Macromolecules

Quasi-Block Copolymers: Design, Synthesis, and Evidence for Their Formation in Solution and in the Melt

Ester Weiss,[†] Kostas Ch. Daoulas,[‡] Marcus Müller,[§] and Roy Shenhar^{*,†}

[†]Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Edmond J. Safra Campus, Givat Ram, Jerusalem 91904, Israel

^{*}Max-Planck-Institute für Polymerforschung, 55128 Mainz, Germany, and Innovation Lab GMBH, 69115 Heidelberg, Germany

[§]Institut für Theoretische Physik, Georg-August-Universität, 37077 Göttingen, Germany

Supporting Information

ABSTRACT: A family of block copolymers featuring dynamically controlled compositions is presented. These copolymers, termed "quasi-block copolymers" (q-BCP), consist of a supramolecular polymer as one of the blocks. A conventional polymer end-capped with a functionality that is complementary to the supramolecular monomer is used to terminate the supramolecular block, giving rise to a block copolymer architecture. In this work we have utilized N, N'-2,4-bis((2-ethylhexyl)ureido)toluene



(EHUT) as the supramolecular monomer and employed two types of modified 2,4-bis(ureido)toluene polystyrenes as the endfunctionalized conventional polymer. Solution viscosity measurements with different solvent compositions and DSC analysis of poly(EHUT)/functionalized-PS blends provide compelling evidence for the formation of self-assembled q-BCP structures both in solution and in the melt. The qualitative role of chain stoppers on the molecular weight distribution is studied by simulations.

INTRODUCTION

Nanostructured materials represent a major research thrust in materials science today because the nanometer scale is relevant to various fields, ranging from microelectronics¹ to catalysis² and medicine.³ Another focus of interest is the so-called "smart" materials,⁴ which respond to changes in environmental parameters such as pH, temperature, and ionic strength. Responsiveness is usually obtained via molecular functionalities that can be reversibly switched between stable states by the application of external stimuli or a change in environmental conditions. In general, polymers can provide solutions to both challenges because they can be synthesized in different architectures, with molecular sizes in the range of nanometers, and tailored with a variety of functionalities that lead to the desired material properties.

Block copolymers consist of two or more sequences of different repeat units and give rise to materials, which phase separate into a variety of useful morphologies on the scale of 10-100 nm. The self-assembly is controlled by the interplay between incompatibility and chain stretching.⁵ Supramolecular polymers, on the other hand, consist of bifunctional molecules ("monomers") that are held together by reversible and highly directional noncovalent interactions (e.g., multiple hydrogen bonding, metal–ligand coordination, aromatic stacking, etc.).^{6–15} Similar to traditional polymers, these materials exhibit strong concentrationdependent viscosities and obey the predictions of the wellestablished theories of polymer physics. The reversibility of the bonding between the monomeric units, however, makes

supramolecular polymers highly sensitive to different factors that affect the bonding such as temperature, type of solvent, and presence of competitive molecules. Supramolecular polymers thus give rise to environmentally responsive materials that can be easily assembled and dismantled under mild conditions, a feature that strongly affects their material properties.^{6–15} The combination between supramolecular polymers and block copolymers should thus afford new materials featuring responsiveness to environmental conditions as well as nanoscale, phase-separated structures.

The simplest design of a block copolymer consisting of a supramolecular block includes two components: a conventional (i.e., covalently bonded) polymer terminated with a supramolecular unit and self-complementary, bifunctional molecules ("supramolecular monomers"), which form the supramolecular block and also feature high affinity to the end group capping the conventional polymer (Figure 1). These copolymers, termed "quasi-block copolymers" (q-BCPs),16 give rise to diblock and triblock copolymers depending on the symmetry of the supramolecular monomer and coexist in the bulk with homopolymers of the supramolecular molecules.

The number-average degree of polymerization $\langle N \rangle$ of supramolecular polymers is dictated by the association constant K and the concentration of the monomer *c*. For sufficiently high values of K and c, $\langle N \rangle \approx 2(Kc)^{1/2}$.¹⁷ While large values of K are a

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Figure 1. Schematic illustration of the formation of a quasi-block copolymer (q-BCP): bifunctional supramolecular monomers first create long supramolecular chains; addition of end-functionalized conventional polymers, acting as chain stoppers, leads to the formation of q-BCPs.

prerequisite for obtaining long polymer chains from supramolecular monomers, they also cause the polydispersity index (PDI) to approach the theoretical value of 2 (in analogy to step polymerization). Better control over molecular weight and PDI can be achieved with the addition of complementary monofunctional units, termed "chain stoppers", which cap the chain ends, block their growth, and additionally suppress the formation of supramolecular macrocycles.^{12g,17,18} When the mole fraction of chain stoppers, *x*, and the monomer concentration exceed the critical value of $(xc^{1/2})_{crit} = n/(2K^{1/2})$, $\langle N \rangle$ becomes independent of *K* and *c* and is totally dictated by *x*: $\langle N \rangle \approx n/x$ (where *n* is the number of chain stoppers that have to be added to the solution to produce one new chain).¹⁷ Hence, in the context of q-BCPs, the end-functionalized conventional polymer acts as a chain stopper to the growing supramolecular chain, which both regulates its length (to some extent) and adds the ability to create micro- and macrophase-separated structures both in solution (e.g., as micelles) and in the melt.

Despite the extensive activity in the field of supramolecular polymers, both experimentally^{6–12} and theoretically,^{13,14} published reports on the formation of nanoscale structures from such polymers are rare^{19,20} and usually deal with block copolymers featuring conventional blocks that are linked by noncovalent interactions (i.e., a fundamentally different concept).^{21,22} So far, only a few papers have reported on systems consisting of supramolecular polymer and conventional polymer components.²⁰ These, however, were either structured as a statistical graft copolymer¹⁹ (i.e., the functionalized conventional polymer did not act as a chain stopper) or involved supramolecular monomers that associate with an exceedingly high association constant, which reduces their dynamic nature.²⁰

Simulations, which we have performed on the behavior of q-BCP systems in the bulk, have revealed a variety of morphologies (bicontinuous networks, cylinders, lamellae, and macrophase separation) that can be obtained by varying the association constant and the level of incompatibility between the conventional and supramolecular blocks.²³ The simulations gave additional insights into the distribution of compositions of the formed chains (among supramolecular homopolymers and di- and triblock q-BCPs) as well as their spatial distributions in the microphase-separated morphology. For example, it was found that short q-BCPs segregate to the phase rich with the conventional polymer blocks while long q-BCPs localize at the interfaces.²³ Recent simulations performed on q-BCP systems on patterned substrates have shown that the dynamic nature lends great versatility to q-BCP systems in the context of pattern replication of nonregular features.²⁴

In this paper we describe an experimental demonstration for the formation of a model q-BCP system based on capped polystyrene (PS) as the conventional block and on N_1N' -2,4bis((2-ethylhexyl)ureido)toluene (EHUT)¹² as the supramolecular monomer. In chloroform (CHCl₃), EHUT forms thin, onedimensional supramolecular filaments with one molecule in the cross section.^{12h} In toluene, EHUT forms long, tubular selfassembled structures, giving rise to very high viscosities.^{12d,f,h} In this tubular structure, the cross section contains three EHUT molecules,^{12f} where the 2-ethylhexyl groups point away from the tube, the core aromatic rings are roughly perpendicular to the tube axis, and the cavity (about 7 Å in diameter) accommodates solvent molecules.^{12c} The tubular form is stable at high concentrations and low temperatures with nonpolar solvents that fit the dimensions of the cavity and undergoes a rather sharp transition with a decrease in concentration (within only 20%) or an increase in temperature (within only 5 °C) to the much shorter, thin filaments.^{12h} Several effective chain stoppers were developed for EHUT;^{12a,b,g} in our case, the chain stopper is modified with a polymer.

RESULTS AND DISCUSSION

Synthesis and Characterization of the End-Functionalized Block. Polystyrene (PS) was polymerized by atom transfer radical polymerization (ATRP) from modified initiators²¹ to ensure that every chain is capped with the end-functionality. Figure 2 shows the synthesis of two types of end-functionalized polystyrenes, containing either two or three butyl substituents on the urea groups (denoted as PS-DiBUT and PS-TriBUT, respectively), and Table 1 summarizes their data, including that of a nonfunctionalized PS used for comparison throughout this study. As these capped polymers serve as chain stoppers for poly(EHUT), the comparison between these end-functionalities was meant to provide insights into the mode of interaction and the effectiveness of chain stopper action on the poly(EHUT) chains.

Figure 3 shows the GPC traces of PS-DiBUT polymers obtained after different time intervals. The linear dependence between the number-average molecular weight (M_n) and the conversion as well as the relatively narrow molecular weight distributions attest to the controlled nature of the ATRP polymerization using the DiBUT-modified initiator. Nonetheless, polymers obtained under extended polymerization times exhibit bimodal molecular weight distributions with an increasing fraction of a high molecular weight component (from 13% for the 2k polymer to 21% in the 7k polymer), featuring molecular weights that are approximately double the molecular weight of the majority fraction. We attribute these higher molecular weight fractions to undesired coupling reactions, which terminate the growing chains and double their lengths. It should be noted that such a termination reaction is not detrimental for the purpose of preparing a q-BCP, since it gives rise to chains that are capped at both ends with the supramolecular unit (i.e., of the structure DiBUT-PS-DiBUT). Such polymers should still act as chain stoppers for poly(EHUT), giving rise to multiblock q-BCPs with

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Figure 2. Synthesis scheme for the formation of DiBUT and TriBUT-capped PS.

Table 1. Polymerization Data of the Covalent (PS-Based)Polymers

notation	polymerization time (min)	conv (%)	$M_{ m n}$ $({ m kDa})^a$	PDI	
PS-DiBUT 2k	15	3.5	2.5	1.12	
PS-DiBUT 4k	30	22	3.9	1.14	
PS-DiBUT 6k	45	48	6.0	1.18	
PS-DiBUT 7k	60	49	7.0	1.24	
PS-TriBUT 4k	30	22	3.9	1.22	
PS 4k			4.2	1.38	
^a According to SEC with PS standards.					

the same compositions as the intended diblock q-BCPs. Nevertheless, to strike a compromise between the desire to avoid this complication and the need to use as long a polymer as possible (to reduce the influence of the end-functionality on the general nature of the polymer),²¹ we used PS-DiBUT and PS-TriBUT obtained after 30 min of polymerization, featuring M_n of ca. 4 kDa.

The PS-DiBUT and PS-TriBUT were characterized by infrared (IR) and NMR spectroscopy. Figure 4 shows a comparison between the IR spectra of the PS-DiBUT, the DiBUT-modified initiator (denoted as DiBUT for brevity), and a mixture of the latter with non-end-functionalized PS (denoted as PS/DiBUT). While the N-H stretching modes of the pure initiator and the PS/DiBUT appear to be identical, there is a noticeable shift in the NH vibration peaks in the case of the end-functionalized polymer



Figure 3. GPC traces of PS-DiBUT polymers obtained after different polymerization times. Inset shows the dependence between the resulting M_n and the conversion.

(PS-DiBUT), indicating that the DiBUT functionality is indeed attached to the PS chain.

Further support for the presence of the DiBUT functionality terminating the PS chains was obtained from NMR measurements performed on the PS-DiBUT (Figure 5). Evidently, the methylene proton peaks in the region of 3–4.5 ppm, which are indicative of the DiBUT functionality, appear also in the spectrum of the PS-DiBUT. A similar spectrum was obtained for the analogous PS-TriBUT. The line broadening observed for these peaks, as well as the failure to obtain polymers in polymerization attempts of styrene performed under the same conditions in the



Figure 4. N-H stretching region in the IR spectra of the DiBUT initiator, PS/DiBUT mixture, and the end-functionalized polymer PS-DiBUT 4k. Curves are offset for clarity.



Figure 5. ¹H NMR of the DiBUT initiator and PS-DiBUT 4k. Peaks indicative of the DiBUT functionality are marked with asterisks.

absence of the DiBUT initiator, precludes the option of a mixture of unreacted initiator and self-polymerized PS.

Formation of the q-BCP in Solution. Compelling evidence for the formation of q-BCPs in solution was obtained from viscosity measurements performed on solutions containing varying amounts of EHUT and employing different solvent compositions. In these experiments, the measured viscosities of solutions containing EHUT with either PS-DiBUT or PS-TriBUT (denoted as PS-DiBUT/EHUT and PS-TriBUT/EHUT, respectively) were compared to solutions containing EHUT and nonfunctionalized PS (denoted as PS/EHUT) and were normalized to the solvent viscosity. This comparison enabled us to study the functioning and efficiency of the supramolecular end-functionality as a chain stopper for poly(EHUT).

Figure 6a shows the relative viscosities measured for the three types of systems as a function of EHUT concentration in 3:7 toluene:chloroform solutions at a constant concentration of the PS-derivative (i.e., the PS, PS-TriBUT, or PS-DiBUT in the respective system). All three systems exhibit rather low and constant relative viscosities up to EHUT concentration of 4.0 mg/mL. This suggests that in this solvent composition at low EHUT concentrations the poly(EHUT) chains formed are rather short and hence do not contribute to a considerable increase in viscosity above that of the solvent. This situation remains the same for the solutions containing the end-functionalized PS-DiBUT and PS-TriBUT polymers also at higher EHUT concentrations. In contrast, the viscosities of the PS/EHUT system with EHUT



Figure 6. Relative viscosities measured for the PS/EHUT, PS-DiBUT/ EHUT, and PS-TriBUT/EHUT systems at constant PS-derivative concentration (7.4 mg/mL) and different EHUT concentrations dissolved in different solvent compositions: (a) 7:3 CHCl₃:toluene, (b) 5:5 CHCl₃:toluene, (c) 3:7 CHCl₃:toluene. The dashed lines represent reaching the maximum detection limit in the viscosity measurements of the next concentration.

concentration exceeding 8 mg/mL become remarkably high (beyond the measurement range of the viscometer), possibly indicating a transition from the short filament structure to the long tubular structure.^{12d,f,h} Since nonfunctionalized PS cannot serve as a chain stopper for poly(EHUT), this indicates that at EHUT concentrations exceeding 8 mg/mL the unperturbed poly(EHUT) chains grow to substantial lengths. The sharp contrast between the behavior of the systems containing PS-DiBUT and PS-TriBUT and the behavior of the control system employing nonfunctionalized PS indicates an effective chain stopper effect displayed by the PS-DiBUT and PS-TriBUT, which result in shorter poly(EHUT) chains (which possibly results also a larger fraction of the filament form). The inevitable consequence of this effective chain stopper functioning of PS-DiBUT and PS-TriBUT is the formation of q-BCPs architectures.



Figure 7. Ratios of IR absorbances at 3344 and 3300 cm⁻¹ as a function of EHUT:PS or EHUT:PS-DiBUT ratio for the 3:7 CHCl₃:toluene solutions corresponding to Figure 6c. The ratios for solutions containing only EHUT at the same concentrations as the q-BCP mixtures are given as reference.

Increasing the toluene fraction in the solvent composition was expected to result in longer poly(EHUT) chains (with an additional change in morphology from short filaments to long tubular structures).^{12d,f,h} Figure 6b,c indeed shows this effect by the general trend of increasing relative viscosities already at lower EHUT concentrations for all systems. Remarkably, under these conditions we observe a difference between the DiBUT and the TriBUT end-functionalities, where it becomes obvious that the DiBUT functionality serves as a much better chain stopper for poly(EHUT) than the TriBUT functionality. Considering the chemical differences between the DiBUT and TriBUT functionalities, this provides evidence that with these macromolecular chain stoppers the chain stopping effect is achieved mostly through the NH groups, acting as hydrogen bond donors, rather than through the carbonyl groups. This finding seemingly stands in contrast to recent findings on molecular chain stoppers for EHUT, where it was shown that the carbonyl groups are responsible to the chain stopping effect and the involvement of existing NH groups may only reduce this effect by making the chain stopper act as a supramolecular comonomer.^{12a,g} More information is required to elucidate the reason for this behavior; we hypothesize that the PS chain tethered to the chain stopper functionality contributes to its ability to serve as a chain stopper, especially in the case of the tubular form of poly(EHUT), where it may disrupt the supramolecular assembly.

Quantitative analysis of the IR spectra at the N–H stretching modes provides insights into the molecular structure of the supramolecular blocks in the q-BCP architecture. Bouteiller and co-workers have identified that the transition from filamentous to tubular morphology of the supramolecular polymer, noted as a change in the linear density calculated from fitting small-angle neutron scattering (SANS) curves, is accompanied by a similar change in the absorption pattern of the hydrogenbonded N–H vibration band at 3344 cm⁻¹.^{12h} Hence, when the intensity of this absorbance is normalized to the intensity of the absorbance at 3300 cm⁻¹, ratios between 1.12 and 1.19 are attributed to the filament form, and ratios between 1.30 and 1.36 are exhibited by the tubular form. Figure 7 shows a marked difference in the measured ratios between analogous PS/EHUT and PS-DiBUT/EHUT systems for high EHUT contents in 3:7



Figure 8. DSC curves of blends of (a) PS and EHUT at different EHUT:PS ratios (x) and (b) PS-DiBUT 4k and EHUT at different EHUT:PS-DiBUT ratios. For comparison, the curves of the neat PS and PS-DiBUT 4k are provided on top (green), and the neat EHUT curve is provided on the bottom (blue). Curves are offset for clarity.

CHCl₃:toluene solutions (see also Supporting Information).²⁵ The high A_{3344}/A_{3300} ratios (in the range of 1.26–1.29) measured for the PS/EHUT solutions, which are close to the values measured for pure EHUT at the same concentrations (1.28-1.29), indicate a tubular morphology of the poly(EHUT) in this system, which is only slightly affected by the presence of the PS chains at low EHUT concentrations. This result is in accord with the high viscosities measured for these solutions (Figure 6c) and corroborates the lack of chain stopping effect in the PS/EHUT system. In contrast, the PS-DiBUT/EHUT solutions display much lower ratios (in the range of 1.17 - 1.22), which align with the much lower viscosities measured for these solutions (Figure 6c) and agree with a filamentous morphology of the supramolecular block within the q-BCP architecture. This finding means that supramolecular chain shortening caused by the DiBUT functionality is also accompanied by a transition from a tubular morphology with three EHUT molecules in the cross section into a filamentous morphology containing only one EHUT molecule in the cross section. A possible explanation for this behavior is the steric hindrance for the formation of the tubular form by the polymeric chain stopper. It should be noted, however, that the A_{3344}/A_{3300} ratios increase with increasing EHUT content for the q-BCP structure, indicating the existence of an increasing fraction of tubular poly(EHUT) assemblies. These assemblies could be either tubular homopolymers coexisting with q-BCPs in solution²³ or tubular portions of the blocks in the q-BCP. At this point we cannot differentiate between these two options, but the strong cooperativity effect observed for the filmant-tube transition ^{12d,h} tends to favor the first.

Formation of the q-BCP in the Melt. Differential scanning calorimetry (DSC) measurements performed on the control system, PS/EHUT, reveals no significant change in the T_g of the PS caused by the increasing amounts of EHUT added to the blend (Figure 8a). In addition, two melting transitions attributed to EHUT appear already from EHUT:PS mole ratio of 2. The low-temperature melting transition occurs at nearly the same temperature as the corresponding transition in pure EHUT regardless of the EHUT concentration in the blend.



Figure 9. Ratios of IR absorbances at 3344 and 3300 cm⁻¹ as a function of EHUT:PS, EHUT:PS-TriBUT, and EHUT:PS-DiBUT ratios measured for films cast from CHCl₃ solutions corresponding to the same compositions as in Figures 6 and 8. The ratio measured for a pure EHUT film cast from CHCl₃ solution is given as reference.

The high-temperature melting transition in the blends occurs at lower temperatures than the corresponding transition in pure EHUT, but their temperatures increase steadily with the EHUT: PS ratio in the direction of the $T_{\rm m}$ of the corresponding transition in pure EHUT. These observations indicate a small influence of the EHUT phase on the PS phase and vice versa, leading to the conclusion that these control blends are phase separated on a macroscopic scale, where the shifts in the high $T_{\rm m}$ transitions in these blends is attributed to the increasing size of pure EHUT domains with EHUT:PS ratios. In sharp contrast to these findings, PS-DiBUT/EHUT blends exhibit a strong decrease of the $T_{\rm g}$ of the PS-DiBUT with increasing EHUT:PS-DiBUT ratios (Figure 8b). Additionally, only the low $T_{\rm m}$ transition of EHUT appears and only at high EHUT:PS-DiBUT mole ratios. These observations demonstrate strong mutual influence between PS-DiBUT and EHUT, resulting from an interaction between EHUT and the DiBUT end group and, consequently, the formation of a q-BCP. The reduction in T_g of the PS domains²⁶ and the absence of the high temperature melting transition suggest the formation of rather small PS and poly-(EHUT) domains, respectively, which are consistent with a microphase-separated structure typical of a block copolymer.

In analogy to the solution phase study, insights into the molecular structure of poly(EHUT) in the q-BCP structure in the melt were obtained by measuring the ratios of A_{3344}/A_{3300} of the IR intensities (Figure 9; see also Supporting Information). Here again, the PS/EHUT exhibited ratios exceeding 1.30, only slightly lower than of pure EHUT, indicating the formation of tubular poly(EHUT) assemblies also in the melt.²⁷ The PS-TriBUT/ EHUT and PS-DiBUT/EHUT systems demonstrated much lower ratios, which increased with increasing EHUT content in the film. Similar to the situation in solution, the stronger chain stopping effect of the DiBUT functionality compared to the TriBUT functionality is manifested by lower ratios measured for the former, indicating the existence of a smaller fraction of tubular poly(EHUT) assemblies. If the assumption made above regarding the identity of tubular poly(EHUT) assemblies as homopolymers coexisting with q-BCP structures is correct,²³ then the lower fraction of such homopolymers in the PS-DiBUT/EHUT melts supports a pronounced intervention of the PS-DiBUT in the poly(EHUT) assemblies and thus an enhanced formation of the q-BCP structures in the melt.

Effect of Functionalized PS Chain Stoppers on the Molecular Weight of Poly(EHUT): Coarse-Grained Simulations. To illustrate qualitatively the effect of the functionalized PS (i.e., the PS-DiBUT or the PS-TriBUT) as chain stoppers on the molecular weight distribution, we considered a simple model system with similar properties as the experimental system using hybrid density functional theory (DFT)/particle-based simulations. This mesoscopic modeling strategy combines concepts from classical DFT of liquids with standard particle-based simulation techniques (e.g., Monte Carlo simulations). It has been extensively discussed in earlier publications^{28,29} and has been applied to supramolecular polymers.^{23,24} Here we consider $n_{\rm PS}$ PShomopolymer chains dissolved in n_{EHUT} EHUT molecules so that $n_{\rm EHUT}/n_{\rm PS}$ = 19, which corresponds to the limit of high EHUT concentrations in this study. Each PS homopolymer is described through a bead-spring model with $N_{\rm PS}$ = 13 coarsegrained segments, while each EHUT molecule is represented by a single coarse-grained bead. In the case of nonfunctionalized PS, the EHUT monomers can reversibly bind only between themselves, forming a polydisperse melt of linear poly(EHUT) homopolymers (h-EHUT) mixed with PS homopolymers. When modeling functionalized PS, we allow the EHUT monomers to associate with one of the two termini of the PS-chains as well. Thus, in addition to the h-EHUT polymers, the system contains PS-EHUT diblock and PS-EHUT-PS triblock copolymers.

The energy due to the connectivity of the chains is given by

$$H_{\rm b} = \sum_{\rm bonds} \left[E_{\rm b} + \frac{3k_{\rm B}T|\Delta r|^2}{2b^2} \right]$$
(1)

where the summation is performed over all the bonds in the system (covalent and supramolecular). $\Delta \mathbf{r}$ denotes the distance of the neighbors forming the considered bond, *b* sets the characteristic length scale of the segments (PS and EHUT), and *E*_b represents the bonding strength of the supramolecular association. The systematic mapping of the strength of the EHUT/EHUT, EHUT/DiBUT, and the EHUT/TriBUT bonding on the phenomenological *E*_b parameter is out of the scope of the simulations performed within the current work. Here, we used $E_{\rm b} = -6k_{\rm B}T$, which corresponds to strong supramolecular association²³ and is representative of the situation encountered in the experimental systems. The nonbonded interactions are described through the functional

$$\frac{H_{\rm nb}}{\rho_0 k_{\rm B} T} = \frac{\kappa_0}{2} \int \,\mathrm{d}\mathbf{r} \left[\hat{\phi_{\rm PS}}(\mathbf{r}) + \hat{\phi_{\rm EHUT}}(\mathbf{r}) - 1\right]^2 \tag{2}$$

where $\hat{\varphi}_{PS}(\mathbf{r})$ and $\hat{\varphi}_{EHUT}(\mathbf{r})$ are the local volume fractions of the PS and the EHUT monomers calculated directly from the coordinates of the corresponding monomers with the help of a grid.²⁸ The quantity $\rho_0 = (N_{PS}n_{PS} + n_{EHUT})/V \approx 23.73b^{-3}$ stands for the average number density of the monomers while κ_0 controls the compressibility of the liquid. Here, we employ $\kappa_0 \approx 1.56$, which is sufficiently large to suppress fluctuations of the total density on the mesoscale.²⁸ A cubic system of size of 27.83*b* with periodic boundary conditions is considered in the following simulations.

The polymer conformations in the supramolecular system are sampled using "smart Monte Carlo" monomer displacements,³⁰ while the chain connectivity is altered with the help of supramolecular Monte Carlo moves.¹⁴ Figure 10a shows a semilogarithmic plot of the molecular weight distribution (MWD)

of the supramolecular poly(EHUT)-containing chains in systems involving either nonfunctionalized (solid symbols) or functionalized (open symbols) PS. In the "no-stoppers" case involving only nonfunctionalized PS chains, the supramolecular assemblies include only h-EHUT macromolecules, which are markedly longer than the h-EHUT homopolymers, PS-EHUT diblocks, and PS-EHUT-PS triblocks observed in the presence of functionalized-PS. This is manifested by the significant difference in the slope of the decay of the MWD in the two cases. The solid red line corresponds to a simple theoretical prediction for the MWD in the limit where $E_{\rm b}$ is sufficiently high so that each supramolecular chain has two stoppers (i.e., when only PS-EHUT-PS triblocks are formed). In this case one can assume an exponential MWD of the supramolecular EHUT part:¹⁷ $P(N) = \langle N \rangle^{-1} e^{-N/\langle N \rangle}$. Taking into account that in these simulations we have an average of 19 EHUT molecules per functionalized PS chain stopper (N_{av}) , we obtain $\langle N \rangle = 2N_{av} = 38$. This simple analytical argument follows the simulation results closely; the minor discrepancy stems from the fact that for $E_{\rm b} = -6k_{\rm B}T$ not all supramolecular chains are terminated by two stoppers; i.e., h-EHUT chains and PS-EHUT diblocks are still present in the system. Our result nicely agrees with a similar argument described in ref 17. To highlight the influence of the strength of the supramolecular association on the effect of chain stoppers on the MWD, Figure 10b illustrates the MWD for an analogous system with $E_{\rm b} = -2k_{\rm B}T$. In this case the effect of the functionalized PS on the stoichiometry of the supramolecular system is much less pronounced. The system contains more PS-EHUT diblocks than PS-EHUT-PS triblocks (manifested by the relative position of the plots of the corresponding MWD), emphasizing the fact that there are many supramolecular chains having only one stopper and one "dangling" active end. The discrepancy between the analytical prediction and the simulation results shows that the simple argument¹⁷ used to derive the MWD in the case of strong association (i.e., assuming that both ends of a poly(EHUT) chain are capped by functionalized PS chain stoppers) is no longer valid in the weak association case.

CONCLUSIONS

The design and synthesis of a model q-BCP based on a hydrogen-bonded supramolecular monomer and the corresponding end-functionalized conventional polymer were described. Evidence for the formation of the q-BCP, both in solution and in the melt, was obtained by viscosity measurements and DSC analyses, respectively. The crucial effect of the end-functionalized polymer on the average length and molecular weight distribution of the EHUT chains was described by simulations. We anticipate that the formation of these dynamic block copolymer architectures may lead to new opportunities in the field of environmentally responsive materials, with possible applications ranging from tunable micelles to "smart" coatings and self-assembled, nanostructured resists.²⁴

EXPERIMENTAL SECTION

Instrumentation. NMR measurements were performed on a 400 MHz Bruker spectrometer. Infrared (IR) measurements were performed at room temperature on Nicolet FT-IR spectrometers (models 380 or 6700, Thermo Scientific, Boston, MA) using either KBr disks (1 mm thickess) or CaF₂ disks (2 mm diameter; including a 100 μ m spacer in



Figure 10. Semilogarithmic plots depicting the molecular weight distributions of the supramolecular EHUT-containing chains as obtained by hybrid DFT/particle-based simulations. Systems contain either end-functionalized PS (open symbols) or nonfunctionalized PS (solid symbols). In the former case, the system is comprised of h-EHUT homopolymers, PS-EHUT diblocks, and PS-EHUT-PS triblocks, while in the latter only h-EHUT homopolymers can be created. The red solid line marks a simple theoretical prediction for the molecular weight distribution in the case of end-functionalized PS, derived under the assumption that only PS-EHUT-PS triblocks are formed (see main text for details). The energy of bond formation is (a) $E_{\rm b} = -6k_{\rm B}T$ and (b) $E_{\rm b} = -2k_{\rm B}T$.

the case of a solution cell). Solution and film measurements were taken using either 2 or 4 cm⁻¹ resolution and averaging 64 scans. Gel permeation chromatography (GPC) was performed using a Thermo SpectraSYSTEM HPLC equipped with a P200 pump, SDV linear M column (5 μ m particle size, 8 × 300 mm; Polymer Standards Service), and a SpectraSYSTEM RI-150 detector. The column was calibrated against PS standards (PSS ReadyCal kit), and samples were analyzed at a flow rate of 1 mL/min using 5% triethylamine in THF as the mobile phase. Glass transition temperatures were determined using differential scanning calorimetry (DSC), performed on 5–12 mg samples under continuous nitrogen purge (50 mL/min) on a Mettler Toledo DSC822 (Greifensee, Switzerland). Data were collected in the range of –50 to 200 °C at a heating scan rate of 10 °C/min and represent the second heating cycle. Viscosity measurements were performed at room temperature on a DV-II+ viscometer (Brookfield, Middleboro, MA) at a shear rate of 264 s⁻¹.

Synthesis. All reagents were purchased from either Acros or Sigma-Aldrich and were used without further purification, apart from styrene, which was dried for 2 days on calcium hydride and distilled before use.

1: Dibutylamine (0.957 mmol) was dissolved in 30 mL of dry CHCl₃ and slowly added under a nitrogen atmosphere to toluene-2,4-diisocyante (11.48 mmol) dissolved in 40 mL of dry CHCl₃. The solution was let to stir overnight. Column chromatography (SiO₂, 4:1 hexane:ethyl acetate, $R_f = 0.48$) provided 1.5 g (50%) of the titled compound as a yellow-white solid; mp 64–66 °C. The isomer resulting from the modification of the other isocyanate group was obtained in minor quantities;³¹ structural verification of the major isomer as 1 was obtained from NOE spectroscopy. ¹H NMR (CDCl₃): δ 7.29 (d, J = 2 Hz, 1 H, OCN–C=CH), 7.05 (d, J = 8.4 Hz, 1 H, Me–C=CH), 7.00 (dd, J = 8.2, 2.2 Hz, 1 H, Me–C=CH–CH), 6.21 (br s, 1 H, N–H), 3.27 (t, J = 7.6 Hz, 4 H, N–CH₂), 2.25 (s, 3 H, Ph–CH₃), 1.60 (m, 4 H, N–CH₂CH₂), 1.36 (m, 4 H, CH₂CH₃).

Compounds 2a and 2b. 2-Aminoethanol or 2-butylaminoethanol (7.42 mmol) was added to a solution of 1 (4.94 mmol) in 40 mL of dry CHCl₃ to obtain compound **2a** or **2b**, respectively. The mixture was stirred for 4 h under nitrogen. After solvent evaporation the product was dissolved in dichloromethane, washed with water, NaHCO₃, and brine, and dried over sodium sulfate. Evaporation of the solvent provided a yellow-white solid product of either **2a** (1.35 g, 75%, mp 85 °C) or **2b** (1.55 g, 75%, mp 65 °C).

2a: ¹H NMR (CDCl₃): δ 7.67 (d, J = 2.0 Hz, 1 H, NH–C=CH– C–NH), 7.02 (d, J = 8.0 Hz, 1 H, Me–C=CH), 6.68 (dd, J = 8.0, 2.2 Hz, 1 H, Me–C=CH–CH), 6.31 (br s, 1 H, NH), 6.24 (br s, 1 H, NH), 5.93 (br s, 1 H, NH–CH₂), 4.20 (t, J = 6.3 Hz, 1 H, OH), 3.74 (dd, J =9.7, 5.9 Hz, 2 H, HO–CH₂), 3.40 (dd, J = 9.6, 5.5 Hz, 2 H, HO–CH₂CH₂), 3.28 (t, J = 7.6 Hz, 4 H, N–CH₂), 2.06 (s, 3 H, Ph–CH₃), 1.60 (m, 4 H, N–CH₂CH₂), 1.38 (m, 4 H, CH₂CH₃), 0.97 (t, J = 7.3 Hz, 6 H, CH₂CH₃).

2b: ¹H NMR (CDCl₃): δ 7.49 (s, 1 H, NH–C=CH–C–NH), 7.43 (br s, 1 H, NH), 7.21 (d, *J* = 8.8 Hz, 1 H, Me–C=CH–CH), 6.99 (d, *J* = 8.0 Hz, 1 H, Me–C=CH), 6.33 (br s, 1 H, NH), 3.75 (m, 2 H, HO–CH₂), 3.43 (m, 2 H, HO–CH₂CH₂), 3.25 (m, 6 H, N–CH₂), 2.08 (s, 3 H, Ph–CH₃), 1.58 (m, 6 H, N–CH₂CH₂), 1.34 (m, 6 H, CH₂CH₃), 0.96 (m, 9 H, CH₂CH₃).

DiBUT and TriBUT. To a 40 mL THF solution of either 2a or 2b (3.56 mmol), triethylamine (5.35 mmol) and pyridine (1.16 mmol) were added under a nitrogen atmosphere to obtain DiBUT or TriBUT, respectively. After 10 min of stirring the flask was cooled using an ice bath, and stirring was continued for an additional 10 min. 2-Bromopropionyl bromide (5.35 mmol) was added, and the resulting cloudy solution was stirred overnight. The crude product was dried, dissolved in dichloromethane, washed with water, NaHCO₃, and brine, dried over sodium sulfate, and purified by flash chromatography (SiO₂, 1:2 hexane: ethyl acetate, $R_f = 0.25$) to yield as a white solid (DiBUT: 400 mg, 20%, mp 135–139 °C; TriBUT: 450 mg, 25%, mp 66–69 °C).

DiBUT: ¹H NMR (CDCl₃): δ 7.30 (d, J = 2 Hz, 1 H, NH–C=CH– C–NH), 6.96 (br s, 1 H, NH), 6.86 (d, J = 8.4 Hz, 1 H, Me–C=CH), 6.77 (dd, J = 8.0, 2.0 Hz, 1 H, Me–C=CH–CH), 6.37 (br s, 1 H, NH), 6.21 (t, J = 5.6 Hz, 1 H, NH–CH₂), 4.36 (q, J = 6.9 Hz, 1 H, Br–CH), 4.19 (t, J = 5.8 Hz, 2 H, O–CH₂), 3.40 (m, 2 H, O–CH₂CH₂), 3.26 (t, J = 7.6 Hz, 4 H, N–CH₂) 1.85 (s, 3 H, Ph–CH₃), 1.80 (d, J = 7.2 Hz, 3 H, CH₃CH–Br), 1.57 (m, 4 H, N–CH₂CH₂), 1.34 (m, 4 H, CH₂CH₃), 0.96 (t, J = 7.2 Hz, 6 H, CH₂CH₃).

TriBUT: ¹H NMR (CDCl₃): δ 7.64 (d, *J* = 2.4 Hz, 1 H, NH–C=CH–C–NH), 7.32 (dd, *J* = 8.1, 2.0 Hz, 1 H, Me–C=CH–CH), 7.07 (d, *J* = 8.8 Hz, 1 H, Me–C=CH), 6.56 (br s, 1 H, NH), 6,33 (br s, 1 H, NH), 4.37 (m, 3 H, Br–CH + O–CH₂), 3.64 (m, 2 H, O–CH₂CH₂),

 $\begin{array}{l} 3.33 \ (t,J=7.8 \ Hz, 2 \ H, N-CH_2), 3.23 \ (t,J=7.6 \ Hz, 4 \ H, N-CH_2), 2.20 \\ (s, 3H, Ph-CH_3), 1.82 \ (d,J=6.9 \ Hz, 3 \ H, CH_3CH-Br), 1.63 \ (m, 6 \ H, N-CH_2CH_2), 1.37 \ (m, 6 \ H, CH_2CH_3), 0.96 \ (m, 9 \ H, CH_2CH_3). \end{array}$

Polymerization. CuBr (0.048 mmol), PMDETA (0.096), styrene (19.14 mmol), and DiBUT or TriBUT (0.048 mmol) dissolved in 0.5 mL of DMF were inserted into a pressure tube. The tube was connected to a high vacuum line, and degassing using three cycles of freeze—pump—thaw was performed. Purified nitrogen was then added to the frozen mixture, and the tube was closed under slightly less than 1 atm. The tube was inserted into an oil bath preheated to 110 °C for different time intervals (from 15 to 60 min), after which the resulting polymer was cooled to ambient temperature, opened to the atmosphere, diluted with dichloromethane, and precipitated in methanol. The precipitation procedure was repeated until the polymer obtained was white.

Sample Preparation for Viscosity, DSC, and IR Measurements. Mother solutions of EHUT and PS, PS-DiBUT, and PS-TriBUT polymer were prepared in dry CHCl₃, stirred for 3 h, and filtered. Portions of the EHUT solution and the desired PS-derivative solution were mixed in chloroform to obtain 7 mL solutions of 0.5 wt %(7.4 mg/mL) concentration of the PS derivative and different mole ratios between EHUT and the PS derivative (x; 0 < x < 20). The mixtures were stirred for 16 h. Prior to the viscosity measurements and solution IR measurements, the chloroform was evaporated and the mixture was further dried under high vacuum for 2 days, dissolved in 7 mL of CHCl₃:toluene at the desired volume ratio (either 3:7, 5:5, or 7:3), and stirred for 2.5 h. Prior to DSC measurements, solution mixtures were evaporated and dried for 3 days under high vacuum, weighed into standard aluminum pans, and sealed. Films for IR measurements were created by drop-casting chloroform solutions onto CaF₂ disks and drying in air.

ASSOCIATED CONTENT

Supporting Information. NMR spectra of all synthesized compounds (Figures S1–S5) and IR spectra of the different systems in 3:7 CHCl₃:toluene solutions and in the melt (Figures S6 and S7). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: roys@chem.ch.huji.ac.il.

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