Introduction

Challenges in polymer science have increased in recent years thanks to a growing demand for new functional materials presenting a wide range of properties, such as the self-healing to mechanical stress and the ability to reversibly adapt to external stimuli. Supramolecular polymer chemistry addresses the multifaceted tasks of designing smart materials and expanding polymer applications through the rational implementation of non-covalent interactions in polymer chemistry. The nature of the secondary weak interactions and the types of building blocks involved in the supramolecular polymer systems are pivotal to determine the responsiveness of the resulting materials. In this context, host–guest chemistry can offer a palette of non-covalent interactions, within a large variety of interacting species. Molecular receptors such as cyclodextrins, calixarenes, crown ethers and pillararenes are ideal components of supramolecular polymers thanks to their synthetic and binding versatility. Moreover the host–guest interactions endow the final supramolecular materials with some attractive features like stimuli responsiveness to pH, temperature, electrons and light. A further class of molecular receptors that fulfills the requirement of high association constants necessary for polymerization is the one of tetraphosphonate cavitands (Tiiii). These resorcincarne based cavitands functionalized at the upper rim with four phosphonate groups – oriented inward with respect to the cavity – are appealing receptors thanks to remarkable recognition properties towards positively charged species. In particular the ability of tetraphosphonate cavitands to recognize the N-alkyl ammonium hydrochloride moieties have been demonstrated by our group in several papers including the complexation of the series of N-alkyl ammonium salts, for molecules of biological interest like sarcosine and the antitumor drug procarbazine hydrochloride. The observed selectivity is the results of the synergic action of three interaction modes: (i) multiple ion–dipole interactions between the inward facing P=O groups and the positively charged guest; (ii) hydrogen bonding interactions between the –NH2 group of the guest and the phosphonate groups; (iii) CH–π interaction involving the methyl group of the guest and the electron rich cavity of the receptor. The high association constants and pH dependence of the tetraphosphonate cavitand/N-methyl ammonium complexes prompted us to use them as building block to construct new supramolecular materials. Herein, we report the relevance of such host–guest interaction to form reversible supramolecular polymers and blends.
In the first part of the work a new pH dependent supramolecular homopolymer was self-assembled. An AB-type self-complementary heteroditopic monomer based on tetraphosphonate cavandit was synthesized introducing a sarcosine moiety at the lower rim of the receptor. In this case the supramolecular polymerization was promoted by the complexation of the protonated secondary amine by the tetraphosphonate cavandit. The pH dependence of the polymerization was demonstrated using several complementary techniques, such as $^1$H and $^{31}$P NMR spectroscopy, NMR diffusometry (DOSY) and light scattering measurements.

In the second section of the paper the molecular recognition properties of the supramolecular complex were used to introduce supramolecular cross-links and, in turn, to induce the compatibilization of two immiscible polymers: polystyrene (PS) and poly(butyl methacrylate) (PBMA). Indeed, an interesting property of secondary interactions is the ability to form reversible bonds between macromolecules.24-26 Blending two or more polymer in such a fashion allows the development of new materials that present combined properties of both polymers.27 Recently, our group has reported the compatibilization of PS and PBMA embedding tetraphosphonate cavandit and N-methylpyridinium moiety along the backbone of the polymers.28 In this work, tetraphosphonate cavandit and N-methyl ammonium salt molecules (sarcosine) were randomly copolymerized into the polymer chains of PS and PBMA respectively to investigate the ability of this complex to drive the formation of an amorphous blend. The formation of an homogeneous polymer blend was unambiguously confirmed in solution and at the solid state by complementary analytical tools, namely: NMR, differential scanning calorimetry (DSC) and atomic force microscopy (AFM).

Results and discussion

Self-assembly of the supramolecular homopolymer

Our target monomer was designed placing the sarcosine group at the lower rim of the tetraphosphonate cavandit connected through a short tether, to avoid intramolecular self-association processes. The monomer Tiili[3C$_3$H$_7$, 1 sarcosine, CH$_3$, Ph] [5] was synthesized in four steps (22% overall yield, Scheme 1): the key step of the synthesis was the insertion of the Boc-sarcosine moiety at the lower rim of the silyl cavandit 1 under Steglich conditions.29

The carbamate protecting group allowed an orthogonal deprotection of the upper rim of 2 using tetra butylammonium fluoride. The four inward phosphonate groups were introduced by reacting the resorcinarene 3 with $P$,P-dichlorophenylphosphine and oxidizing the tetraphosphonate intermediate in situ with hydrogen peroxide. Finally, cavandit 4 was treated with trifluoroacetic acid to remove the carbamate protecting group and protonate the amine (Scheme 2). Once protonated, this molecule underwent polymerization to the corresponding homopolymer 5. The intermolecular inclusion process between the methylammonium moiety of one cavandit monomer and the cavity of another was monitored by $^{31}$P and $^1$H NMR spectroscopy. The $^{31}$P signal of 4 was split in two singlets because the four phosphorous of the cavandit are not magnetically equivalent (Fig. S1†). After the acidic treatment the $^{31}$P signal of the phosphate groups of the cavandit 5 experienced a downfield shift due to the inclusion of the cationic part of the guest in the cavity. Upon complexation, the methyl protons of the sarcosine group shifted upfield from 2.90 ppm in 4 to $-0.7$ ppm in 5 (Fig. S2†).19 These data confirmed the inclusion of the sarcosine group of the monomer within the cavity of another receptor, together with the broadening of all

Scheme 1. Synthesis of Tiili[3C$_3$H$_7$, 1 sarcosine BOC protected, CH$_3$, Ph] 1: (a) N-Boc-sarcosine, DCC/DMAP, CHCl$_3$, r.t., 12 h, 40%; (b) TBAF, THF, r.t., 1 h, 60%; (c) (1) PhPCl$_2$, Py, 75 °C, 3 h; (2) H$_2$O$_2$, r.t., 1 h, 92% (over two steps); (d) TFA, DCM, r.t., 3 h, quantitative.

Scheme 2. Formation of homopolymer of Tiili[3C$_3$H$_7$, 1 sarcosine salt, CH$_3$, Ph] 5 upon deprotection of precursor 4.
the signals of the $^1$H NMR spectra – indicating the formation of large aggregates. Quantitative measurement of the association constants ($K_{ass}$) for Tiili–guest systems were obtained using isothermal titration calorimetry (ITC). The complexation of sarcosine methyl ester hydrochloride in methanol solution (†) by the parent Tiili$[C_{3}H_{7}, C_{3}H_{5}, Ph]$ showed a $K_{ass}$ value of $6.8 \times 10^{3}$ M$^{-1}$, while a higher $K_{ass}$ of $2.6 \times 10^{6}$ M$^{-1}$ was measured in dichloromethane for the same cavitand and $N,N$-methylbutyl ammonium chloride, that is a proxy for sarcosine (Fig. S3†). To obtain further insights into the self-assembly process, many static (SLS) and dynamic light scattering (DLS) experiments were performed. SLS measurements provided the weight-average molecular weight ($M_w$) of the aggregates in solution by measuring the intensity of the scattered light. In the case of Tiili supramolecular homopolymer, SLS measurements were performed in chloroform in the 9.0–40.0 mg mL$^{-1}$ concentration range. Due to the presence of complexation equilibria within the supramolecular polymer, $M_w$ estimations by SLS measurements were made in narrower concentration windows, to have an approximate value of the average molecular weight in the considered concentration regime. In particular the Debye plots for the 9.2–14.1 mg mL$^{-1}$ ($M_w = 7 \pm 1$ kDa) and 25.5–36.7 mg mL$^{-1}$ ($M_w = 11 \pm 1$ kDa) concentration windows are reported in ES† (Fig. S4 and S5, incremental r. i. dn/dc = 0.152 mL g$^{-1}$, toluene as scattering standard). The DLS experiments on Tiili homopolymer showed a smooth shifting towards larger size as the concentration was increased – as expected for a supramolecular polymer. Average hydrodynamic diameters starting from 5 nm (2.8 mg mL$^{-1}$) were obtained, with size distributions showing monodisperse aggregates, with low and reproducible polydispersity index (PDI < 0.2) in the full concentration range that was investigated (Fig. 1). These size distributions found at various concentrations are in agreement with $M_w$ obtained from the SLS data.

SLS and DLS measurements obtained with our instrumentation are – with very good approximation – independent upon the shape of the homopolymer chains in solution, since the measured average hydrodynamic diameter was always lower than 60 nm. The rather narrow degree of polymerization (DP) window (7–11), that can be inferred from these data probably indicates that for Tiili, the formation of cyclic structures$^{22}$ – rather than more longer and flexible linear chains – is strongly favoured, as already demonstrated in the case of A-B supramolecular polymers$^{23}$ with similar $K_{ass}$ and given the discrete flexibility of the Tiili–Tiili linking.

The size distribution of the homopolymer was also measured at various temperatures to verify the stability of the aggregates (Fig. S6†). These experiments were performed in 1,1,2,2-tetrachloroethane, which has an high boiling point than chloroform, using two different concentrations (4.2 and 36.7 mg mL$^{-1}$) and a wide range of temperature: for both concentrations we observed stable aggregates with quite low PDI and an hydrodynamic diameter of about 10 nm from 15 °C to 80 °C.

Then we turned to investigate the responsive properties of the supramolecular homopolymer employing NMR spectroscopy and DLS (Fig. 2), since homopolymer 5 is able to respond to a simple chemical stimuli such as an acid–base treatment, causing the assembly and disassembly of the aggregates. Compound 5 was easily deprotonated with 3 equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), a non-nucleophilic hindered tertiary amine that, once protonated, does not fit into the receptor cavity. Additionally the deprotonated cavitand can be reconverted to the homopolymer upon subsequent exposure to 5 eq. of trifluoroacetic acid (TFA). The $^{31}$P and $^1$H NMR spectroscopy recorded an high-field shift of the signal after the basic treatment and consequent reappearance of the characteristic pattern of the phosphorous signal similar to that of the protected monomer 5, while the addition of TFA restored the phosphorous signal at low-field. The pH-responsive properties of the supramolecular homopolymer was also confirmed by DLS studies: as depicted in Fig. 2. DLS size distribution presents a sudden drop of the average hydrodynamic diameter of the homopolymer after the treatment with DBU, with a size consistent with the one of the Tiili monomer. Subsequently, the addition of TFA restored the initial size distribution demonstrating the reproducible responsiveness of this system. The self-assembly process at 25 °C was also monitored by $^1$H NMR diffusometry (DOSY, Fig. S6, S8 and S9†). For this analysis, 5.26 mg of Tiili pre-treated with TFA were dissolved into 750 mL of CDCl$_3$ to give a 5 mM sample (monomer concentration). The diffusion coefficient of the homopolymer in this sample was estimated by means of a LED-STE pulse sequence featuring bipolar gradients of 1 ms duration ($\delta = 2$ ms) and a 100 ms diffusion delay ($\Delta$). The resulting gradient-attenuated transients (32) were processed both by regression fits and by inverse Laplace transform (ILT) of selected peak intensities. Possible convection flow in the 5 mm tube was ruled out by comparing the estimated diffusion coefficient of residual CHCl$_3$ in the sample ($2.59 \times 10^{-9}$ m$^2$ s$^{-1}$) with literature data ($2.58 \times 10^{-9}$ m$^2$ s$^{-1}$).$^{13}$ This analysis provided an apparent diffusion coefficient of $4.22 \times 10^{-10}$ m$^2$ s$^{-1}$ for the homopolymer. To minimize the interference from extra NMR signals, the monomers were restored by adding to the previous sample 4 eq. of aqueous NaOD dissolved in MeOD. The resulting mixture was stable over hours, and provided an estimated diffusion coefficient of $2.67 \times 10^{-9}$ m$^2$ s$^{-1}$ for residual CHCl$_3$.

The apparent diffusion coefficient of the monomer estimated by the same protocol outlined before was $7.49 \times 10^{-10}$ m$^2$ s$^{-1}$, roughly corresponding to a hydrodynamic diameter of 1.0 nm. These data taken in concert, also with the DLS size distribution of the monomer, confirmed that the polymerization degree of the aggregates can be straight forwardly modified altering the pH of the solution.

**Compatibilization of two immiscible polymers**

Supramolecular self-assembly of the homopolymer has proven that the proposed host-guest interaction is amenable to construct responsive materials driven by non-covalent interactions.
In this section we test the cavitand–sarcosine hydrochloride binding mode for the compatibilization of two immiscible polymers, namely PS and PBMA. For this purpose we prepared a PS functionalized with tetraphosphonate cavitand (PS–Host, Scheme 3a) and PBMA decorated with a sarcosine hydrochloride moiety (PBMA–Sarc, Scheme 3b). The non-covalent interactions between the host–guest counterparts brought to a cross-link of the polymer chains of the copolymers and consequently the formation of an homogeneous blend. The PS–Host was synthesized and characterized according to protocols previously published by our group.  

The PBMA–Sarc was synthesized by copolymerization of butyl methacrylate with the corresponding sarcosine-functionalized monomer, 6-((methylglycyl)oxy)hexyl methacrylate 9, prepared

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**Fig. 1**  DLS analysis (CHCl₃, 25 °C): (a) hydrodynamic diameter and PDI of the homopolymer 5 as function of concentration; (b) and (c) examples of size intensity distributions at different concentrations.

**Fig. 2**  (1) DLS experiments (hydrodynamic diameter, CHCl₃, 10.5 mM, 25 °C): (a) homopolymer; (b) homopolymer + 3 eq. DBU; (c) homopolymer + 3 eq. DBU + 5 eq. triflic acid; (2) ³¹P{¹H}NMR spectra (CDCl₃, 400 MHz, 10 mM, 25 °C) of: (d) homopolymer; (e) homopolymer + 3 eq. DBU; (f) homopolymer + 3 eq. DBU + 5 eq. of TFA.
in three steps as reported in Scheme S1.† At first, monoesterification of 1,6-hexanediol with methacryloyl chloride introduced a single methacrylate group, then the monomer was reacted with bromoacetyl chloride using a DCC/DMAP coupling procedure affording the diester 8. Subsequently, 8 underwent a nucleophilic substitution with methylamine to afford the monomer 9 in 27% overall yield. The free radical copolymerization of 9 with butyl methacrylate in treatment with hydrochloric acid afforded the copolymer PBMA–Sarc (Scheme S2†). The ratio between 9 and butyl methacrylate in the reaction was 4 : 96. The polymer was fully characterized by several techniques. 1H NMR (Fig. S10†) spectroscopy and FT-IR (Fig. S11†) assured the formation of the desired copolymer. The percentage of the guest monomer in the copolymer was estimated through elemental analysis and 1H NMR integration. The initial molar composition of butyl methacrylate and 9 was not fully retained inside the polymer. In fact, elemental analysis led to a value of 2.9% molar incorporation. This value was confirmed from 1H NMR integration ratio of the methyl group of sarcosine (2.29 ppm) and OCH2 groups (3.96 ppm).

The weight-average molecular weight $M_n$, the number-average molecular weight $M_n$ and the PDI were assessed by gel permeation chromatography (GPC) in chloroform with standard polystyrene calibration. The results are summarized in Table 1 and the refractive index chromatographic trace of 10 is reported in Fig. S12.† The average number of host–guest units per chain ($F$) was calculated from the experimentally determined monomer molar ratios and $M_n$ of the polymers, obtained respectively by elemental analysis and GPC. Inter-molecular association between the two copolymers in solution was monitored by 31P NMR. This technique proved the association between PS–Host and PBMA–Sarc by recording a downfield shift of the phosphorous signal of the cavitand: the 7.8 ppm signal of free PS–Host moved to 11.7 ppm in the presence of PBMA–Sarc (Fig. S13†). The 31P NMR analysis indicated that the $F$ values reported in Table 1 are correct for the determination of the 1 : 1 host–guest molar ratio between the two polymers. The next step was to study the blend at the solid state: PS–Host and PBMA–Sarc were dissolved in dichloromethane and the two solutions were mixed together in the right proportion to obtain a 1 : 1 molar ratio of cavitan host and sarcosine hydrochloride guests attached to the polymer backbone (see Experimental section). The miscibility of the two copolymers was assessed using two different methods, differential scanning calorimetry (DSC) on the powder and atomic force microscopy (AFM) on spin cast films. Materials formed by a single phase structure exhibit only one glass transition temperature ($T_g$) that can be determined via DSC. The 1 : 1 molar mixture of PS–Host and PBMA–Sarc showed one endothermic relaxation peak, in between the $T_g$ of the two functionalized polymers, indicative of an homogeneous blend (Table 2, Fig. 3 and S14†).

AFM experiments were performed in contact mode on spin cast films to determine the morphological homogeneity of the mixture of PS–Host and PBMA–Sarc. It is well known that in case of films prepared from blends of immiscible polymers, the topography consists of segregated islands and depressions, while on the contrary, a flat and homogeneous surface indicates good miscibility of the polymers. In the pristine PBMA/PS mixture, PBMA, having higher mobility, migrate to the silicon surface, while PS tends to segregate forming the islands above PBMA. The phase segregation results from the combination of the low chemical affinity between the two polymers, and the great difference in terms of their surface energy. A thin film was prepared from a 0.5 mM solution of a 1 : 1 molar mixture of PS–Host and PBMA–Sarc and was deposited on Si/SiO, surface by spin coating (1500 rpm for 30 s, dichloromethane as solvent). As the $T_g$ of the two polymers are completely different (PS $\sim$ 100 °C, PBMA $\sim$ 23 °C), it was necessary to work at 15 °C, to avoid any dewetting-related phenomenon.

Fig. 4a shows a typical morphology corresponding to the immiscible PS–PBMA blend, while Fig. 4b, by contrast, reports the homogeneous and flat topographic image of compatibilized PS–Host and PBMA–Sarc blend. These two evidences

![Scheme 3](image)

Scheme 3 (a) PS–Host; (b) PBMA–Sarc.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$T_g$ (°C)</th>
</tr>
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<tbody>
<tr>
<td>PS–Host</td>
<td>97.1</td>
</tr>
<tr>
<td>PBMA–Sarc</td>
<td>14.6</td>
</tr>
<tr>
<td>PS–Host/PBMA–Sarc</td>
<td>37.3</td>
</tr>
</tbody>
</table>

Table 2 Glass transition temperatures of copolymers PS–Host, PBMA–Sarc and mixture

<table>
<thead>
<tr>
<th>Polymers</th>
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</tr>
</thead>
<tbody>
<tr>
<td>PS–Host</td>
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</tr>
<tr>
<td>PS–Host/PBMA–Sarc</td>
<td>37.3</td>
</tr>
</tbody>
</table>

Table 1 GPC characterization of the polymers and average number of host–guest units $F$

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$M_n$</th>
<th>$M_n$</th>
<th>PDI</th>
<th>mol% $F$ units</th>
<th>Average no. of $F$ units per chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS–Host–4%</td>
<td>20 800</td>
<td>27 100</td>
<td>1.30</td>
<td>3.9</td>
<td>5.3</td>
</tr>
<tr>
<td>PBMA–Sarc–4%</td>
<td>23 200</td>
<td>36 600</td>
<td>1.58</td>
<td>2.9</td>
<td>4.6</td>
</tr>
</tbody>
</table>

$^a$ Relative molecular weights against PS standards obtained from GPC in CHCl$_3$. $^b$ Determined by elemental analyses and 1H NMR integration. $^c$ Calculated from the number-average molecular weights ($M_n$) and mol% recognition unit of the polymers.
demonstrate the mixing of the two copolymers at the molecular level, hence their compatibilization driven by host–guest interactions between the cavitand and the sarcosine hydrochloride units, present in low amounts in the two copolymers.

Conclusions

In summary, the molecular recognition properties of the tetraphosphonate cavitand/N-methyl ammonium complex were successfully translated in supramolecular polymer chemistry in two different settings. By first a new stimuli responsive supramolecular homopolymer were designed and synthesized, exploiting the monomer Tiiii[3C3H7, 1 sarcosine, CH3, Ph] as building block based on the resorcinarene scaffold, and presenting four P≡O groups at the upper rim and a sarcosine moiety at the lower rim. The self-assembly properties of this supramolecular polymer were investigated with several techniques which provided numerous evidences on the formation of supramolecular homopolymer in solution. Furthermore, the polymers assembly was controlled by means of acid–base treatment demonstrating the reversibility of the system. In the second study, the host–guest counterpart was embedded in polymeric materials to test its ability to promote polymer blending. The formation of an homogeneous blend was unambiguously confirmed by several and complementary analytical tools, such as NMR, DSC and AFM. The precise response to pH constitutes a significant advantage for controlling and driving polymer blending. The present findings lead us to propose this pH responsive host–guest system as an useful tool to manipulate the properties of polymeric species and to generate pH responsive polymeric interfaces.

Experimental section

Materials and methods

All reagents and chemicals were obtained from commercial sources and used without further purification. Compound 1 was prepared according to the published procedure. Dry pyridine was distilled from KOH before use. n-Butyl methacrylate (Aldrich) was distilled under vacuum to remove stabilizers. 2,2’-Azobis(2-methylpropionitrile) (AIBN, Fluka), was purified by crystallization in acetone. Column chromatography was performed using silica gel 60 (MERCK 70-230 mesh). Electrospray ionization ESI-MS experiments were performed on a Waters ZMD spectrometer equipped with an electrospray interface. Exact masses were determined using a LTQ ORBITRAP XL Thermo spectrometer equipped with an electrospray interface. MALDI-TOF spectra was performed using AB SCIEX MALDI TOF-TOF 4800 Plus (matrix: α-cyano-4-hydroxycinnamic acid). 1H NMR spectra were obtained using a Bruker AVANCE-300 (300 MHz) or a Bruker AVANCE 400 (400 MHz). All chemical shifts (δ) were reported in ppm relative to the proton resonances resulting from incomplete deuteration of the NMR solvents. 31P NMR spectra were obtained using a Bruker AVANCE-300 (300 MHz) or a Bruker AVANCE 400 (400 MHz). All chemical shifts (δ) were recorded in ppm relative to external 85% H3PO4 at 0.00 ppm. FT-IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One Spectrometer on films obtained by solution casting onto KBr windows of polymers diluted CHCl3 solution. DSC thermograms were recorded by using a Mettler Toledo Star System, model DSC 822e differential scanning calorimeter equipped with a Stare software.

Fig. 3  DSC thermogram of 1 : 1 molar mixture PS–Host/PBMA–Sarc.

Fig. 4  (a) AFM topographic image of PS/PBMA mixture, deposited by spin coating of a dichloromethane solution, displaying large lateral in homogeneities; (b) the same for a film made of 1 : 1 molar mixture PS–Host/PBMA–Sarc, exhibiting an homogeneous and flat morphology.
AFM measurements
Surface topography was examined using an atomic force microscope Thermomicroscope Autoprobe CP Research. All measurements were performed either in contact mode or in tapping mode employing respectively Silicon Nitride probes (Veeco OTR4-35, typical spring constant 0.05 N m\(^{-1}\)) or silicon probes (Bruker, MPP-12100, typical spring constant 3 N m\(^{-1}\)), and to preserve the initial structure, the films were not annealed. Given the low T\(_g\) of PBMA, to minimize artifacts due to tip-sample interactions, all samples were measured at 15 °C using a Peltier cell in a dry chamber to prevent humidity condensation. The collected images were analyzed using the proprietary software or Gwyddion, an Open Source software, covered by GNU General Public License (http://Gwyddion.net).

GPC measurements
GPC System apparatus equipped with Jasco PU-2089 Plus pump, Jasco RI 2031 Plus as Refractive Index Detector, Jasco CO_2063 GPC System apparatus equipped with Jasco PU-2089 Plus pump, GPC measurements covered by GNU General Public License (http://Gwyddion.net). Annealed. Given the low and to preserve the initial structure, the solution were prepared. PS whereas 40 mg of PBMA was made with polystyrene standards and calculations were carried out with software Borwin 1.21.61 (JMBS DEVELOPMENT).

Light scattering measurements
SLS and DLS measurements were performed using a Malvern Nano ZS instrument, equipped with a 633 nm laser source. All the solution were filtered with PTFE filters (4 mm × 0.2 μm, Supelco). The width of DLS hydrodynamic diameter distribution is indicated by Pdi (Polydispersion Index). In case of a mono-modal distribution (gaussian) calculated by means of cumulant analysis, Pdi = (σ/Z\(_{av}\))^2, where σ is the width of the distribution and Z\(_{av}\) is average diameter of the particles population respectively.

Polymer blending and film deposition
Solutions of the different polymers (0.5 mM) in CH2Cl2 were prepared. PS–Host–4% (42 mg) was dissolved in 4 mL of CH2Cl2, whereas 40 mg of PBMA–Sarc-4% were dissolved in 4 mL of CH2Cl2. 1 mL aliquot of PS–Host solution was mixed with 1.38 mL of PBMA–Sarc solution, and 100 μL of the resulting solution was filtered over 0.45 μm PTFE filter and spin-coated on a silicon slice at 1500 rpm for 30 seconds. The films were analyzed without any further modification.

NMR diffusometry
NMR diffusometry experiments were performed on a Bruker AVANCE III (500 MHz) spectrometer equipped with a BBI Zy-gradient probe (max. gradient = 55 G cm\(^{-1}\)). DOSY maps were obtained with Bruker Dynamics Center 2.2.1 after spectra preprocessing in TopSpin 3.1. Both fitting and inverse Laplace transform (ILT) methods were employed to check for consistency of the results. The final values for the apparent diffusion coefficients (free and oligomer) were obtained by averaging the values relative to selected signals.

N-Boc-sarcosine
To a solution of sarcosine (0.4 g, 4.49 mmol) in acetonitrile, triethylamine (0.68 mL, 4.94 mmol) and di-tert-butyl dicarbonate (1.13 mL, 4.94 mmol) were added. The solution was heated to reflux for 4 hours and the solvent removed in vacuo. The crude oil was dissolved in dichloromethane and extracted with water (2 × 30 mL). The organic phase was dried with anhydrous CaCl\(_2\) and evaporated under reduced pressure to give the product as colorless oil (0.4 g, 2.15 mmol, 48%). \(^1\)H NMR (CDCl\(_3\), 400 MHz): δ (ppm) = 9.56 (s, 1H, OH), 3.87 (d, J = 33.4 Hz, 2H, NCH\(_2\)), 2.83 (s, 3H, NCH\(_3\)), 1.34 (s, 9H, C(CH\(_3\))\(_3\)); ESI-MS: m/z 190.1 [M + H]+.

N-Boc-sarcosine based silyl-cavitand (2)
N-Boc-sarcosine (0.31 g, 1.68 mmol), DCC (0.34 g, 1.68 mmol) and DMAP (0.2 g, 1.68 mmol) were dissolved in dry chloroform under stirring for 15 minutes. Successively, monohydroxy footed silylcavitand 1 (0.8 g, 0.83 mmol) was added into the reaction mixture and stirred overnight at room temperature. Saturated NH\(_4\)Cl solution was added and the organic phase was extracted with water (2 × 20 mL) dried with anhydrous Na\(_2\)SO\(_4\), filtered and the solvent was removed in vacuo. Purification by silica gel column chromatography (hexane : ethyl acetate 85:15) yielded the desired product as white solid (0.37 g, 0.33 mmol, 40%). \(^1\)H NMR (CDCl\(_3\), 300 MHz): δ (ppm) = 7.20 (s, 2H, ArH), 7.18 (s, 2H, ArH), 4.64 (t, J = 8 Hz, 4H, ArCH\(_2\)), 4.28–4.20 (2H, CH\(_2\)OC(O)), 3.96 (d, J = 40 Hz, 2H, NCH\(_2\)), 2.85 (d, J = 10.3 Hz, 3H, NCH\(_3\)), 2.27–2.01 (m, 10H, CH\(_2\)CH\(_2\)CH\(_2\)OC(O), CH\(_2\)CH\(_2\)CH\(_3\)), 1.85 (s, 12H, ArCH\(_3\)); 1.67–1.14 (m, 17H, CH\(_3\)CH\(_2\)OC(O), C(CH\(_3\))\(_3\), CH\(_2\)CH\(_2\)CH\(_3\)), 0.98–0.82 (m, 9H, CH\(_2\)CH\(_2\)CH\(_3\)), 0.54 (s, 12H, SiCH\(_3\)out), –0.64 (s, 12H, SiCH\(_3\)in); ESI-MS: m/z 1164.1 [M + K]+.

N-Boc-sarcosine based resorcinarene (3)
To a solution of N-Boc-sarcosine based silyl-cavitand 2 (0.39 g, 0.34 mmol) in dry THF, TBAF (1.36 g, 5.2 mmol) was added under argon atmosphere at 0 °C. After 1 hour the reaction mixture was quenched by adding saturated NH\(_4\)Cl solution, the crude mixture was diluted with ethyl acetate and the organic phase was extracted with sat. aq. NaHCO\(_3\) and water. The organic phase was dried with anhydrous Na\(_2\)SO\(_4\) and evaporated under reduced pressure to give the product as yellow pale solid (0.18 g, 0.2 mmol, 60%). \(^1\)H NMR ((CD\(_3\))\(_2\)CO, 300 MHz): δ (ppm) = 7.84 (s, 2H, ArH), 7.46 (s, 2H, ArH), 7.44 (s, 2H, ArH), 4.41 (t, J = 9 Hz, 4H, ArCH\(_2\)), 4.24–4.11 (m, 2H, CH\(_2\)OC(O)), 3.97 (d, J = 14.5 Hz, 2H, NCH\(_2\)), 2.91 (d, J = 9 Hz, 3H, NCH\(_3\)), 2.45–2.00 (m, 20H, CH\(_2\)CH\(_2\)CH\(_2\)OC(O), CH\(_2\)CH\(_2\)CH\(_3\), ArCH\(_3\)), 1.71–1.55 (m, 2H, CH\(_2\)CH\(_2\)OC(O)), 1.50–1.18 (m, 15H, C(CH\(_3\))\(_3\), CH\(_2\)CH\(_2\)CH\(_3\)), 0.95 (t, J = 9 Hz, 9H, CH\(_2\)CH\(_2\)CH\(_3\)); ESI-MS: m/z 922.8 [M + Na]+, 939 [M + K]+.
Tiiii[3C,H, 1 Boc-sarcosine, CH₃, Ph] (4)

To a solution of N-Boc-sarcosine based resorcinarene 3 (0.19 g, 0.21 mmol) in freshly distilled pyridine, dichlorophenylphosphine (0.13 mL, 0.88 mmol) was slowly added at room temperature under argon atmosphere. After 3 hours of stirring at 75 °C, the solution was allowed to cool at room temperature and aqueous H₂O₂ (2 mL, 30%) was added. The resulting mixture was stirred for 1 hour at room temperature, then addition of water resulted in the precipitation of a white powder. The solid was recovered by suction filtration to give pure 4 (0.45 g, 0.33 mmol, 92%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.15–8.01 (m, 8H, P(0)ArHₐ), 7.72–7.61 (m, 4H, P(0)ArHₖ), 7.61–7.47 (m, 8H, P(0)ArHo), 7.24–7.13 (m, 4H, ArH), 4.85–4.72 (m, 4H, ArCH), 4.35–4.24 (m, 2H, CH₂OC(O)), 3.97 (d, J = 36 Hz, 2H, NCH₂), 2.90 (s, 3H, NCH₃), 2.44–2.30 (m, 8H, CH₂CH₂CH₂, CH₂CH₂CH₂OC(O)), 2.14 (s, 12H, ArCH₃), 1.50–1.20 (m, 15H, C(CH₃)₃, CH₂CH₂CH₃), 1.12–0.98 (m, 9H, CH₃), 1.16 (s, 3P, P=O); ¹³P ¹H NMR (CDCl₃, 161.9 MHz): δ (ppm) = 8.44 (s, 1P, P=O) 8.34 (s, 3P, P=O); HR-ESI-MS: m/z calecd for C₇₆H₈₁NO₁₆P₄Na: 1410.4403; found: 1410.4398.

Tiiii[3C,H, 1 sarcosine salt, CH₃, Ph] (5)

Cavitand 4 (20 mg, 0.014 mmol) was treated with 10 equivalent of trifluoroacetic acid in CHCl₃. After 3 hours the solvent was removed in vacuo and the crude was dried under reduced pressure [quantitative yield]. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.17–7.96 (m, 8H, P(0)ArHₐ), 7.89–7.42 (m, 16H, P(0)ArHₐ, P(0)ArHₖ, ArH), 4.85–4.61 (m, 4H, ArCH), 4.25 (s, 2H, CH₂OC(O)), 3.30 (s, 2H, NCH₂), 2.66–2.30 (m, 8H, CH₂CH₂CH₂, CH₂CH₂CH₂OC(O)), 2.14 (s, 12H, ArCH₃), 1.79–1.59 (m, 2H, CH₂CH₂OC(O)), 1.51–1.20 (m, 8H, CH₂CH₂CH₃), 1.16–0.81 (m, 9H, CH₃), −0.68 (s, 3H, NCH₃); ¹³P ¹H NMR (CDCl₃, 161.9 MHz): δ (ppm) = 11.01 (s, P=O); MALDI TOF-TOF: calecd for C₇₄H₆₁NO₁₄P₄Na: 1288.4054 Da, found: 1288.3879 Da.

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Notes and references