Chiral Nanostructures

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Nanospheres, Nanotubes, Toroids, and Gels with Controlled Macroscopic Chirality**

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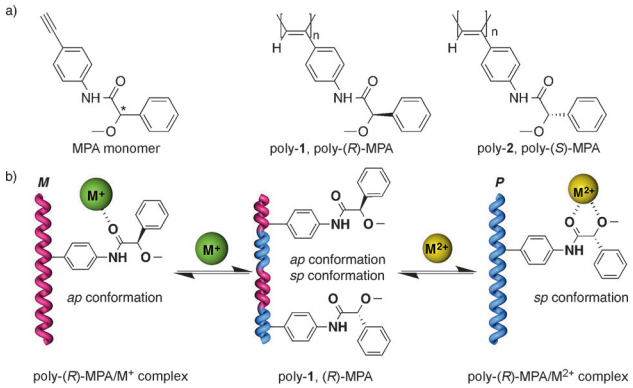
Abstract: *The interaction of a highly dynamic poly(aryl acetylene) (poly-**1**) with Li^+, Na^+, and Ag^+ leads to macroscopically chiral supramolecular nanospheres, nanotubes, toroids, and gels. With Ag^+, nanospheres with M helicity and tunable sizes are generated, which complement those obtained from the same polymer with divalent cations. With Li^+ or Na^+, poly-**1** yields chiral nanotubes, gels, or toroids with encapsulating properties and M helicity. Right-handed supramolecular structures can be obtained by using the enantiomeric polymer. The interaction of poly-**1** with Na^+ produces nanostructures whose helicity is highly dependent on the solvation state of the cation. Therefore, structures with either of the two helicities can be prepared from the same polymer by manipulation of the cosolvent. Such chiral nanotubes, toroids, and gels have previously not been obtained from helical polymer–metal complexes. Chiral nanospheres made of poly(aryl acetylene) that were previously assembled with metal(II) species can now be obtained with metal(I) species.*

The introduction of chirality into nanostructures (nanospheres, nanofibers, nanotubes, etc.) has attracted great interest during the last decade because it might lead to new applications in fields such as chiral sensing, chiral separation, and chiral nanoreactors.[1] Different approaches have been developed, and for example, chiral nanospheres and chiral nanofibers have been prepared from metal–organic frameworks (MOFs),[2] from metal–peptide complexes,[3] or by the self-assembly of small molecules,[4] dendrimers,[5] and polymer chains.[6]

Recently, a new strategy to generate chiral nanostructures from helical polymer–metal complexes (HPMCs) has been presented,[6c] leading to nanospheres with tunable chiral content (i.e., helicity) and particle size. The polymer used to generate these nanospheres was a poly(aryl acetylene)[7] (poly-**1**; Scheme 1 a), having a polyene skeleton with high *cis* content[7s] and (*R*)-α-methoxyphenylacetic acid (MPA) units as the chiral pendants.



Scheme 1. a) Structures of the MPA monomer, poly-**1**, and poly-**2**. b) Chiral amplification of poly-**1** induced by mono- and divalent metal ions.

In solution (e.g., $CHCl_3$, THF), this polymer is present in a 1:1 equilibrium mixture of both helical senses (*M* and *P* helicity; i.e., no circular dichroism (CD)).[8] When monovalent metal cations are added, the equilibrium shifts to the left-handed sense of helicity because the metal cations bind to the carbonyl group, promoting an antiperiplanar conformation (*ap*; dihedral angle of O=C–C–OMe ca. 180°), whereas with divalent metal ions, the polymer adopts a right-handed helical structure because the metal cations coordinate to both the methoxy and carbonyl groups promoting a synperiplanar conformation (*sp*; dihedral angle of O=C–C–OMe ca. 0°; Scheme 1 b).[8] In both cases, a chiral amplification phenomenon is operative, and a minute amount of the metal ion is enough to trigger the maximum helicity of the polymer.

Divalent cations (e.g., Ba^{2+}, Ca^{2+}, Ni^{2+}, and Co^{2+}) also act as crosslinking agents.[6c] In THF, they induce the aggregation of HPMCs into nanospheres whose size and chirality (right-handed helices for poly-**1**) depend on the polymer/metal ratio. Unfortunately, aggregation could not be achieved with monovalent metal ions in THF, and therefore, nanospheres with the opposite helicity (left-handed) were not available from poly-**1**.

We herein describe that the interaction of poly-**1** with Ag^+, Li^+ and Na^+ ions in $CHCl_3$ can produce chiral nanospheres, nanotubes, gels, and toroids that consist of either left- or right-handed polymeric helices. For instance, we will show that nanostructures with opposite helicities can be prepared from a single polymer (poly-**1**) and Na^+ when the action of the cation is modulated by the presence of certain cosolvents. We

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now describe the specific behavior of poly-**1** in the presence of each of those monovalent metal cations.

The addition of silver perchlorate that had been dissolved in THF (e.g., 10.0 mg mL^{-1}) to a chloroform solution of poly-**1** (e.g., 0.1 mg mL^{-1}) yielded well-defined, stable, and monodisperse nanospheres with a diameter of 94 nm [polydispersity index (PDI) = 0.197; polymer (mru)/metal ion mole ratio: 1.0:1.0, mru = monomer repeating unit] with left-handed helicity as expected for the interaction of poly-**1** with monovalent ions (Figure 1). Both their size and helical content could be tuned by changing the polymer (mru)/metal ion ratio (for details, see the Supporting Information).

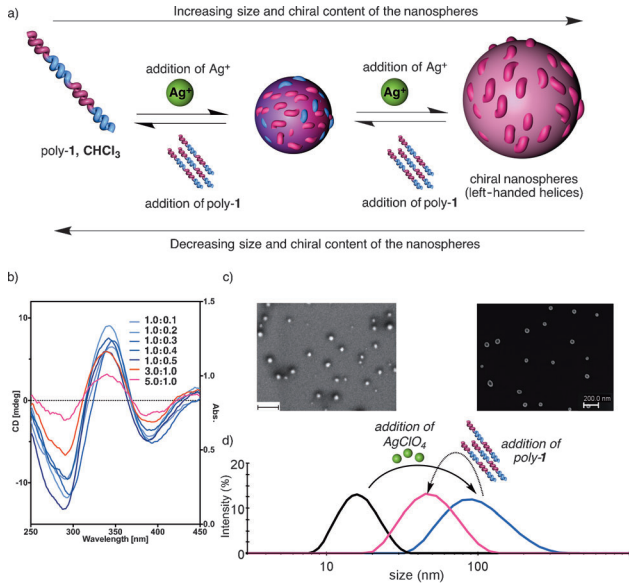
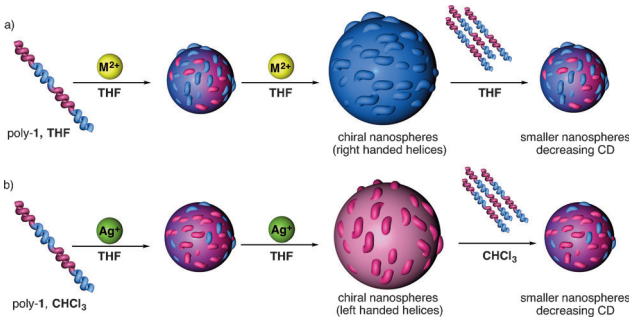


Figure 1. a) Schematic representation of the size and chirality control of poly-**1**/Ag$^+$ HPMCs in $CHCl_3$. b) CD spectra of poly-**1**/Ag$^+$ complexes with different polymer/metal ratios (given as polymer (mru)/metal ion). c) SEM images of HPMCs with poly-**1** (mru)/Ag$^+$ mole ratios of 1.0:0.3 (left, 59 nm, PDI = 0.134, scale bar: 200 nm) and 1.0:1.0 (right, 106 nm, PDI = 0.197, scale bar: 200 nm). d) Dynamic light scattering (DLS) traces showing the size modulation of the poly-**1**/Ag$^+$ nanospheres by changing the polymer (mru)/M$^+$ ratios. Black trace: poly-**1**, Zave: 38 nm, PDI: 0.124; pink trace: poly-**1**/Ag$^+$: 3.0:1.0, Zave: 66 nm, PDI: 0.194; blue trace: poly-**1**/Ag$^+$: 1.0:1.0, Zave: 106 nm, PDI: 0.197.

Therefore, the aggregation of HPMCs formed by poly-**1** and Ag$^+$ in $CHCl_3$ produced chiral nanospheres that can be compelled to grow or shrink, similar to those obtained with divalent metal cations in THF.[6c] However, in poly-**1**/Ag$^+$ nanospheres, the polymer adopts a left-handed helical structure, whereas in the nanospheres made with divalent ions (i.e., poly-**1**/M^{2+}), the inverted macromolecular helicity is observed (i.e., right-handed helicity; Scheme 2). A single polymer (i.e., poly-**1**) thus produces nanospheres with opposite helicities just by selecting an appropriate metal ion and solvent.

The left-handed nanospheres from poly-**1**/Ag$^+$ present virtually the same encapsulation properties as their right-handed counterparts from poly-**1**/M^{2+} (see the Supporting Information).[8]



Scheme 2. Chiral amplification of poly-**1** induced by a) divalent metal ions in THF and by b) monovalent metal ions in $CHCl_3$. Cosolvents given under the arrows are those employed to solubilize the metal salts or poly-**1** in subsequent additions.

Similar to the previous case, the addition of small amounts of lithium perchlorate dissolved in THF, MeOH, or MeCN to a chloroform solution of poly-**1** [poly-**1** (mru)/Li$^+$ mole ratio: 1.0: < 1.0] produced aggregates in the form of unstable polydisperse nanospheres with diameters that vary from 60 to 100 nm and the expected left-handed helicity (Figure 2; see

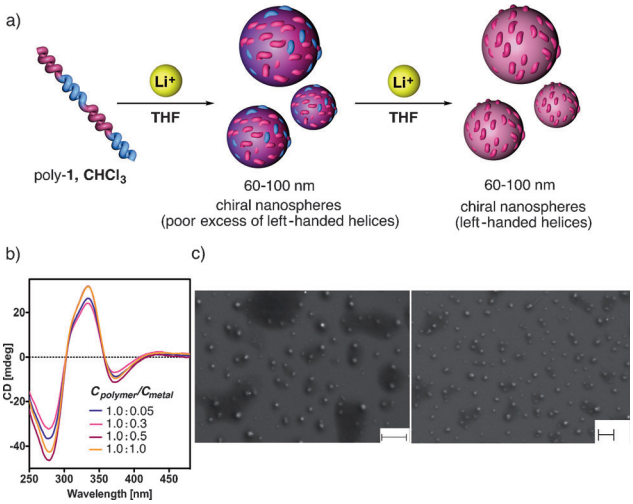


Figure 2. a) Schematic representation of poly-**1**/Li$^+$ complex nanostructures in $CHCl_3$ (THF was used as the cosolvent to solubilize the lithium salt). b) CD spectra of poly-**1**/Li$^+$ complexes with different polymer/metal ratios. c) SEM images of polydisperse nanospheres obtained from HPMCS with poly-**1** (mru)/Li$^+$ mole ratios of 1.0:0.3 (left, scale bar: 300 nm) and 1.0:1.0 (right, scale bar: 200 nm).

also the Supporting Information).[9] Although the helical content of those nanospheres could be increased by the addition of more lithium salt, their size is not tunable by modification of the polymer/metal ratio (contrary to what was observed with Ag$^+$).

These chiral nanospheres spontaneously collapsed during drop-casting and/or solvent evaporation onto a silicon wafer substrate (Figure 3), which generated 1D aggregates that grow to form nanotubes consisting of left-handed helical chains. SEM images of these nanotubes with a diameter close to that of the starting nanospheres are shown in Figure 3.

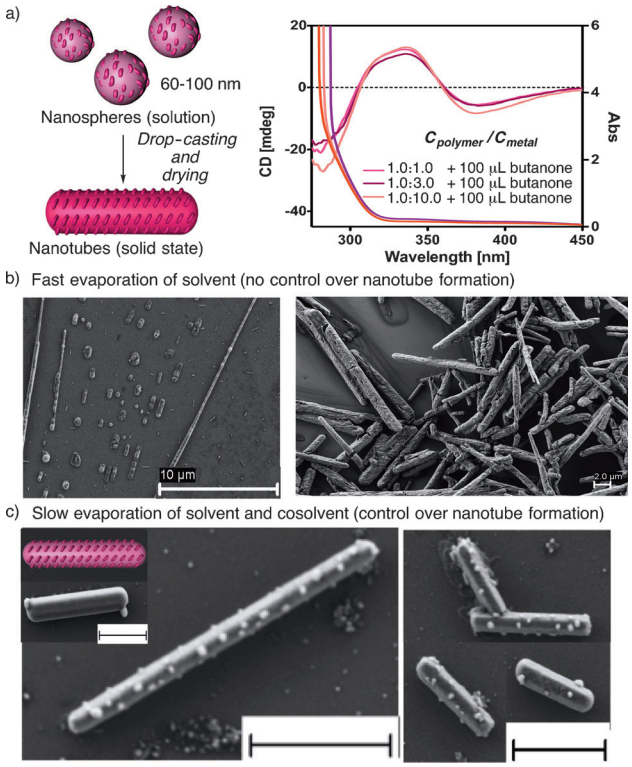


Figure 3. a) Schematic representation of nanotube formation. Nanotubes of poly-**1**/Li^+ were obtained by b) fast or c) controlled evaporation of the solvent. Scale bars: 10 µm (b left), 2 µm (b right, c), 1 µm (c inset). Additional images are shown in Figure S40 in the Supporting Information (encapsulation of iron oxide magnetic nanoparticles, fluorescein, and quantum dots).

When solvent (i.e., $CHCl_3$) evaporation from the substrate was fast, the aggregation could not be controlled, and the nanotubes formed with different sizes and shapes (Figure 3b). However, well-defined nanotubes with left-handed chirality could be obtained when the process was slowed down by incorporation of a higher-boiling-point cosolvent, such as 2-butanone (Figure 3c).

It should be noted that these nanospheres and nanotubes present a macroscopically chiral (helical) surface that is defined by the left-handed interaction of poly-**1** (containing (*R*)-MPA as the pendants) with Li^+. To obtain the corresponding "enantiomeric" right-handed nanospheres and nanotubes, poly-**2** (with the enantiomeric skeleton and (*S*)-MPA as the pendants) should be used.

The aggregation process that leads to nanospheres and nanotubes can be compelled to reach a gel structure when the polymer/metal ratio and the polymer concentration are increased above certain values, for example, for a poly-**1** (mru)/Li^+ mole ratio of 1.0:>1.0 and [poly-**1**]> 0.2 mg mL^{-1} (see the Supporting Information, Figure S36d). The macroscopically enantiomeric gel (right-handed) is obtained by using poly-**2** instead of poly-**1**. Detailed information on the encapsulation abilities of these nanostructures can be found in the Supporting Information.

Finally, when the aggregation of the poly-**1**/Li^+ complex was carried out in the presence of a solvent in which the polymer is poorly soluble, toroidal nanostructures were formed,[10] probably as a result of the polymer surrounding solvent droplets and keeping that form during evaporation (Figure 4). Detailed information on the formation of these toroids can be found in the Supporting Information.

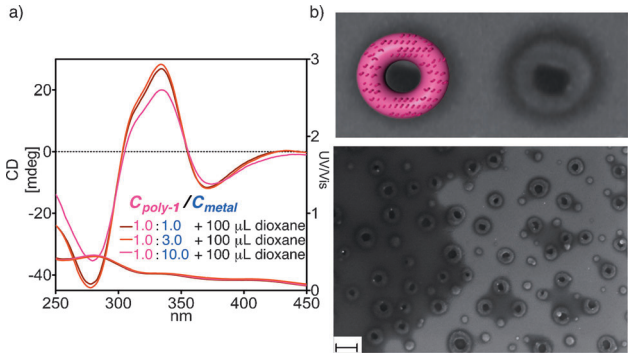


Figure 4. a) CD and UV spectra of poly-**1** for different amounts of $LiClO_4$ (THF) and 100 µL of dioxane. b) SEM images of toroidal nanostructures formed from HPMCs with a poly-**1** (mru)/Li^+ mole ratio of 1.0:1.0 in $CHCl_3$ (1 mL) and dioxane (100 µL). Scale bar: 200 nm; [poly-**1**] = 0.03 mg mL^{-1}.

Similar to Li^+, the addition of small amounts of sodium perchlorate to a solution of poly-**1** produced poly-**1**/Na^+ HPMC aggregates in the form of polydisperse nanospheres (60–100 nm). Their size was not tunable by the polymer/metal ratio, but interestingly, the helicity of the nanospheres could now be controlled or even inverted by changing the solvent, in particular by varying the amount and type of cosolvent that was used to deliver the Na^+ salt (e.g., THF, MeOH, or MeCN).

Thus, when the formation of nanospheres and nanotubes was carried out by the addition of a solution of $NaClO_4$ in MeOH to a solution of poly-**1** in $CHCl_3$ (polymer (mru)/Na^+/MeOH mole ratio: 1.0:0.1:20.0), the expected "left-handed" nanospheres and nanotubes were obtained (CD and SEM images in Figure 5b). Nevertheless, when the amount of methanol in which the sodium salt had been dissolved was increased (polymer (mru)/Na^+/MeOH mole ratio: 1.0:0.1:140), the "enantiomeric" right-handed nanospheres and nanotubes were formed (CD and SEM images in Figure 5c). The corresponding "enantiomeric" right-handed gel was obtained as before when the concentration of the polymer was increased (Figure 5).

In summary, macroscopically enantiomeric left- and right-handed nanospheres, nanotubes, and gels can be obtained from the same polymer (i.e., poly-**1**) by using an appropriate amount of the right cosolvent to deliver the metal ion.

This phenomenon is not exclusively observed for the formation of aggregates, but also for poly-**1**/Na^+ complexes generated at low concentrations and in the presence of small amounts of Na^+ ion, which present left-handed or right-handed helicity depending on the amount of cosolvent.

More precisely, we have determined that the main factor in the control of the helicity of poly-**1** by Na^+ is the degree of solvation of the Na^+ ion that is provided by the cosolvent.

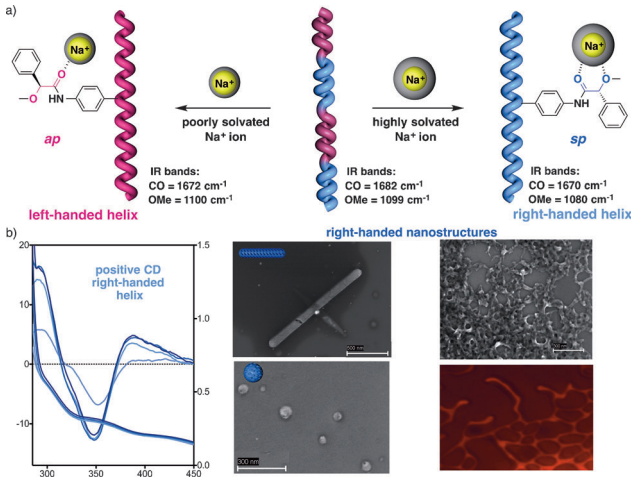


Figure 5. a) Schematic representation of the control of the chirality of the poly-**1**/Na^+ HPMCs by the degree of solvation of the metal ion. b) CD spectra and images of the chiral nanotubes, nanospheres, and nanogels with encapsulation properties that consist of right-handed helical structures, which were obtained owing to different degrees of solvation of the Na^+ ion. Scale bars: 500 nm (top left), 300 nm (top right and bottom left). Additional images in Figure S41 show CD spectra and images of the chiral nanotubes, nanospheres, and nanogels with encapsulation properties that consist of the left-handed helical structures.

Thus, when the metal ion was added to the polymer only slightly solvated, that is, only small amounts of THF, MeOH, or MeCN were used to dissolve the salt, it coordinated to the carbonyl group of the MPA pendants (IR band at 1672 cm^{-1}), shifting the conformational equilibrium to *ap* and the polyene skeleton to a left-handed helical structure.[8] On the contrary, when the Na^+ ion was highly solvated, it chelated both the carbonyl and methoxy groups of MPA (IR bands at 1670 and 1080 cm^{-1}, respectively), so that a *sp* conformation and a polymer backbone with a right-handed helical structure were preferred.[8]

In conclusion, poly-**1** can produce macroscopically chiral supramolecular nanospheres, nanotubes, toroids, and gels by aggregation of the corresponding HPMCs with Ag^+, Li^+, and Na^+. With Ag^+, poly-**1** generated nanospheres with left-handed helicity and tunable size. As poly-**1** interacted with divalent metal ions yielding tunable nanospheres with right-handed helicity,[7] our finding enables the synthesis of nanospheres from a single helical polymer with encapsulation abilities and both tunable size and chiral sense (right-handed with divalent ions and left-handed with Ag^+).

The interaction of poly-**1** with Li^+ or Na^+ generated chiral polydisperse nanospheres that could be converted into chiral nanotubes and gels (Li^+ or Na^+) or toroids (Li^+) with encapsulation properties and left-handed helicity in a controlled way. The corresponding right-handed superstructures can be obtained using poly-**2** as the starting polymer. Moreover, the interaction of poly-**1** with Na^+ has been shown to produce nanostructures whose helicity depends on the solvated state of the metal ion. In this way, nanostructures with either of the two helicities (left- or right-handed) could be prepared from the same polymer by manipulating the amount of an appropriate cosolvent accompanying the metal ion.

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[1] For reviews on supramolecular chirality, see: a) P. Duan, H. Cao, L. Zhang, M. Liu, *Soft Matter* **2014**, *10*, 5428 – 5448; b) L. Zhang, L. Qin, X. Wang, H. Cao, M. Liu, *Adv. Mater.* **2014**, DOI: 10.1002/adma.201305422; c) Y. Yang, Y. Zhang, Z. Wei, *Adv. Mater.* **2013**, *25*, 6039 – 6049; d) Y. Wang, J. Xu, Y. Wang, H. Chen, *Chem. Soc. Rev.* **2013**, *42*, 2930 – 2962; e) H. Miyake, H. Tsukube, *Chem. Soc. Rev.* **2012**, *41*, 6977 – 6991; f) D. K. Smith, *Chem. Soc. Rev.* **2009**, *38*, 684 – 694; g) S. S. Buabu, C. Vijayakumar, R. Varghese, A. Ajayagosh, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1196 – 1211; h) A. R. A. Palmans, E. W. Meijer, *Angew. Chem. Int. Ed.* **2007**, *46*, 8948 – 8968; *Angew. Chem.* **2007**, *119*, 9106 – 9126; i) M. A. Mateos-Timoneda, M. Crego-Calama, D. N. Reinhoudt, *Chem. Soc. Rev.* **2004**, *33*, 363 – 372.

[2] a) Q. -Zhu, Q. Xu, *Chem. Soc. Rev.* **2014**, *43*, 5468 – 5512; b) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444; c) A. Carné-Sánchez, I. Imaz, M. Cano-Sarabia, D. Maspoch, *Nat. Chem.* **2013**, *5*, 203 – 211; d) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105 – 1125; e) N. Stock, S. Biswas, *Chem. Rev.* **2012**, *112*, 933 – 969.

[3] a) M. Rubio-Martínez, J. Puigmartí-Luis, I. Imaz, P. S. Dittrich, D. Maspoch, *Small* **2013**, *9*, 4160 – 4167; b) E. Gazit, *Chem. Soc. Rev.* **2007**, *36*, 1263 – 1269; c) X. Fu, Y. Wang, L. Huang, Y. Sha, L. Gui, L. Lai, Y. Tang, *Adv. Mater.* **2003**, *15*, 902 – 906.

[4] a) C. Ren, J. Zhang, M. Chen, Z. Yang, *Chem. Soc. Rev.* **2014**, DOI: 10.1039/c4cs00161c; b) Z. Huang, S.-K. Kang, M. Lee, *J. Mater. Chem.* **2011**, *21*, 15327 – 15331; c) I. Danila, F. Riobé, F. Piron, J. Puigmartí-Luis, J. D. Wallis, M. Linares, H. Ågren, D. Beljonne, D. B. Amabilino, N. Avarvari, *J. Am. Chem. Soc.* **2011**, *133*, 8344 – 8353; d) V. Percec, D. A. Wilson, P. Leowanawat, C. J. Wilson, A. D. Hughes, M. S. Kaucher, D. A. Hammer, D. H. Levine, A. J. Kim, F. S. Bates, K. P. Davis, T. P. Lodge, M. L. Klein, R. H. DeVane, E. Aqad, B. M. Rosen, A. O. Argintaru, M. J. Sienkowska, K. Rissanen, S. Nummelin, J. Ropponen, *Science* **2010**, *328*, 1009 – 1014; e) T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2009**, *109*, 5687 – 5754; f) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491 – 1546; g) N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821 – 836.

[5] a) B. M. Rosen, C. J. Wilson, D. A. Wilson, M. Peterca, M. R. Imam, V. Percec, *Chem. Rev.* **2009**, *109*, 6275 – 6540; b) V. Percec, M. R. Imam, M. Peterca, D. A. Wilson, R. Graf, H. Spiess, V. S. K. Balagurusamy, P. A. Heiney, *J. Am. Chem. Soc.* **2009**, *131*, 7662 – 7677; c) V. Percec, M. R. Imam, M. Peterca, D. A. Wilson, P. A. Heiney, *J. Am. Chem. Soc.* **2009**, *131*, 1294 – 1304; d) V. Percec, M. Peterca, A. E. Dulcey, M. R. Imam, S. D. Hudson, S. Nummelin, P. Adelman, P. A. Heiney, *J. Am. Chem. Soc.* **2008**, *130*, 13079 – 13094.

[6] a) W. Li, H. Huang, Y. Li, J. Deng, *Polym. Chem.* **2014**, *5*, 1107 – 1118; b) C. Song, X. Liu, D. Liu, C. Ren, W. Yang, J. Deng, *Macromol. Rapid Commun.* **2013**, *34*, 1426 – 1445; c) F. Freire, J. M. Seco, E. Quiñoá, R. Riguera, *J. Am. Chem. Soc.* **2012**, *134*, 19374 – 19383; d) D. Zhang, H. Zhang, C. Song, W. Yang, J. Deng, *Synth. Met.* **2012**, *162*, 1858 – 1863; e) Y. Yan, R. Wang, X.

Qiu, Z. Wei, *J. Am. Chem. Soc.* **2010**, *132*, 12006 – 12012; f) H.-J. Kim, J.-K. Kim, M. Lee, *Chem. Commun.* **2010**, *46*, 1458 – 1460; g) V. Percec, A. E. Dulcey, V. S. K. Balagurusamy, Y. Miura, J. Smidrkal, M. Peterca, S. Nummelin, U. Edlund, S. D. Hudson, P. A. Heiney, H. Duan, S. N. Magnov, S. S. Vinogradov, *Nature* **2004**, *430*, 764 – 768.

[7] a) S. Leiras, F. Freire, J. M. Seco, E. Quiñoá, R. Riguera, *Chem. Sci.* **2013**, *4*, 2735 – 2743; b) K. Maeda, S. Wakasone, K. Shimomura, T. Ikai, S. Kanoh, *Chem. Commun.* **2012**, *48*, 3342 – 3344; c) Z. Tang, H. Iida, H.-Y. Hu, E. Yashima, *ACS Macro Lett.* **2012**, *1*, 261 – 265; d) S. Ohsawa, S.-I. Sakurai, K. Nagai, K. Maeda, J. Kumaki, E. Yashima, *Polym. J.* **2012**, *44*, 42 – 50; e) K. Maeda, M. Muto, T. Sato, E. Yashima, *Macromolecules* **2011**, *44*, 8343 – 8349; f) G. M. Miyake, H. Iida, H.-Y. Hu, Z. Tang, E. Y.-X. Chen, E. Yashima, *J. Polym. Sci. Part A* **2011**, *49*, 5192 – 5198; g) E. Schwartz, M. Koepf, H. J. Kitto, R. J. M. Nolte, A. E. Rowan, *Polym. Chem.* **2011**, *2*, 33 – 47; h) I. Louzao, J. M. Seco, E. Quiñoá, R. Riguera, *Angew. Chem. Int. Ed.* **2010**, *49*, 1430 – 1433; *Angew. Chem.* **2010**, *122*, 1472 – 1475; i) E. Yashima, K. Maeda, H. Lida, Y. Furusho, K. Nagai, *Chem. Rev.* **2009**, *109*, 6102 – 6211; j) J. Liu, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.* **2009**, *109*, 5799 – 5867; k) T. Sierra in *Chirality at the Nanoscale: Nanoparticles, Surfaces, Materials and More* (Ed.: D. B. Amabilino), Wiley-VCH, Weinheim, **2009**, pp. 115 – 190; l) E. Yashima, K. Maeda, Y. Furusho, *Acc. Chem. Res.* **2008**, *41*, 1166 – 1180; m) J. G. Rudick, V. Percec, *Acc. Chem. Res.* **2008**, *41*, 1641 – 1652; n) E. Yashima, K. Maeda, *Macromolecules* **2008**, *41*, 3 – 12; o) E. Yashima, K. Maeda in *Foldamers: Structure, Properties, and Applications* (Eds.: S. Hecht, I. Huc), Wiley-VCH, Weinheim, **2007**, pp. 331 – 366; p) K. Maeda, E. Yashima, *Top. Curr. Chem.* **2006**, *265*, 47 – 88; q) H. Nakako, R. Nomura, M. Tabata, T. Masuda, *Macromolecules* **1999**, *32*, 2861 – 2864; r) M. Tabata, Y. Tanaka, Y. Sadahiro, T. Sone, K. Yokota, I. Miura, *Macromolecules* **1997**, *30*, 5200 – 5204; s) C. I. Simionescu, V. Percec, S. Dumitrescu, *J. Polym. Sci. Polym. Chem. Ed.* **1977**, *15*, 2497 – 2509.

[8] F. Freire, J. M. Seco, E. Quiñoá, R. Riguera, *Angew. Chem. Int. Ed.* **2011**, *50*, 11692 – 11696; *Angew. Chem.* **2011**, *123*, 11896 – 11900.

[9] The strong affinity towards alkali metals (e.g., Li^+, Na^+) shown by the coordinating solvent that dissolves the salt disrupts the crosslinking among the polymer chains, thus generating polydisperse nanospheres.

[10] a) G. T. Carroll, M. G. M. Jongejan, D. Pijper, B. L. Feringa, *Chem. Sci.* **2010**, *1*, 469 – 472; b) S. Yagai, S. Mahesh, Y. Kikkawa, K. Unoike, T. Karatsu, A. Kitamura, A. Ajayaghosh, *Angew. Chem. Int. Ed.* **2008**, *47*, 4691 – 4694; *Angew. Chem.* **2008**, *120*, 4769 – 4772.