Introducing self-healing capability into block copolymers would significantly improve the performance and expand the scope of applications for this important family of materials. Herein, we report a supramolecular block copolymer design for new multiphase self-healing materials (Figure 1). We reasoned that the supramolecular block copolymer should retain the hard/soft two-phase morphology found in conventional covalent block copolymer architectures, affording advantageous mechanical properties (such as thermoplastic elastomeric). Meanwhile, the supramolecular healing motifs located within the soft phase should remain dynamic and reversible, providing self-healing capability (Figure 1).

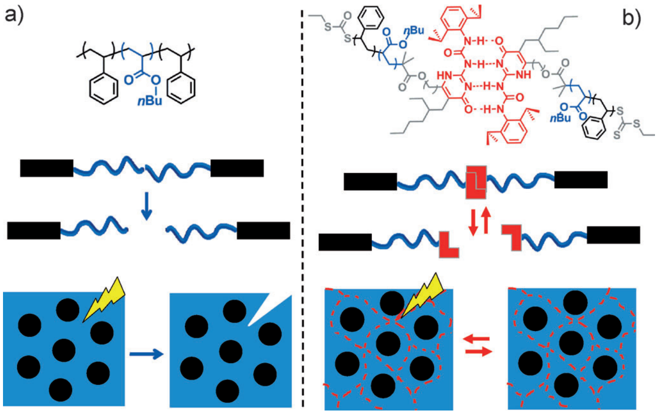

Figure 1. The concept of self-healing supramolecular block copolymer design. a) Conventional PS-*b*-PBA-*b*-PS triblock copolymers form a microphase-separated thermoplastic elastomer. In these systems, mechanical fracture results in irreversible covalent bond rupture and permanent loss of properties. b) Supramolecular triblock copolymers combine the advantageous thermoplastic elastomeric properties of microphase-separated block copolymer systems with the reversible H-bonding interactions at the junction of the soft PBA block to afford dynamic, self-healing properties.

To demonstrate our concept, we chose a block copolymer system having poly(*n*-butyl acrylate) (PBA; T_g = ca. −40 °C) as the soft block and polystyrene (PS; T_g = ca. 100 °C) as the hard block. Previous studies have shown that covalent PS-*b*-PBA-*b*-PS triblock copolymers exhibit microphase-separated morphology and unique thermoplastic elastomer properties.[19] However, mechanical fracture of this covalent system would result in irreversible covalent bond rupture and permanent loss of properties (Figure 1 a). We reasoned that by replacing the covalent linkage in the center of the PBA soft block with a dynamic quadruple H-bonding junction, the supramolecular block copolymer should be able to self-heal after mechanical damage. To demonstrate this, we synthesized PBA-*b*-PS diblock copolymers end-functionalized with a well-defined quadruple H-bonding motif, 2-ureido-4-pyrimidinone (UPy). Dimerization between UPy motifs leads to the formation of supramolecular ABA triblock copolymers with the flexible PBA blocks connected by a single reversible UPy dimer (Figure 1 b). Importantly, this architecture places the dynamic H-bonding interaction within the soft phase of the two-phase system after microphase separation, where chain motion should facilitate reversible H-bond formation in the solid state. Whereas several supramolecular block copolymers have been developed,[20,21] to the best of our knowledge,

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[**] We thank the US Department of Energy, Division of Materials Sciences (DE-FG02-04ER46162), and the National Science Foundation (DMR-1217651) for financial support. The Alexander von Humboldt foundation is thanked for financial support through a Feodor Lynen research fellowship for J.H.

Supporting information, including polymer synthesis and characterizations, material characterizations by DMA, DSC, tensile tests and polymer morphology study by AFM, for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201204840.

no self-healing properties have been reported for such systems.

We selected the UPy dimer[22] as our reversible interaction motif because it offers an attractive combination of relatively high thermodynamic stability (ΔG = ca. 10 kcal mol^{-1}) and rapid kinetic reversibility (k_{off} = ca. 8 s^{-1}),[23] and when incorporated into polymers, results in adaptive and responsive supramolecular materials.[24–29] However, the rigid, flat aromatic structure of the UPy dimer makes it prone to fibrillar assembly[30,31] in the condensed phase, which can hinder the dynamics of reversible H-bond formation. To avoid undesired long-range aggregation and vitrification of the dynamic elements, we adapted a design[32] utilizing a 2,6-diisopropylphenyl group to disrupt π–π stacking between UPy dimers, yielding a new “stack-blocked” UPy motif (SB-UPy) (Supporting Information, Scheme S1). Single crystal X-ray analysis of the SB-UPy-olefin intermediate confirms that the bulky isopropyl substituents are oriented perpendicular to the dimer plane, thus sterically shielding the UPy-dimer from co-facial long-range assembly (Figure 2).

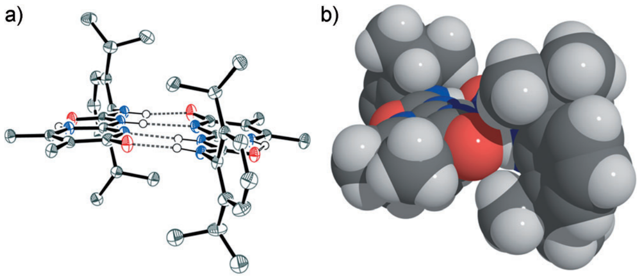
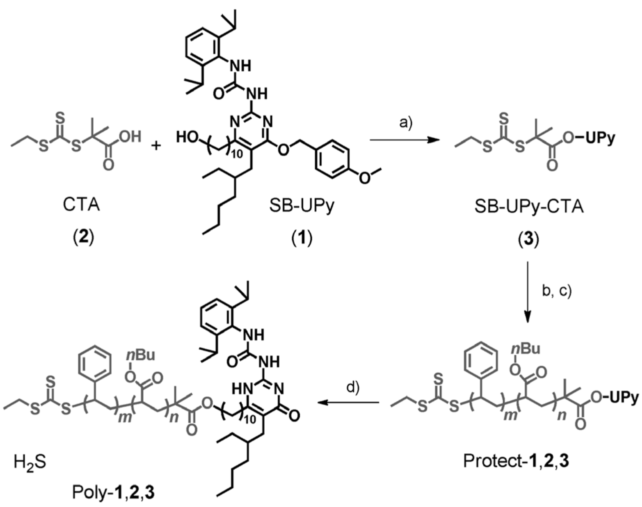


Figure 2. a) X-ray structure of SB-UPy showing the perpendicular out-of-plane orientation of the isopropyl groups. b) Space-filling model showing steric blockage of co-facial aggregation. Oxygen shown in red, nitrogen shown in blue.

We employed radical addition fragmentation chain transfer (RAFT)[33] polymerization, a living/controlled radical polymerization method, to construct our UPy-terminated block copolymers (Scheme 1). For this purpose, a RAFT chain transfer agent (CTA) functionalized with a protected version of our designed SB-UPy motif was first synthesized following literature procedures. The specific CTA, *S*-ethyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (**2**), which is known to be a very efficient and versatile CTA,[34] was synthesized in a one-pot reaction from carbon disulfide, ethanethiol, and acetone. This CTA was coupled to the protected SB-UPy (**1**) through the hydroxy linker by standard *N*,*N*′-dicyclohexylcarbodiimide (DCC) coupling protocols and the resulting SB-UPy-CTA (**3**) was characterized by NMR spectroscopy and ESI-MS (see the Supporting Information).

With SB-UPy functionalized CTA **3** in hand, we carried out sequential RAFT polymerization of *n*-butyl acrylate and styrene to form the desired diblock copolymer with a single protected SB-UPy at the PBA terminus (Scheme 1). The CTA was designed in such a way that the PBA block could be formed first, avoiding the low cross-over initiation efficiency observed for block copolymerization with the opposite order of monomer incorporation.[35] Three block copolymers with high (Protect-**1**), medium (Protect-**2**), and low (Protect-**3**) relative PS hard-phase fractions were synthesized, varying the ratio of PBA and PS block size while maintaining a similar PS block length (Table 1).



Scheme 1. Synthesis of SB-UPy end-functionalized PS-*b*-PBA diblock copolymers (Poly-**1**,**2**,**3**). Conditions: a) DCC, DMAP, CH_2Cl_2; b) *n*-butyl acrylate, AIBN, DMF, 60 °C; c) styrene, AIBN, toluene, 70 °C; d) 20 vol.% TFA in CH_2Cl_2. AIBN = azobisisobutyronitrile, DCC = dicyclohexylcarbodiimide, DMAP = dimethylaminopyridine, DMF = dimethylformamide, TFA = trifluoroacetic acid.

Table 1: Molecular weight characterizations of protected SB-UPy functionalized PS-*b*-PBA diblock copolymers (Protect-**1**,**2**,**3**) as well as covalent PS-*b*-PBA-*b*-PS (SBAS)[a] triblock copolymer control.

Polymer	$M_{n,\text{GPC}}$[b]	M_w/M_n[b]	$M_{n,\text{NMR}}$[c]	[St]/[*n*BA][d]
Protect-**1**	23 000	1.19	31 000	48:52
Protect-**2**	29 000	1.27	41 000	37:63
Protect-**3**	36 000	1.27	50 000	32:68
SBAS[a]	73 000	1.18	80 000	37:63

[a] SBAS = covalent PS-*b*-PBA-*b*-PS triblock copolymer; Polymer Source Inc. (Canada). [b] M_n determined by GPC calibrated with PS standards. [c] Calculated by integration of chain end group and repeat unit from ^{1}H NMR spectra. [d] Calculated by integration of both PS and PBA repeat units from ^{1}H NMR spectra.

The benzyl protecting group on the SB-UPy attached to the block copolymers was removed by treating Protect-**1**,**2**,**3** with 20 % trifluoroacetic acid (TFA). Quantitative deprotection and dimerization of the unprotected SB-UPy was evidenced by the disappearance of the benzyl peaks and the appearance of three new peaks in the UPy H-bonding region (11.9–13.0 ppm) with the expected intensity (Figure S2-A).[28] Furthermore, gel permeation chromatography (GPC) in toluene showed the doubling of number-average molecular weight (M_n) for the copolymers after benzyl deprotection, confirming the transformation from protected diblock copolymers into supramolecular triblock copolymers (Figure S2-B). Thin films were prepared from both protected and deprotected SB-UPy-copolymers by slow evaporation of concentrated chloroform solutions. As a control, a covalent PS-*b*-PBA-*b*-PS (SBAS) triblock copolymer having an identical ratio of hard/soft blocks was used in comparative studies. The solid polymer samples were investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). As shown by DSC, the T_g values of the PBA blocks range from −37 to −42 °C. The T_g values of the PS blocks were determined by DMA measurements (Table S3) because they were not obvious by DSC. Our values are consistent with previously reported T_g values of PS-*b*-PBA-*b*-PS triblock copolymers.[35] The two distinct T_g values suggest that the block copolymers are microphase separated.

Poly-**2** will be used as a representative example for further discussion, because it has a similar composition ([St]/[*n*BA] = 37:63) to the commercially available control polymer (basic mechanical characterization of Poly-**1** and Poly-**3** can be found in the Supporting Information). First, the microphase morphology of the block copolymers was investigated by tapping mode AFM on dip-coated films (Figure 3). Poly-**2** and its covalent analogue, PS-*b*-PBA-*b*-PS (SBAS), show a very similar cylindrical morphology. AFM micrographs of Poly-**3** show a comparable cylindrical morphology to Poly-**2** (Figure S3c), whereas the images of Poly-**1** (Figure S3a) show different phase morphology, owing to the differences in PS/PBA ratio.

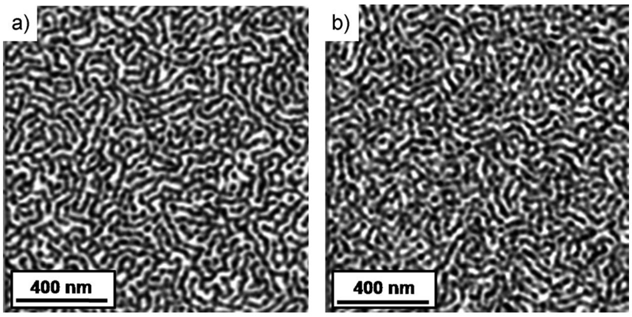


Figure 3. AFM phase-contrast image of a) the SBAS control copolymer and b) Poly-**2**. A cylindrical styrenic microphase is observed in both cases, aligned both parallel and perpendicular to the film surface.

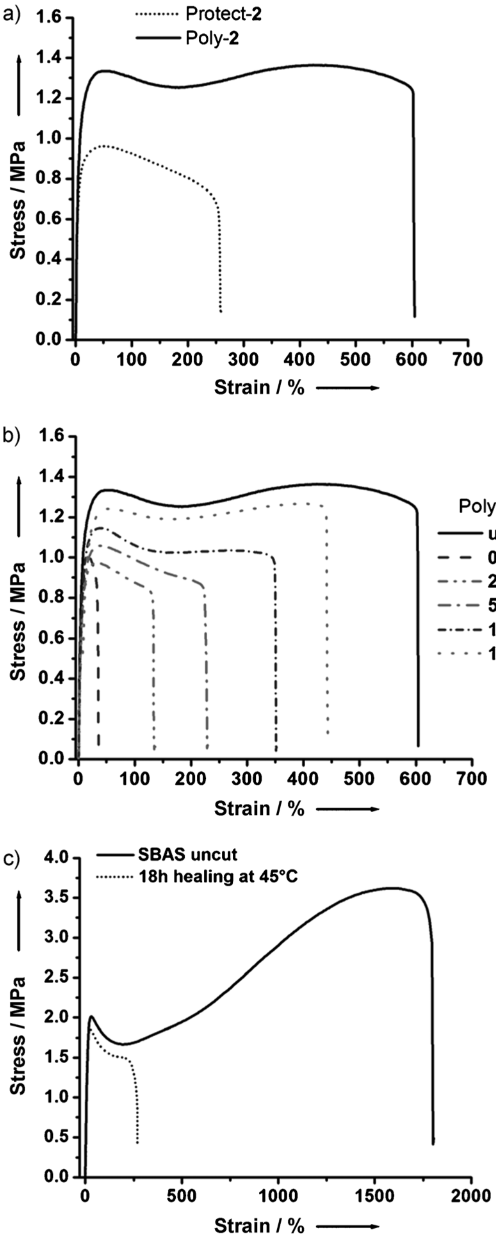


Figure 4. Stress-strain experiments and self-healing tests on both supramolecular and covalent control triblock copolymers. a) UPy-protected (Protect-**2**) vs. deprotected polymer (Poly-**2**). b) Poly-**2** after different time periods of healing at 45 °C. c) Covalent triblock copolymer SBAS uncut and after 18 h healing at 45 °C.

Basic mechanical tests were carried out on both the protected and deprotected block copolymer samples. All three deprotected samples show the characteristic stress-strain behavior of thermoplastic elastomers (Figure S4). As expected, the volume fraction of the hard PS phase has a dramatic effect on the bulk mechanical properties. With increasing volume fraction of the PS hard domain, both the Young's modulus (stiffness) and the yield strength of the sample increase. Figure 4 a compares the tensile properties for Protect-**2** and deprotected Poly-**2**. Protect-**2** is relatively weak and unable to maintain stress after yield. In contrast, the deprotected Poly-**2** is much stronger and displays a distinct post-yield strain-hardening from 170–450 % strain, before the sample finally breaks at around 600 % strain (Figure 4 a). Notably, this dramatic enhancement in mechanical strength and extensibility results from a single deprotection on the terminal SB-UPy on each diblock copolymer chain, and therefore can only be attributed to the spontaneous dimerization of SB-UPy to form dynamic crosslinks between the hard domains. The dramatic increase in mechanical properties following deprotection was observed in all samples, as shown by their storage modulus (G′), Young's Modulus (E), and yield strength (Table S4).

The dynamic nature of the supramolecular triblock copolymers is revealed by the load-rate dependence of the mechanical properties in the strain-hardening region. Films of polymer Poly-**2** were stretched at four different load rates ranging from 10 mm min^{-1} to 1000 mm min^{-1} (Figure S5). The slope of the post-yield tensile curve rises with increasing load rate, indicating that the timescale for the dynamic supramolecular polymer formation is on the order of seconds to minutes, correlating well with the known equilibrium association/dissociation dynamics of the UPy motif.[23] On the other hand, no significant change in the slope of the post-yield curve is observed when measuring the stress/strain behavior of the covalent PS-*b*-PBA-*b*-PS triblock copolymer (SBAS) at different load rates (Figure S5), indicating that no dynamic association is present. It should be noted that the commercial SBAS control polymer has significantly higher molecular weight than Poly-**2** (Table 1), affording higher tensile strength and strain at breaking than Poly-**2**.

Finally, we tested the self-healing ability for the supramolecular triblock copolymers in bulk without adding any solvent, plasticizer, or healing agent. In a typical test procedure, the specimens were bisected by a razor blade, then the cut faces were gently pressed together for 1 min and left for a certain time at 45 °C before they were stretched to failure in a standard stress/strain tensile experiment. Previous studies have indicated that UPy-dimers attached to a polymer backbone show a significant increase in their association/dissociation dynamics at 40–50 °C.[24] Thus, the self-healing properties of our supramolecular triblock copolymers were investigated at 45 °C, a temperature sufficiently high for rapid SB-UPy on/off dynamics but still well below the T_g of the PS hard domain. Indeed, a significant recovery of tensile strength ($>90\%$) and strain at break (ca. 75 %) was observed for Poly-**2** after healing at 45 °C for 18 h (Figure 4 b). In addition, the time-dependent healing of Poly-**2** eventually leads to recovery of post-yield strain hardening, in sharp contrast to the covalent control, the SBAS covalent triblock copolymer (Figure 4 c). For the control, despite the significantly higher molecular weight, owing to the lack of any dynamic interactions, the bisected sample shows only minimal healing capacity ($<15\%$ recovery of strain at break) and fails immediately after yield.

All three supramolecular block copolymers (Poly-**1,2,3**) show significant healing capability (Figure S6). After healing at 45 °C for 18 h, Poly-**1**, which is mechanically the strongest of the three samples, showed almost quantitative recovery of both the Young's modulus and peak strength, and about 45 % recovery of extensibility, making it useful for many elastomer applications. With an increasing PBA/PS ratio, Poly-**3** was more dynamic and showed quantitative recovery of the Young's modulus, tensile strength, and strain at break after 18 h of healing at 45 °C.

In summary, we have demonstrated the first example of self-healing block copolymers in bulk solid state. Specifically, we have designed a novel multiphase self-healing material employing supramolecular block copolymer architecture. Simple terminal functionalization of PBA-*b*-PS diblock copolymers with supramolecular SB-UPy groups results in thermoplastic elastomers with dynamic and self-healing properties. The hard/soft microphase-separated supramolecular block copolymers can combine the stiffness and toughness of thermoplastic elastomers with the dynamics and healing capabilities of supramolecular materials. Efficient recovery of mechanical strength and extensibility was observed with mild thermal treatment. We envision that this concept can be generally applicable to a wide range of block copolymer systems having different hard/soft blocks and various types of supramolecular healing motifs for the design of stiff, strong, and tough self-healing polymers.

Received: June 20, 2012

Keywords: block copolymers · multiphase · polymer design · self-healing · supramolecular chemistry

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[1] 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.
[2] B. Ghosh, M. W. Urban, *Science* **2009**, *323*, 1458.
[3] Y. Amamoto, J. Kamada, H. Otsuka, A. Takahara, K. Matyjaszewski, *Angew. Chem.* **2011**, *123*, 1698; *Angew. Chem. Int. Ed.* **2011**, *50*, 1660.
[4] X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran, F. Wudl, *Science* **2002**, *295*, 1698.
[5] P. J. Boul, P. Reutenauer, J.-M. Lehn, *Org. Lett.* **2005**, *7*, 15.
[6] K. Imato, M. Nishihara, T. Kanehara, Y. Amamoto, A. Takahara, H. Otsuka, *Angew. Chem.* **2012**, *124*, 1164; *Angew. Chem. Int. Ed.* **2012**, *51*, 1138.
[7] P. Zheng, T. J. McCarthy, *J. Am. Chem. Soc.* **2012**, *134*, 2024.
[8] M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan, C. Weder, *Nature* **2012**, *472*, 334.
[9] P. Cordier, F. Tournilhac, C. Soulie-Ziakovic, L. Leibler, *Nature* **2008**, *451*, 977.
[10] A. B. South, L. A. Lyon, *Angew. Chem.* **2010**, *122*, 779; *Angew. Chem. Int. Ed.* **2010**, *49*, 767.
[11] 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.
[12] Q. Wang, J. L. Mynar, M. Yoshida, E. Lee, M. Lee, K. Okuro, K. Kinbara, T. Aida, *Nature* **2010**, *463*, 339.
[13] A. Phadke, C. Zhang, B. Arman, C.-C. Hsu, R. A. Mashelkar, A. K. Lele, M. J. Tauber, G. Arya, S. Varghese, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 4383.
[14] G. M. L. van Gemert, J. W. Peeters, S. H. M. Söntjens, H. M. Janssen, A. W. Bosman, *Macromol. Chem. Phys.* **2012**, *213*, 234.
[15] W. C. Yount, D. M. Loveless, S. L. Craig, *Angew. Chem.* **2005**, *117*, 2806; *Angew. Chem. Int. Ed.* **2005**, *44*, 2746.
[16] N. R. Sottos, J. S. Moore, *Nature* **2011**, *472*, 299.
[17] P. Reutenauer, E. Buhler, P. J. Boul, S. J. Candau, J. M. Lehn, *Chem. Eur. J.* **2009**, *15*, 1893.
[18] Y. Chen, A. M. Kushner, G. A. Williams, Z. Guan, *Nat. Chem.* **2012**, *4*, 467.
[19] Y. W. Luo, X. G. Wang, Y. Zhu, B. G. Li, S. P. Zhu, *Macromolecules* **2010**, *43*, 7472.
[20] X. Yang, F. Hua, K. Yamato, E. Ruckenstein, B. Gong, W. Kim, C. Y. Ryu, *Angew. Chem.* **2004**, *116*, 6633; *Angew. Chem. Int. Ed.* **2004**, *43*, 6471.
[21] E. Weiss, K. C. Daoulas, M. Maller, R. Shenhar, *Macromolecules* **2011**, *44*, 9773.
[22] F. H. Beijer, R. P. Sijbesma, H. Kooijman, A. L. Spek, E. W. Meijer, *J. Am. Chem. Soc.* **1998**, *120*, 6761.
[23] S. H. M. Söntjens, R. P. Sijbesma, M. H. P. van Genderen, E. W. Meijer, *J. Am. Chem. Soc.* **2000**, *122*, 7487.
[24] A. M. Kushner, J. D. Vossler, G. A. Williams, Z. Guan, *J. Am. Chem. Soc.* **2009**, *131*, 8766.
[25] J. Li, J. Viveros, M. Wrue, M. Anthamatten, *Adv. Mater.* **2007**, *19*, 2851.
[26] C. L. Elkins, T. Park, M. G. McKee, T. E. Long, *J. Polym. Sci. Part A* **2005**, *43*, 4618.

[27] K. Yamauchi, J. R. Lizotte, T. E. Long, *Macromolecules* **2003**, *36*, 1083.

[28] K. E. Feldman, M. J. Kade, T. F. A. de Greef, E. W. Meijer, E. J. Kramer, C. J. Hawker, *Macromolecules* **2008**, *41*, 4694.

[29] K. E. Feldman, M. J. Kade, E. W. Meijer, C. J. Hawker, E. J. Kramer, *Macromolecules* **2009**, *42*, 9072.

[30] W. P. J. Appel, G. Portale, E. Wisse, P. Y. W. Dankers, E. W. Meijer, *Macromolecules* **2011**, *44*, 6776.

[31] N. E. Botterhuis, D. J. M. van Beek, G. M. L. van Gemert, A. W. Bosman, R. P. Sijbesma, *J. Polym. Sci. Part A* **2008**, *46*, 3877.

[32] S. H. M. Söntjens, R. P. Sijbesma, M. H. P. van Genderen, E. W. Meijer, *Macromolecules* **2001**, *34*, 3815.

[33] J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1998**, *31*, 5559.

[34] A. J. Convertine, B. S. Lokitz, Y. Vasileva, L. J. Myrick, C. W. Scales, A. B. Lowe, C. L. McCormick, *Macromolecules* **2006**, *39*, 1724.

[35] S. Robin, O. Guerret, J. L. Couturier, R. Pirri, Y. Gnanou, *Macromolecules* **2002**, *35*, 3844.