Poly(ε-caprolactone)–Poly(isobutylene): A Crystallizing, Hydrogen-Bonded Pseudo-Block Copolymer

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ABSTRACT: The crystallization of block copolymers (BCPs) under homogeneous and heterogeneous nucleation is currently well understood revealing the strong interplay of crystallization in competition to microphase separation. This article reports investigations on synthesis and crystallization processes in weakly interacting supramolecular pseudo-BCPs, composed of poly(ε-caprolactone) (PCL) and poly(isobutylene) (PIB) blocks, connected by a specifically interacting hydrogen bond (thymine/2,6-diaminotriazine). Starting from ring opening polymerization of ε-caprolactone, the use of "click"-chemistry enabled the introduction of thymine endgroups onto PCL polymer, thus generating the fully thymine-substituted pure PCLs (**1a**, **1b**) as judged via NMR and MALDI analysis. Physical mixing of **1a**, **1b** with a bivalent, bis(2,6-diaminotriazine)-containing molecule (**2**) generated the bivalent polymers **BC1** and **BC2**, whereas mixing of **1a** or **1b** with the 2,6-diaminotriazine-substituted PIB (**3**) generated the supramolecular pseudo-BCPs **BC3** and **BC4**. Thermal investigations (DSC, Avrami analysis) revealed only minor changes in the crystallization behavior of **BC1**–**BC4** with Avrami exponents close to three, indicative of a confluence of the growing crystals during the crystallization process. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3404–3416, 2011

KEYWORDS: "click"-chemistry; crystallization; hydrogen bonds; pseudo-block copolymer; poly(ε-caprolactone); poly(isobutylene); poly(ε-caprolactone)–poly(isobutylene); self-assembly; supramolecular polymer; supramolecular structures

INTRODUCTION Crystallization processes constitute a fundamental structure formation in homopolymers, which have been investigated experimentally intensely within the past years.[1,2] Even more complex ordering processes take place if one (or both) blocks within a microphase-separated block copolymer (BCP) are crystalline, leading to crystallization phenomena under constraint, thus in turn generating a significantly richer phase behavior as compared to purely amorphous BCPs.[3–5] Based on a multitude of investigations, the crystallization[6] in BCPs under homogeneous and heterogeneous nucleation is currently well understood revealing the strong influence of microphase separation in competition to crystallization.[5,7] Especially, the cases of either "templated" or "confined" crystallization are important, as now the Flory–Huggins parameter (χN), as well as the chain length of the polymer blocks are determining the crystallization process. A prominent example is poly(ε-caprolactone-*block*-polybutadiene) BCPs (PCL-*b*-PB), where crystallization dominates over microphase separation at low molecular weights ($M_n < 19{,}000$ g/mol)[8] (leading to "breakout-crystallization"), whereas at significantly higher molecular weights ($M_n >$ 44,000 g/mol^{-1}) the microphase-separated structure is retained and over-rules crystallization.[9] Similar cases have been described on a large variety of other BCPs (i.e., poly(ethylene)-*b*-poly(3 methyl-1-butene) (PE-*b*-PME),[10,11] poly(ethylene)-*b*-poly(styrene-ethylene-butene) (PE-*b*-PSEB),[12] poly(ethylene oxide)-*b*-poly(butadiene) (PEO-*b*-PB[13])) as well as BCP blends (i.e., poly(ethylene oxide)-*b*-poly(butylene oxide)/poly(butylene oxide) (PEO-*b*-PBO/PBO).[14] Another factor[15] is related to the nature of the microphase from which crystallization occurs. Thus not only the Flory–Huggins-parameter (χN) but also the volume fraction of the respective blocks (and therefore the resulting microphase) determines whether crystallization under confined or templated conditions takes place, resulting in changes of the crystallization in cylindrical or spherical phases[15] or a significant distortion of the (hexagonal) phase if templated crystallization occurs.[16–18] In contrast to conventional BCPs, supramolecular polymers[19] are interconnected by thermally reversible bonds (such as a hydrogen bonds,[20] metal/metal

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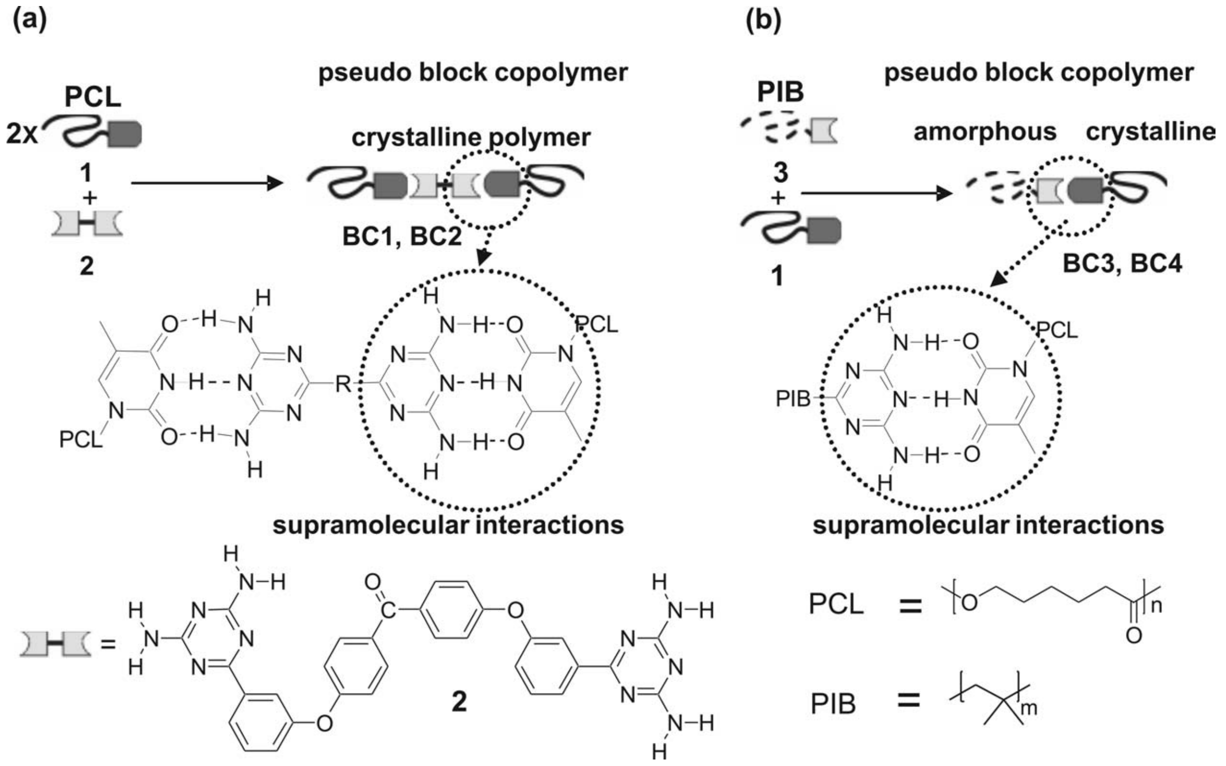


FIGURE 1 Structure of the supramolecular pseudo-block copolymers: **BC1**, **BC2**, **BC3**, **BC4**.

complexes,[21] or just charge/charge interactions[22]), thus being subject to breaking and reformation on a defined timescale. Therefore, in supramolecular polymer science an additional dynamic element[23] is placed between polymer chains, thus generating BCPs different from the covalently linked counterparts. The chemical nature of the respective supramolecular bond determines the extent to which the bonds between the polymer chains are broken, being a strong function of temperature (*T*) and—if present—solvent molecules.

Structure formation and dynamics of (solid) supramolecular BCPs with at least one crystalline part have not been investigated systematically. Investigations on the crystallization of polymers in dynamic structures (i.e., supramolecular polymers) have revealed contradicting results with respect to nucleation and crystallization behavior, if studied systematically. In most cases, an increased fraction of the crystalline part (i.e., PCL,[24–28] PEO,[25,29,30] PDMS,[31] PBD[32–35]) in linear supramolecular polymers has been described, pointing at confinement effects and constraints exerted by the supramolecular interaction within the polymer structure. However, uncontrolled phase separation and nucleation effects in all of these cases lead to difficult interpretations of the nucleation behavior and thus the underlying crystallization process. However, it was demonstrated,[28] that PCL polymers with hydrogen-bonded moieties can exhibit the formation of sheets, consisting of layered supramolecular H-bonds and PCL chains if weak hydrogen bonds are used, leading to Avrami values during the PCL crystallization between two and three. Moreover, these effects may result from a variety of effects known during the crystallization of conventional systems (confinement effects, fractionated crystallization, and nucleation effects).

This article will put these investigations on a more defined basis, revealing new insights into the basics of crystallization processes in weakly interacting supramolecular BCPs. So-called pseudo-BCPs[36–38] consisting of PCL-*b*-PIB blocks, connected by a specifically interacting hydrogen bond are prepared for the first time, and subsequently structure formation and crystallization are investigated (see Fig. 1). As now the two blocks are connected only transiently via a hydrogen bond; the microphase separation of the immiscible blocks is not acting permanently but depends on the aggregation strengths of the intermediate hydrogen bonds linking the two fragments. In our case, the thymine/2,6-diaminotriazine bond was chosen, which constitutes a hydrogen bond of weak strength. As the engineering of the two blocks is achieved by living polymerization techniques, exact chain length control of the blocks is possible. Moreover, the use of the azide/alkyne "click" reaction allows a complete endgroup affixation in high fidelity.

EXPERIMENTAL

Materials and Measurements

All chemicals were purchased from Sigma-Aldrich. ε-Caprolactone was stirred and distilled over calcium hydride (110 °C, 10 mbar), tin(II) 2-ethylhexanoate was distilled two times under high vacuum conditions (140 °C, 0.010 mbar), and 5-hexyn-1-ol was distilled (80 °C, 12 mbar) prior to use. Cu(I)Br was stirred for 2 days in acetic acid/anhydride, washed with dry diethyl ether several times, and dried *in vacuo* under an argon atmosphere. *N*,*N*-diisopropylethylamine (DIPEA) and 2,2′-bipyridyl were used without further purification. Dichloromethane (DCM) was predried over $CaCl_2$, refluxed over calcium hydride, distilled and degassed with argon before use. Hexane was refluxed over concentrated sulfuric acid to remove olefinic impurities, followed by extraction with water solution of NaOH and then refluxed over calcium hydride. Toluene and tetrahydrofuran (THF) were predried over NaOH for several days followed by refluxing over sodium/benzophenone and distillation under an argon atmosphere before use. Microwave irradiation supported reactions were performed on a CEM Discover LabMate using SPS control option switching the power on and off at the defined temperature and pressure.

NMR spectroscopy was measured on Varian Gemini 2000 FT-NMR spectrometer (400 MHz). Chloroform (99.8 atom % D) and dimethyl sulfoxide-d$_6$ (99.9 atom % D) were used as solvents. For FIDs, analysis software Mestrec 4.7.0.0 was used. Chemical shifts (δ) were recorded in parts per million (ppm) and referenced to residual protonated solvent [$CDCl_3$: 7.26 ppm (^{1}H), 77.0 ppm (^{13}C), $(CD_3)_2SO$: 2.54 ppm (^{1}H), 39.52 ppm (^{13}C)]; coupling constants (J) are given in Hertz (Hz) using standard abbreviations (s = singlet, d = doublet, t = triplet, and m = multiplet).

GPC measurements were done on a Viscotek GPCmax VE 2001 with a Styragel linear column GMH$_{HR}$. THF was used as a carrier solvent at 1 mL/min at room temperature. The sample concentration was approximately 3 mg/mL. For PCL samples, polystyrene standards (in the range of 1050–1,870,000 g/mol) were used for conventional external calibration, using a Waters RI 3580 refractive index detector. For PIB samples, polyisobutylene standards (in the range of 340–87,600 g/mol) were used for conventional external calibration, using a VE3580 refractive index detector.

FTIR spectra were recorded with a Bruker Vertex70MIR spectrometer using an ATR Golden Gate unit with a diamond crystal. The scan number was 32 scans per spectra with a resolution of 2 cm^{-1}.

MALDI-TOF MS was done on a Bruker Autoflex III Smartbeam using a nitrogen laser source (λ = 337 nm) in reflection and linear modes. The polymer samples were dissolved in THF at a concentration of 20 mg/mL; 1,8,9-anthracenetriol in THF (20 mg/mL) was used as matrix material; sodium trifluoroacetate (NaTFA) and silver TFA (AgTFA) in THF (20 mg/mL) were used as salt for PCL and PIB samples, respectively. The solutions of the polymer, the matrix, and the salt were mixed in a volume ratio of 100:20:2 and 2 μL of this mixture were spotted on the MALDI target plate. The instrument were calibrated with a poly(ethylene glycol) standard (M_p = 2000 g/mol) using a quadratic calibration method.

DSC measurements were carried out with a Perkin Elmer DSC7 calibrated with indium and mercury. Samples with a mass of about 10 mg were encapsulated in standard aluminium pans. Nitrogen was used as purge gas. The evaluation of the data was conducted using the Pyris Thermal Analysis software package (version 3.81). For nonisothermal measurements, the samples were heated with a heating rate of 20 K/min to 80 °C, held at 80 °C for 20 min, cooled down to −85 °C with a cooling rate of 10 K/min, held at −85 °C for 10 min, heated to 80 °C with a heating rate of 10 K/min, and held for 5 min. The melting temperature was evaluated from the peak maximum of the second heating run, and the crystallization temperature was evaluated from the peak maximum of the first cooling run. For isothermal measurements, the samples were heated to 80 °C at a heating rate of 20 K/min, held for 20 min, cooled down to the selected crystallization temperatures with a nominal cooling rate of 200 K/min, held for 120 min, and heated to 80 °C with a heating rate of 10 K/min.

Rheology measurements were carried out with a MCR 501 rheometer from Anton Paar in a parallel plate geometry with 8 mm diameter plates. This small diameter was chosen because of the limited amount of sample material available, although this causes somewhat higher uncertainties in the absolute values for modulus or viscosity. For the same reason, the gap width used was in the range 0.3–0.5 mm. Temperature was controlled by a Peltier oven in a range of 60–140 °C. The sample chamber was purged by nitrogen gas during all the measurements.

Synthesis

Synthesis of the Alkyne-Functionalized Poly(ε-caprolactone) (4)

Alkyne-functionalized PCL **4a** was prepared via coordination-insertion ring opening polymerization (ROP) using ε-caprolactone as a monomer, 5-hexyn-1-ol as an initiator, and tin(II) 2-ethylhexanoate $Sn(Oct)_2$ as a catalyst according to the literature.[39] Briefly, a Schlenk flask was carefully dried by heating (500 °C), purged with argon, cooled down, and charged with the initiator 5-hexyn-1-ol (55 μL, 5.0 × 10^{-4} mol), the catalyst tin (II) 2-ethylhexanoate (6.0 × 10^{-6} mol, 2 μL), and a solvent mixture of 3 mL toluene and 1 mL THF. This mixture was stirred at room temperature for 30 min to promote the complex formation between catalyst and initiator. Afterward, the solution was treated with ε-caprolactone (3 mL, 0.026 mol) and stirred at 110 °C for 3 h. Finally, the product was dissolved in dry DCM (10 mL) and precipitated into cold (5 °C) methanol (150 mL), filtered off and dried *in vacuo* overnight.

Yield: 75%. ^{1}H NMR (400 MHz; $CDCl_3$): δ (ppm) = 4.04 (t, 74H, J = 6.7 Hz), 3.63 (t, 2H, J = 6.5 Hz), 2.28 (t, 74H, J = 7.5 Hz), 1.91 (s, 1H), 1.65(m, 148 H), 1.38 (m, 72 H).

The synthesis of **4b** was conducted in analogy to the synthetic strategy of **4a**.

Synthesis of 1-(6-Azidohexyl) Thymine (5)

The preparation of (**5**) includes three steps starting from thymine.[40,41] The first step is the protection of the amino group between the two carbonyl groups using an excess of hexamethyldisilazane and a catalytic amount of trimethylchlorsilane. The product of this reaction (5-methyl-2,4-bis-(trimethyl-silanyloxy)-pyrimidine) reacts in the second step with an excess of freshly distilled 1,6-dibromohexane to introduce the Br group. The last step is the exchange of Br against N_3 group which was conducted in analogy to the literature.

Yield: 89%. ^{1}H NMR (400 MHz; $CDCl_3$): δ (ppm) = 8.06 (s, 1H), 6.94 (s, 1H), 3.67 (t, 2H, $J = 7.4$ Hz), 3.26 (t, 2H, $J = 6.7$ Hz), 1.91 (s, 3H), 1.68 (m, 2H), 1.59 (m, 2H), 1.30–1.45 (m, 4H).

Synthesis of Thymine-Functionalized PCL (1) via Click-Reaction

The functionalization of PCL with a thymine endgroup (**1**) was conducted via azide/alkyne click-reaction, using 2,2′-bipyridyl as base and Cu(I)Br as a catalyst. The reaction was done in a one-necked flask carefully dried and purged with argon. Alkyne-functionalized PCL (**4a**; 200 mg, 4.8×10^{-5} mol) and azide-functionalized thymine (**5**; 36 mg, 1.4×10^{-4} mol) were dissolved in 4 mL of dry toluene, then a solution of 2,2′-bipyridyl (148 mg, 9.5×10^{-4} mol) in toluene (2 mL) was added via a syringe and the mixture was degassed with argon to remove the oxygen for 30 min. Subsequently, a catalytic amount of Cu(I)Br (4.7 mg, 3.3×10^{-5} mol) was weighed in, the flask was closed by a cap with a septum, and the mixture was degassed with argon again. The reaction proceeded for 24 h by stirring at 80 °C. Afterwards, the reaction mixture was cooled down to room temperature and filtered over a short neutral Al_2O_3 column to remove the Cu(I)Br. The solvent was removed by distillation; the crude product was dissolved in 10 mL of DCM, slowly added in methanol (200 mL) and left overnight for complete precipitation. The precipitation step was repeated two times to remove the excess of azide-functionalized thymine (**5**) and 2,2′-bipyridyl, which are well soluble in methanol. The pure product **1a** was filtered off and dried in high vacuum.

Yield: 72% .^{1}H NMR (400 MHz $(CD_3)_2SO$): δ (ppm) = 11.14 (s, 1H), 7.82 (s, 1H), 7.49 (s, 1H) 4.31 (t, 2H, $J = 5.3$ Hz), 4.27 (t, 2H, $J = 7.2$ Hz), 3.98 (t, 72H, $J = 6.4$ Hz), 3.58 (t, 2H, $J = 7.2$ Hz), 2.61 (t, 2H, $J = 6.6$ Hz), 2.27 (t, 72H, $J = 7.2$ Hz), 1.74 (s, 3H), 1.55 (m, 152 H), 1.29 (m, 76H).

The synthesis of the PCL-polymer **1b** was conducted in analogy to **1a**.

Synthesis of 4,4-Bis-[3-(2,4-Diamino-[1,3,5]triazin-6-yl)-phenoxy]benzophenone (2)

Compound (**2**) was synthesised in analogy to the strategy reported by Beijer et al.[42] The synthetic approach includes two steps: (a) synthesis of 4,4-bis-(3-cyano-phenoxy)-benzophenone and (b) the conversion with dicyandiamide.

Synthesis of 4,4-Bis-(3-Cyano-phenoxy)benzophenone. 4,4-Difluorobenzophenone (0.450 g, 0.002 mol), 3-cyanophenole (0.476 g, 0.002 mol), K_2CO_3 (0.830 g, 0.002 mol), dry toluene (20 mL), and dry DMA (20 mL) were placed into a 50 mL round-bottom flask equipped with a Dean-Stark trap and a condenser and purged with argon. The reaction mixture was heated to 110 °C via an oil bath for the period of 6 h while liberated water was condensed and separated using a Dean-Stark apparatus. Afterward, the toluene was removed by distillation, and the reaction mixture was stirred to reflux for 72 h at 170 °C. Finally, the mixture was cooled down to 100 °C and filtered over filter paper. In addition, DMF was removed by distillation, and the brown residue was dissolved in chloroform (20 mL) and extracted two times with water (60 mL). The organic phase was collected, dried with Na_2SO_4, filtered over a glass frit, concentrated by evaporation, and the crude product was purified via silica gel column chromatography (R_f: 0.12, $CHCl_3$).

Yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.84 (d, 4H, $J = 8.6$ Hz), 7.46 (m, 4H), 7.33 (m, 4H) 7.07 (d, 4H, $J = 8.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 197.71, 159.65 156.50, 133.37, 132.37, 130.97, 127.70, 124.01, 122.53, 118.26, 117.85, and 114.01.

Conversion with Dicyandiamide. 4,4-Bis-(3-cyano-phenoxy)-benzophenone (0.454 g, 1.09 mmol), dicyandiamide (0.366 g, 1.09 mmol), and KOH (0.03 g, 1.09 mmol) were suspended in dry isopropanol, degassed with argon, and stirred for 6 days at 90 °C. Afterwards, the reaction mixture was cooled down to room temperature, and the crude product (**2**) was collected by filtration over a frit, washed with water and isopropanol three times, and dried in high vacuum.

Yield: 75%.^{1}H NMR (400 MHz, DMSO-d_6) ppm: 8.09 (d, 2H, $J = 8.1$ Hz), 7.93 (s, 2H), 7.77 (d, 4H, $J = 8.8$ Hz), 7.53 (t, 2H, $J = 8.0$ Hz), 7.30 (d, 1H, $J = 7.9$ Hz), 7.09 (d, 1H, $J = 8.9$ Hz), 6.72 (s, 8H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 194.00, 169.45, 167.75, 161.86, 154.87, 140.09, 135.72, 130.77, 130.40, 124.85, 123.56, 119.61, and 118.32.

Synthesis of Initiator, Polymerization and Functionalization of PIB

2-Chloro-2,4,4-trimethyl-pentane was used as initiator for the living cationic polymerization and was synthesized according to the literature.[43]

Yield: 90% ^{1}H NMR (400 MHz; $CDCl_3$): δ (ppm) = 1.86 (s, 2H), 1.65 (s, 6H), 1.04 (s, 9H).

Polymerization of isobutylene was conducted in analogy to the literature[44] using 2-chlor-2,4,4-trimethyl-pentane/$TiCl_4$ as initiating system to achieve allyl-telechelic polyisobutylene.

Yield: 90%. ^{1}H NMR (400 MHz; $CDCl_3$): δ (ppm) = 5.85 (m, 1H), 5.00 (m, 2H), 2.01 (d, 1H, $J = 7.4$ Hz), 1.42 (s, 146 H), 1.11 (s, 438 H), 0.99 (s, 15 H). The synthesis of the azide-telechelic polyisobutylen (**6**) was achieved in analogy to the literature[45] starting from allyl-telechelic polyisobutylen and includes three steps. The first step was the reaction between allyl-telechelic polyisobutylen and 9-borabicyclo[3.3.1.]nonane/3-chloroperbenzoicc acid to introduce OH endgroup.[46] The second step was the formation of Br-telechelic PIB via the Appel reaction whereby hydroxy telechelic PIB reacts with triphenylphosphine/carbon tetrabromide. The last step was the exchange of Br against N_3 group using trimethylsilyl azide/tetrabutylammonium fluoride.[45]

Yield: 90% ^{1}H NMR (400 MHz; $CDCl_3$): δ (ppm) = 3.23 (t, 2H, $J = 6.9$ Hz), 1.42 (s, 146H), 1.11 (s, 438 H), 0.99 (s, 15H)

Synthesis of 6-(4-Ethynylbenzyl)-1,3,5-triazine-2,4-diamine (7)

The synthesis was conducted in analogy to the strategy reported by Herbst et al.[47] In a two-neck round-bottom flask, equipped with a reflux condenser, carefully dried at 500 °C in vacuum and purged with argon several times, 4-ethynylphenylacetonitrile (100 μL, 0.74 mmol), dicyandiamide (0.24 g, 2.9 mmol), and sodium hydroxide (15 mg, 0.38 mmol) were added. Isopropanol (30 mL) was degassed with argon and added via a syringe. The mixture was refluxed for 30 h while the formation of a precipitate was observed. The crude product was filtered off, refluxed with dry isopropanol again for 20 min, and cooled in a freezer over night. Finally, the product was filtered off and dried in high vacuum.

Yield: 85% ^{1}H NMR (400 MHz; DMSO-d$_6$): 7.39 (d, 2H, J = 8.1 Hz), 7.27 (d, 2H, J = 8.2 Hz), 6.60 (br s, 4H), 4.10 (s, 1H), 3.65 (s, 2H). ^{13}C NMR (50 MHz, DMSO-d^6): δ 175.51, 166.82, 138.85, 131.10, 128.87, 119.24, 83.16, 79.65, 44.02.

ESI TOF MS (m/z) calc for $C_{12}H_{11}N_5$ 225.10; found 226.11 $[M+H]^+$.

Synthesis of 2,6-Diaminotriazine–Telechelic Polyisobutylene (3) via Azide/Alkyne "Click"-Chemistry

2,6-Diaminotriazine–telechelic polyisobutylene (**3**) was obtained via click-reaction between azide-telechelic polyisobutylene (**6**) and 6-(4-ethynylbenzyl)-1,3,5-triazine-2,4-diamine (**7**). The synthesis was conducted in a special flask for microwave use, which was dried at 500 °C and purged with argon. Toluene, isopropanol, and water were bubbled with argon for 30 min before use. Azide-telechelic polyisobutylene (100 mg, 2.5×10^{-5} mol) was dissolved in toluene (5 mL), subsequently isopropanol (2 mL), water (1 mL), and DIPEA (0.07 mL, 3.75×10^{-4} mol) were added and the mixture was degassed with argon again. Copper(I)iodide (3 mg, 1.5×10^{-5} mol) and 6-(4-ethynylbenzyl)-1,3,5-triazine-2,4-diamine (**7**; 17 mg, 7.5×10^{-5} mol) were weighed in, the flask was closed by a cap with a septum and placed in the microwave. The reaction was accomplished under constant stirring at 90 °C and microwave irradiation [50 W, SPS control option (see Experimental part)] for 20 h. Afterwards, the reaction mixture was cooled down to room temperature, the solvent was removed, and the residue was dissolved in *n*-hexane and filtered over filter paper. Subsequently, the solution was concentrated in vacuum and the polymer was purified by column chromatography (R_f: 0.25, SiO$_2$, CHCl$_3$/MeOH = 100/3) to remove azide-telechelic polyisobutylene chains. Finally, the product was dissolved in a small amount of *n*-hexane and precipitated in an excess of methanol/acetone (10/2) solution and dried in high vacuum to constant weight.

Yield: 65% ^{1}H NMR (400 MHz, CDCl$_3$): 7.79 (d, 2H, J = 8.1 Hz), 7.71 (s, 1H), 7.44 (d, 2H, J = 7.9 Hz), 5.48 (br s, 4H), 4.35 (t, 2H, J = 7.3 Hz), 3.91 (s, 2H), 1.42 (s, 146 H), 1.11 (s, 438 H), 0.99 (s, 15 H).

Preparation of Supramolecular Pseudo-Block Copolymers via Solution Blending

PCL-b-PCL (BC1, BC2)

Thymine-functionalized PCL (**1a** 100 mg, 2.2×10^{-5} mol/**1b** 100 mg, 1.1×10^{-5} mol) and compound **2** (6.3 mg, 1.1×10^{-5} mol/3.2 mg, 5.7×10^{-6} mol) were dissolved in dry THF separately. Both solutions were mixed together, filtered over filter paper, and the solvent was removed by evaporation. The mixture was dried in high vacuum for 2 days, then purged with argon, and finally heated to 60 °C for 3 days to promote the formation of hydrogen bonds and to achieve equilibrated conditions.

PCL-b-PIB (BC3, BC4)

Thymine-functionalized PCL (**1a** 60 mg, 1.3×10^{-5} mol/**1b** 60 mg, 6.8×10^{-6} mol) and 2,6-diaminotriazine–telechelic polyisobutylene (**3**; 60 mg, 1.3×10^{-5} mol/30 mg, 6.8×10^{-6} mol) were dissolved in dry CHCl$_3$ separately. Both solutions were mixed together, filtered over filter paper, and the solvent was removed by evaporation. The mixture was dried at high vacuum for 2 days, then purged with argon, and finally heated to 45 °C for 2 days to promote the formation of hydrogen bonds.

RESULTS AND DISCUSSION

Polymer Synthesis

We present the synthetic approach of the supramolecular pseudo-BCPs (**BC3**, **BC4**) consisting of thymine-functionalized PCL (**1**) connected via supramolecular interactions with 2,6-diaminotriazine-functionalized PIB (**3**) (Fig. 1). First, we discuss the formation of the thymine-functionalized PCL (**1**) starting from the polymerization of ε-caprolactone, followed by the introduction of the thymine end group. Subsequently, the formation of 2,6-diaminotriazine-functionalized PIB (**3**) is discussed only shortly as it was reported elsewhere.[47]

Synthesis of PCL Blocks (4a, 4b, 1a, 1b)

Alkyne-functionalized PCLs (**4a**, **4b**) were synthesized via coordination-insertion ROP using ε-caprolactone as a monomer, 5-hexyn-1-ol as initiator, and tin(II) 2-ethylhexanoate Sn(Oct)$_2$ as a catalyst as described elsewhere.[39] First, polymerization reactions were conducted at 160 °C for 24 h to favor full conversion. In-depth analysis of the resulting polymers via MALDI-TOF MS (Supporting Information Fig. S1) indicated the formation of mixtures consisting of alkyne-functionalized PCLs as well as PCLs containing hydroxyl endgroup (PCL-OH). As initial trials for separation of this mixture failed, we focused our work on the modification of the reaction conditions to avoid the formation of hydroxyl-telechelic PCLs, as detailed investigations of the mechanism of ε-caprolactone polymerization using Sn(Oct)$_2$ reported by Duda and coworkers[48] showed that even small traces of water present in Sn(Oct)$_2$ can act as initiator and cause the formation of PCL-OH species. Furthermore, we increased the purity of Sn(Oct)$_2$ via two consecutive high vacuum distillations (instead of one distillation as before) and decreased the reaction time and temperature to reduce the reactivity of water as competitive initiator. Both of these changes in the polymerization procedure led to the formation of highly pure alkyne-functionalized PCLs as seen from the MALDI-TOF data (Fig. 2).

Thymine-functionalized PCLs (**1a**, **1b**) were then synthesized via azide/alkyne click reaction between alkyne-functionalized PCLs (**4a**, **4b**) and azide-functionalized thymine (**5**; Scheme 1). To optimize the yield of the final product, we tested different reaction conditions as listed in Table 1. The use of microwave

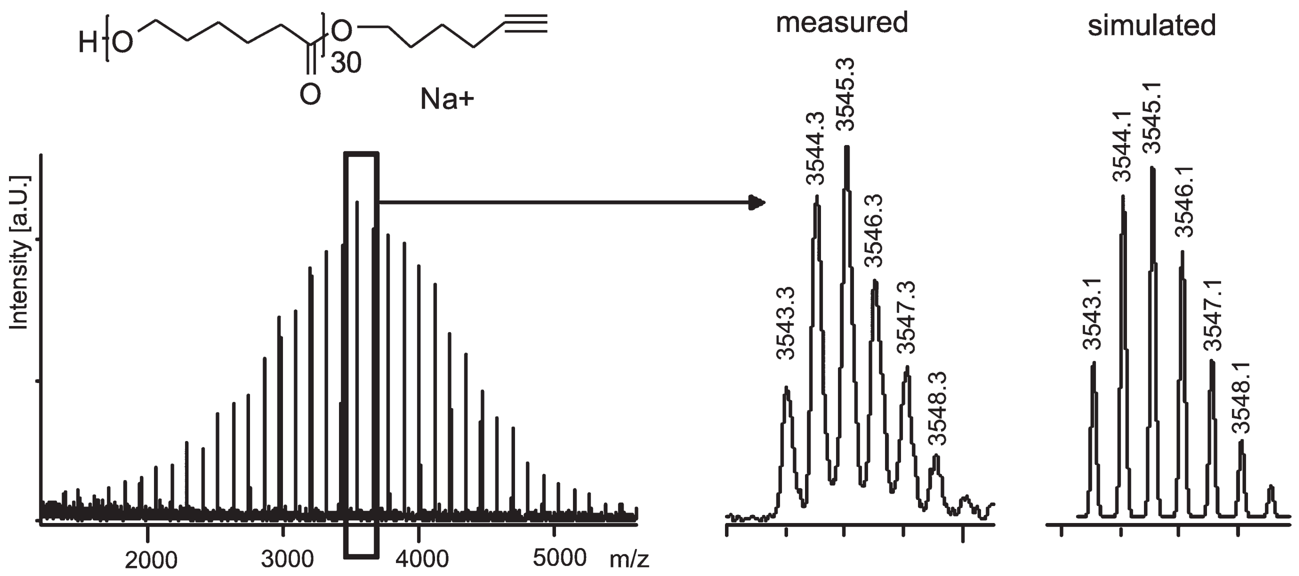
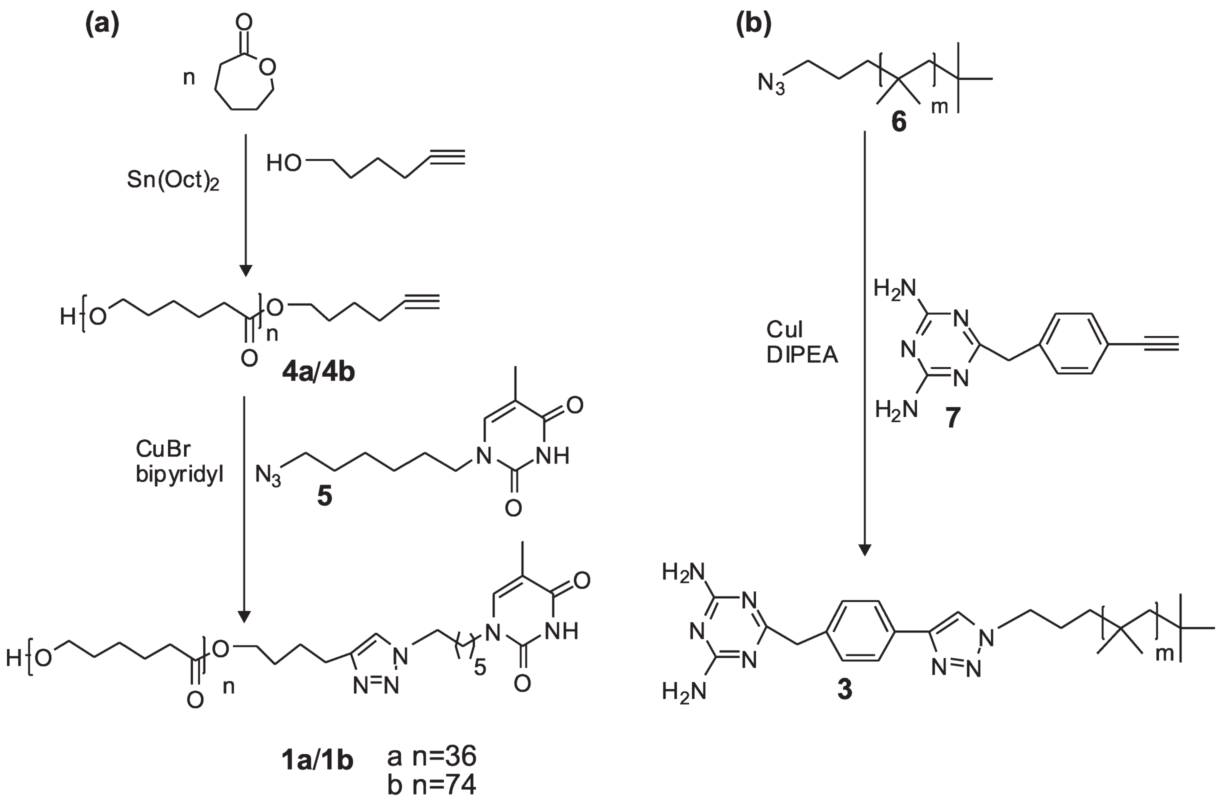


FIGURE 2 MALDI-TOF MS of alkyne-functionalized PCL (**4a**).

irradiation to accelerate the click reactions is well known from the literature.[49] However, in our case after irradiation for 4–5 h it was not possible to isolate the polymer as degradation of PCLs was noticed. Best results were achieved using a reaction mixture of 0.7 equivalents (equiv.) of Cu(I)Br and 20 equiv. of 2,2′-bipyridyl as a base (Table 1, entry 7). All reactions were conducted with 1 equiv. of the alkyne-functionalized PCLs (**4a**, **4b**) by varying the amount of azide-functionalized thymine (**5**) from 1.1 to 6.0 equiv. The molecular weight data of all homopolymers are collected in Table 2.

Characterization of Thymine-Functionalized PCLs (1a, 1b)

Critical for the block formation and their thermal investigations was the synthesis of pure PCLs, truly containing thymine endgroup quantitatively as otherwise the (supramolecular)



SCHEME 1 Synthetic approach for the preparation of the homopolymers (a) **1a**, **1b** and (b) **3**.

TABLE 1 Reaction Conditions of the "Click" Reactions Between Alkyne-Functionalized PCLs (**4a, 4b**) and Azide-Functionalized Thymine (**5**)

Entry	Catalyst[a]	Base[a]	Reaction Time (h)	Temperature (°C)	Amount of 5[a]	Yield (%)
1	Cu(I)Br PPh_3, 0.1 equiv. and TBTA, 0.1 equiv.	DIPEA, 5 equiv.	18	100 °C MW[b]	1.1 equiv.	0
2	Cu(I)Br, 0.1 equiv.	DIPEA, 15 equiv.	15	100 °C MW[b]	2 equiv.	0
3	Cu(I)Br, 0.1 equiv.	DIPEA, 15 equiv.	4.5	100 °C MW[b]	2 equiv.	0
4	Cu(I)I, 0.3 equiv.	DIPEA, 15 equiv.	24	80 °C	3 equiv.	30
5	Cu(I)Br, 0.3 equiv.	DIPEA, 15 equiv.	24	80 °C	6 equiv.	30
6	$CuSO_4{\cdot}5H_2O$/ascorbate, 0.3 equiv./1.5 equiv.	DIPEA, 15 equiv.	18	100 °C	1.1 equiv.	22
7	Cu(I)Br, 0.7 equiv.	Bipyridyl, 20 equiv.	30	120 °C	2 equiv.	70

[a] The amount is given in equivalents (equiv.) relative to the alkyne-functionalized PCLs (**4a**, **4b**).

[b] Microwave irradiation (100 W, SPS control option).

block formation can be prevented by the residual alkyne-functionalized chains. The structures of **1a** and **1b** were confirmed by ^{1}H NMR spectroscopy and MALDI-TOF MS investigations. Figure 3 shows ^{1}H NMR spectra of thymine-functionalized PCL (**1a**). The integral value of the terminal CH_2OH resonance (F) at 2.61 ppm was fixed as two. The appearance of resonance peak (H) at 7.82 ppm with an integral of one indicates the formation of triazol ring typical for the "clicked" product. In addition, the integration values of the thymine endgroup resonances are matching with the number of the corresponding protons, and the disappearance of alkyne protons proves the successful formation of the thymine-telechelic PCLs (Fig. 3).

Synthesis and Characterization of 2,6-Diaminotriazine-Functionalized PIB (3)

The synthesis of allyl-functionalized PIBs was done via living carbocationic polymerization as described elsewhere.[44] 2-Chloro-2,4,4-trimethylpentane was used as initiator, following the transformation of the allyl-functionalized PIB to the azide-functionalized PIB (**6**) accomplished according to the method developed by Binder et al.[45,50] Azide-functionalized PIB (**6**) subsequently was reacted via the azide/alkyne "click"-type reaction with alkyne-functionalized triazine (**7**) using Cu(I)Br as catalyst, DIPEA as a base, and microwave irradiation to yield 2,6-diaminotriazine-functionalized PIB (**3**) as reported by Herbst et al.[47] Similar to the PCL blocks, the purity of the PIB blocks was highly important for the subsequent investigations of the crystallization and melting behavior and therefore critically investigated and proven via ^{1}H NMR spectroscopy and MALDI-TOF MS (see Supporting Information Fig. S3).

Preparation of the Supramolecular Mixtures (BC1, BC2, BC3, BC4)

The first pseudo-BCPs (**BC1**, **BC2**) are a mixture between the mono thymine-functionalized PCL (**1**) and the connecting agent (**2**) bearing two 2,6-diaminotriazine groups (Fig. 1). The supramolecular interaction is based on a triple hydrogen bond, namely the interaction between thymine and 2,6-diaminotriazine. As the molar ratio between the thymine-functionalized PCL (**1**) and the connecting agent (**2**) is two to one, two PCL blocks (**1**) can be connected to one connecting agent (**2**). The mixture between the lower molecular weight thymine-functionalized PCLs (**1a**; $M_n = 4457$ g/mol) and the connecting agent (**2**) are designated as **BC1**, and the mixture between the higher molecular weight thymine-functionalized PCL (**1b**; $M_n = 8795$ g/mol) and **2** was designated **BC2**. **BC1**

TABLE 2 Results of the Synthesis of Homopolymers **1a, 1b, 4a, 4b,** and **3**

Entry	Polymer	$M_{n\ (calc)}$ (g/mol)	DP[a] (NMR)	$M_{n\ (NMR)}$ (g/mol)	$M_{n\ (GPC)}$ (g/mol)	$M_w/M_{n\ (GPC)}$	Yield[b] (%)
1	**4a** (alkyne-PCL)	6,946	36	4,206	6,100	1.2	75
2	**4b** (alkyne-PCL)	9,913	74	8,544	13,200	1.5	77
3	**1a** (thymine-PCL)	7,197	36	4,457	6,000	1.1	72
4	**1b** (thymine-PCL)	10,165	74	8,795	12,900	1.4	67
5	**3** (diaminotriazine-PIB)	4,966	73	4,462	_[c]	_[c]	65

[a] Degree of polymerization obtained via NMR spectroscopy.

[b] Isolated yields after purification.

[c] The molecular weight could not be determined because of adsorptive interactions with the GPC column. GPC curves of homopolymers **1a**, **1b** and of allyl-telechelic PIB are given in supporting information (Fig. S2).

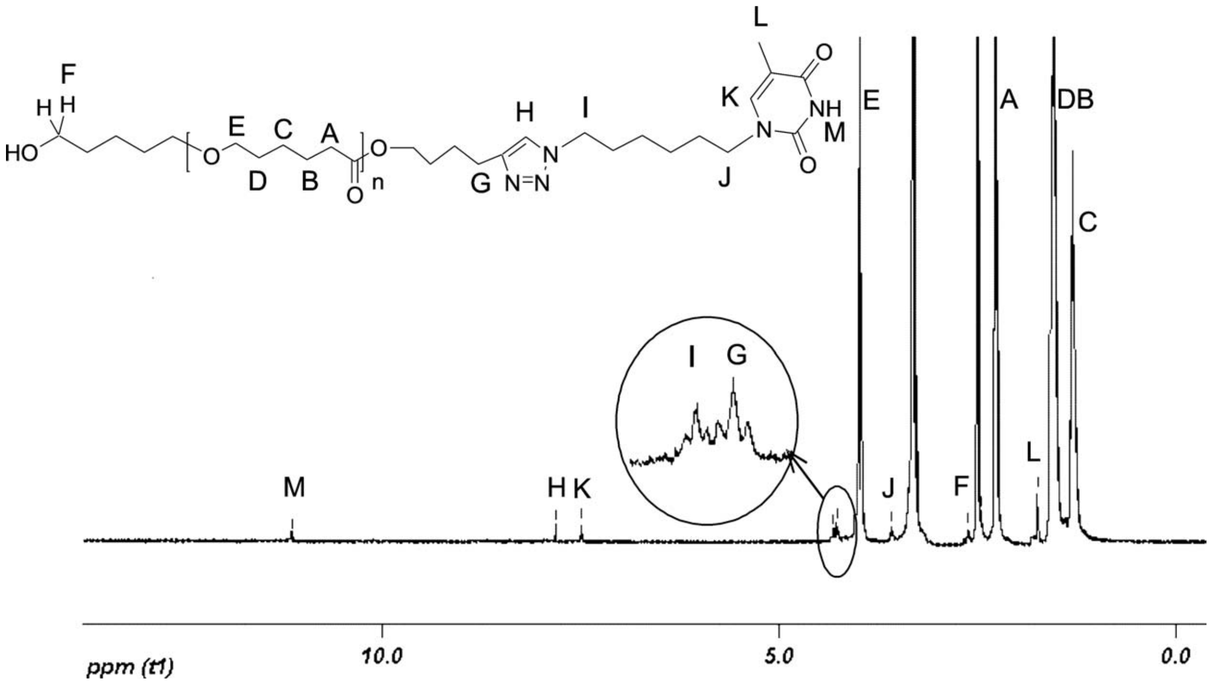


FIGURE 3 ^{1}H NMR spectra of thymine-functionalized PCL (**1a**).

and **BC2** were studied as a model system to investigate the influence of the supramolecular interactions on the crystallization process of polymers.

The second supramolecular BCPs (**BC3** and **BC4**) are a mixture between the thymine-functionalized PCLs (**1**) and the 2,6-diaminotriazine-functionalized PIB (**3**) in a molar ratio of 1/1. Similar to **BC1** and **BC2**, the blocks are connected via supramolecular interactions between thymine and 2,6-diaminotriazine. **BC3** is the pseudo-BCP consisting of the lower molecular weight thymine-functionalized PCL (**1a**) and the 2,6-diaminotriazine-functionalized PIB (**3**); **BC4** comprises the higher molecular weight thymine-functionalized PCL (**1b**) and PIB (**3**). In contrast to **BC1** and **BC2**, **BC3** and **BC4** can be indeed considered as true pseudo-BCPs matching the covalently linked counterpart of a BCP derived from PCL-*b*-PIB.

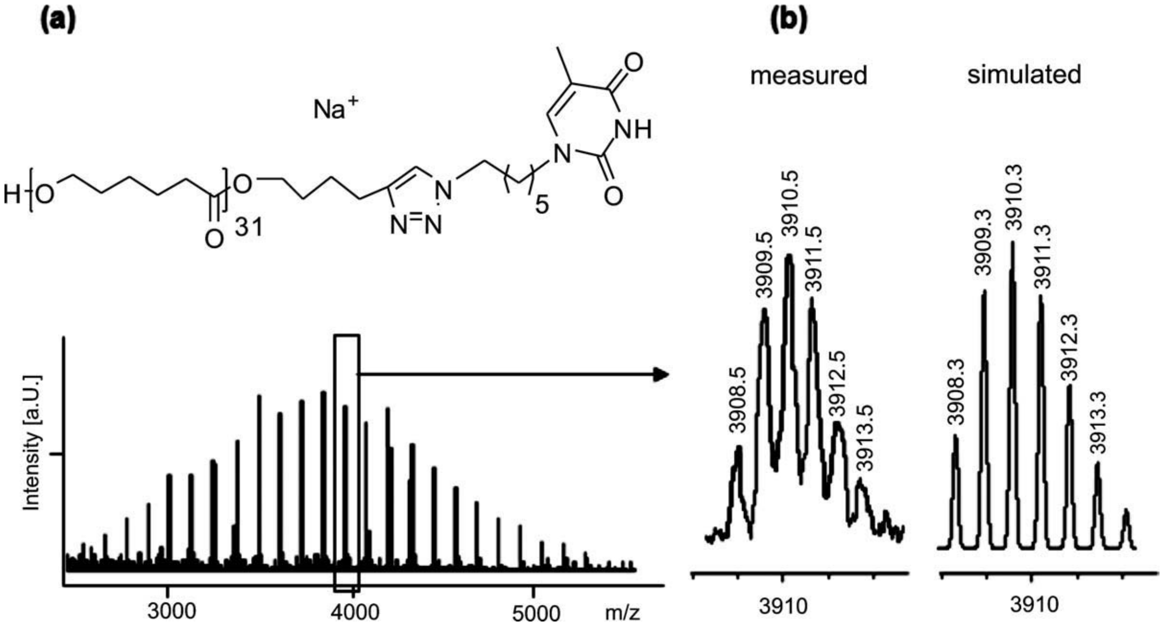


FIGURE 4 MALDI-TOF MS of thymine-functionalized PCL (**1a**) (a) full spectrum, (b) expansion including simulation of the isotope pattern.

TABLE 3 Results of Nonisothermal DSC Measurements of Samples **4a, 4b, 1a, 1b, BC1–BC4**

Entry	Polymer	M_n[a] (g/mol)	T_m[b] (°C)	T_c[c] (°C)	ΔH_m[d] (J/g)	f_c[e]
1	**4a**	4,206	55	38	88	0.62
2	**1a**	4,457	55	36	82	0.61
3	**BC1** (**1a** + **2** + **1a**)	9,474[f]	55	8	70	0.55
4	**4b**	8,544	57	37	86	0.60
5	**1b**	8,795	57	38	82	0.58
6	**BC2** (**1b** + **2** + **1b**)	18,150[f]	57	26	71	0.52
7	**BC3** (**1a** + **3**)	8,919[f]	53/57	27	46	0.68
8	**BC4** (**1b** + **3**)	13,257[f]	56	33	47	0.51

[a] Molecular weights calculated based on NMR data.

[b] Melting temperature (peak maximum) taken from DSC scans performed with heating rates of +10 K/min after cooling with −10 K/min.

[c] Crystallization temperatures (peak maximum) taken from DSC scans performed with a cooling rate of −10 K/min.

[d] Melting enthalpies taken from heating scans.

[e] Degree of crystallinity of the PCL components calculated from $f_c = (\Delta H_m \cdot M_n)/(\Delta H_m^{100\%} \cdot M_{PCL})$ where ΔH_m is the measured melting enthalpy, $\Delta H_m^{100\%} = 146$ J/g is the melting enthalpy of 100% crystalline PCL being an average value of data given in the literature,[51,52] and $M_{PCL} = M_{PCL+endgroup} - M_{endgroup}$ is the molecular weight of the pure PCL component [$M_{endgroup} = 348$ g/mol for thymine used in case of (**1a**) or (**1b**) and $M_{endgroup} = 97$ g/mol for alkyne used in case of (**4a**) or (**4b**)].

[f] Virtual molecular weights calculated by adding up the molecular weights of all constituent parts.

Thermal Analysis

Standard DSC Scans

To study the crystallization behavior of all our samples, nonisothermal crystallization measurements by DSC were performed. Melting temperatures T_m and melting enthalpies ΔH_m (Table 3) were calculated from a heating run done at a scan rate of 10 K/min after isothermal annealing of the sample 20 K above the melting point of pure PCL (to remove all seeds) and cooling the sample at a rate of −10 K/min to −85 °C (Supporting Information Fig. S4). Essentially, all PCL samples displayed single melting peaks with melting temperatures at 55–57 °C. Obviously, neither the thymine endgroup nor the addition of compound **2** have a significant influence on the melting behavior. In the case of PCL-*b*-PIB pseudo-BCPs (**BC3** and **BC4**), the melting transitions are more complex. A dual melting peak occurred for **BC3** (53 and 57 °C) while **BC4** showed a single peak at 56 °C with a small shoulder at the high temperature side [see Supporting Information Fig. S5(a,b)]. For isothermally crystallized **BC3** and **BC4** samples that were annealed at 38 °C for 2 h, however, we observed only one melting peak [see Supporting Information Fig. S5(c,d)]. Dual melting transitions for supramolecular PCLs were also reported by Lin et al.[28] and attributed to the melting of initially formed crystals followed by recrystallization and final melting of these crystals grown during heating. An alternative explanation for a dual-melting peak could be the existence of different crystal structures formed under the nonisothermal conditions. This interpretation was given by Gan et al.[53] to explain a double melting transition for PCL-*b*-PEO copolymers.

The cooling curves for different PCL-containing systems are shown in Figure 5. Alkyne-functionalized PCLs (**4a**, **4b**) and

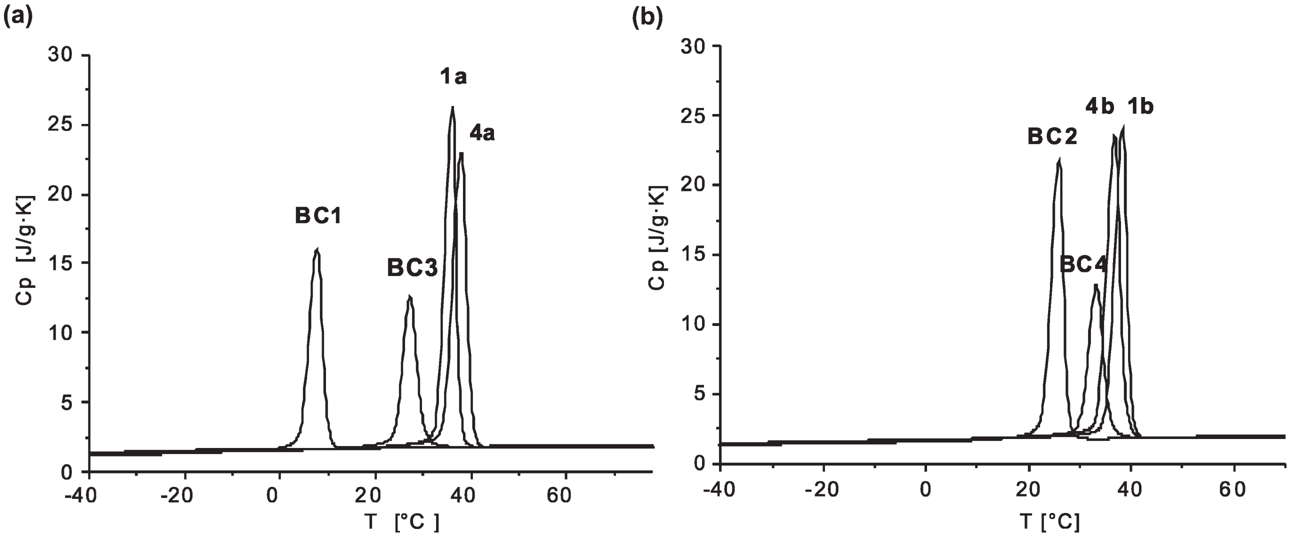


FIGURE 5 Cooling curves of homo and block copolymers obtained from DSC measurements at a cooling rate of 10 K/min. (a) Samples **1a**, **4a**, **BC1**, **BC3** and (b) samples **1b**, **4b**, **BC2**, **BC4**.

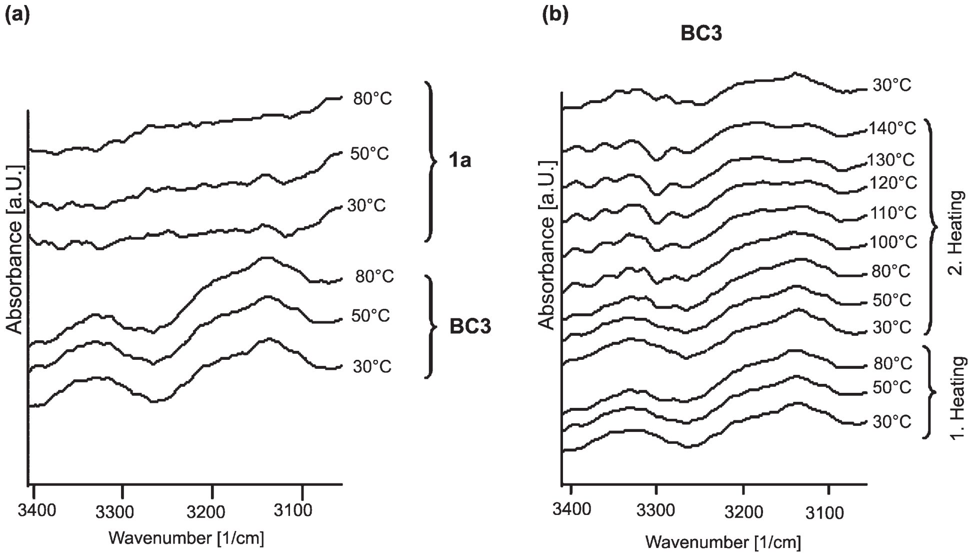


FIGURE 6 Temperature-dependent FTIR spectra of (a) thymine-functionalized PCL (**1a**) and (b) first and second heating of block copolymer **BC3**.

thymine-functionalized PCLs (**1a**, **1b**) display very similar crystallization temperatures at about 36–38 °C. A significant decrease of the crystallization temperatures was observed for all pseudo-BCPs (**BC1**, **BC2**) as well as for **BC3** and **BC4**. While thymine-functionalized PCL **1a** crystallizes at 36 °C, the crystallization temperature is only 8 °C if two thymine-functionalized PCLs (**1a**) are coupled via the connecting moiety **2**. Interestingly, the decrease of the crystallization temperature is less pronounced for the PCL-*b*-PIB pseudo-BCP **BC3** (**1a**+**3**) which crystallizes at 27 °C. The main trends for polymers containing the thymine-functionalized PCL (**1b**) with higher molecular weight are quite similar. We observe a decrease in the crystallization temperature from 38 °C for pure PCL (**1b**) to 26 °C after connecting two PCL blocks (**1b**) with the moiety (**2**) while the crystallization temperature is 33 °C if the PCL block (**1b**) is connected with the PIB block (**3**).

From the melting enthalpies ΔH_m given in Table 3, we have estimated the degree of crystallinity of the PCL component for all samples. We assume here that the experimentally determined melting enthalpy is only because of melting of the PCL component in our polymeric systems, that is, that there are no contributions from PIB, thymine or the connecting moiety **2** (having a melting temperature which is much higher than that of PCL, $T_{m,2} >> 50$ °C). Based on this assumption, the degree of crystallinity f_c of the PCL component can be calculated using the experimentally observed melting enthalpy ΔH_m, the melting enthalpy of 100% crystalline PCL $\Delta H_m^{100\%} = 146$ J/g[51,52] as well as the molecular weights of all components (for details of the calculation see footnote (e) of Table 3). Degrees of crystallinity f_c for the different polymers are given in Table 3. The f_c values for different systems are obviously similar showing that there are no pronounced confinement effects in all investigated pseudo BCPs.

Isothermal Crystallization Kinetics

The kinetics of crystallization processes in microphase-separated block polymers are complex, as exemplified by Avrami exponents n ranging from 1 to 3, indicative of an often constrained growth of the crystals limited by the (glassy) blocks of the microphase-separated second block.[37] As commonly accepted, Avrami exponents close to ~1 are observed for crystallization in strongly confined and disconnected systems where the glassy domains strongly restrict crystal growth. Such systems require strong homogeneous nucleation[54] to initiate crystallization. Avrami exponents of $n \sim 3$ are typically an indication of unrestricted or only weakly restricted crystal growth. Hence, composition and morphology of multicomponent systems will seriously influence the structure-formation processes and the crystallization kinetics. In particular, crystallization rate and Avrami exponent, as a typical parameter describing the time dependence of isothermal crystallization processes,[28] will be strongly affected if a change from homogeneous to (partially) heterogeneous nucleation occurs due to templated crystallization.

To quantify the Avrami exponent n for our PCL containing systems, we conducted isothermal DSC measurements at 42 °C of alkyne-functionalized PCL (**4a**, **4b**), thymine-functionalized PCL (**1a**, **1b**), and PCL-*b*-PIB (**BC3**, **BC4**) pseudo-BCPs. For this purpose, the samples were annealed at 80 °C for 20 min and quenched to 42 °C with a nominal cooling rate of 200 K/min. This temperature was chosen as the time scale of the crystallization allowed measurements on a reasonable time scale. Subsequently, the heat flow was continuously detected during the isothermal crystallization process. The corresponding Avrami plots are shown in the Supporting Information (Fig. S6). Avrami exponents n were determined according to the method described by Lin et al.[28] We obtained Avrami exponents of about $n \sim 3$ for all investigated samples (**1a**, **1b**, **4a**, **4b**, **BC3**, **BC4**) in a wide time interval. In light of the discussion in the literature this can be understood as an indication for a confluence of the growing crystals during the crystallization process in case of the pseudo BCPs (**BC3**, **BC4**).

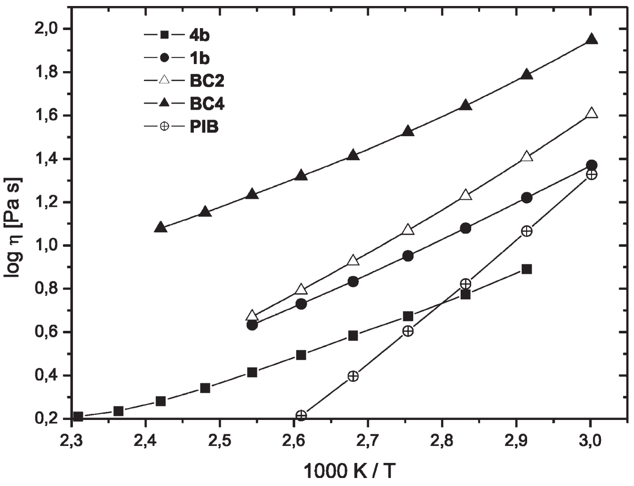


FIGURE 7 Temperature dependence of viscosity of homopolymers **4b**, **1b** and block copolymers **BC2** and **BC4**. For comparison values for PIB, homopolymer of comparable molecular weight as the PIB block **3** in **BC4** are shown.

FTIR Studies

We investigated the state of supramolecular bond of PCL-*b*-PIB BCP **BC3** via FTIR spectroscopy in crystalline and molten state at various temperatures between 30 and 140 °C. Figure 6(a) shows a comparison between the thymine-functionalized PCL (**1a**) and the PCL-*b*-PIB BCP (**BC3**) containing **1a** as a crystalline block. In the case of **BC3**, the broad absorption bands in the range between 3100 and 3400 cm^{-1} indicate bound (associated) N—H stretching vibrations (hydrogen bonds between thymine and 2,6-diaminotriazine). In addition, we have tested the thermal stability of the hydrogen bonds during the melting process [Fig. 6(b)]. On heating from 30 to 140 °C, the peak shape flattened out and the main broad signal shifted toward higher wavenumbers, indicating the opening of the hydrogen bonds.

Rheology

All samples were studied only in the molten state above 60 °C as at lower temperatures in the semicrystalline state the samples are to stiff for measurements in parallel plate geometry as it is used here. For the homopolymer samples **4b**, **1b**, and the mixture **BC2**, the viscosity was so low that meaningful dynamic measurements were not possible. Hence, only steady shear measurements were performed in a range of typically 1–100 rad/s. All samples showed Newtonian behavior with the viscosity being independent of the shear rate.

Figure 7 shows the temperature dependence of viscosity in an Arrhenius diagram. The temperature interval investigated is well above the glass transition temperature. Hence, the temperature dependence of the viscosity is rather weak. The alkyne-functionalized PCL **4b** shows, for instance, only a fourfold increase in viscosity from 140 to 70 °C. The introduction of the thymine functionality in polymer **1b** increases the viscosity somewhat (by a factor of 1.9 at 90 °C). However, the temperature dependence stays similar to the parent polymer **4b**. Either the bulky thymine group could lower the mobility of the whole PCL chain or two thymine functionalities of different PCL chains interact directly to create longer effective molecules. **BC2** (the mixture of **1b** and **2**) shows a stronger temperature dependence than **1b** alone. This is a hint on an increasing influence of hydrogen bonds between PCL chains at lower temperatures, as expected.

The pseudo-BCP **BC4** was distinctly more viscous. In contrast to earlier rheological observations of cluster-effects in hydrogen-bonded polyisobutylenes,[47,55] no transient cluster or networks were observed. This enabled dynamic measurements which give additional information about possible elastic properties. As an example, Figure 8(a) shows dynamic measurements for sample **BC4** with angular frequencies ω of 0.1–20 rad/s at different temperatures. One notices pronounced flow behavior with an imaginary part of the modulus G'' proportional to ω and a small real part of the modulus G' with a stronger frequency dependence. Figure 8(b) shows the real part of the dynamic viscosity, calculated from the data in Figure 8(a). The nearly frequency-independent data prove a nearly perfect Newtonian behavior. The noisy data at low frequencies are caused by the very low

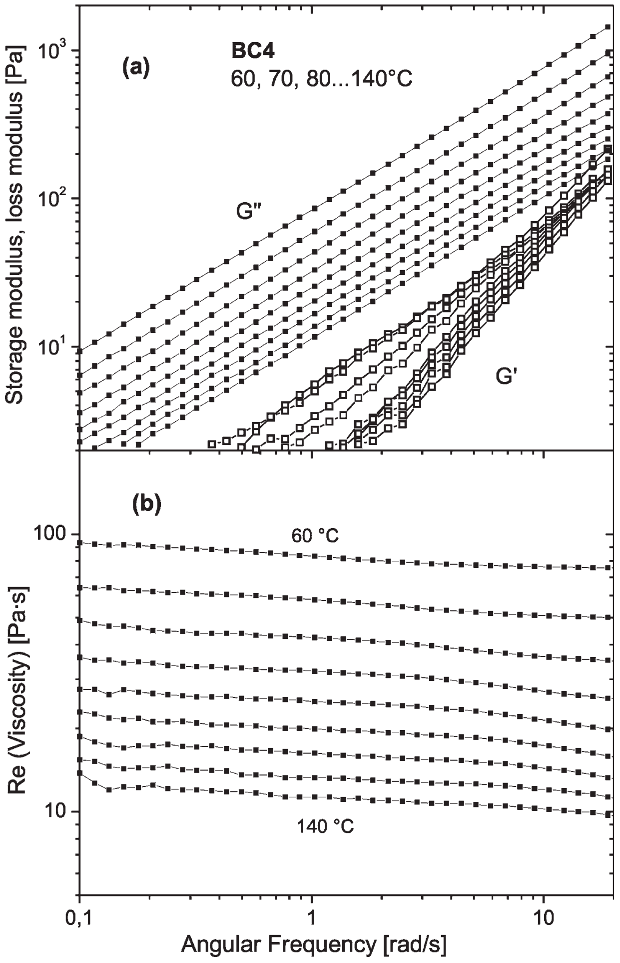


FIGURE 8 Dynamic measurements for sample **BC4**: (a) storage (G') and loss modulus (G'') and (b) real part of viscosity versus angular frequency.

torque values in this range. Correspondingly, at the lowest temperatures and in the lower frequency range one notices some contributions in the real part of the modulus which seem to show a smaller frequency dependence than expected for Newtonian flow. These values are at the limits of resolution. More precise measurements would require larger tools, demanding more sample material.

Based on these measurements, the zero shear rate viscosity for **BC4** was estimated and included in Figure 7. Over the whole temperature range, the viscosity of **BC4** is about a factor of 3.7 higher than the viscosity of the PCL block **1b** alone. The reason for this large increase in viscosity could be a phase separation between the PCL and PIB blocks, aggregation of some PCL chains, or simply the increase of molecular weight of the PCL block because of the attachment of the PIB block. In any case the much higher viscosity of the pseudo-BCP sample **BC4** compared to the PCL block **1b** proves the existence and influence of the supramolecular bond. For comparison, viscosity values of a PIB homopolymer[47] of comparable molecular weight as the PIB block **3** in **BC4** are shown in Figure 7. PIB shows a much stronger temperature dependence in the temperature range investigated, but as the minor component in **BC4** its influence is expected to be limited.

SUMMARY

The preparation of pseudo-BCPs consisting of a crystallizable PCL block and an amorphous (low T_g) block made from PIB both held together by hydrogen bonding systems are described. Starting from ROP of ε-caprolactone, the use of click-chemistry enabled the introduction of thymine endgroups onto the PCL polymer, thus generating the fully thymine-substituted PCLs (**1a** and **1b**). Covalent mixing of **1a**, **1b** with a bivalent, bis(2,6-diaminotriazine)-containing molecule (**2**) generated the supramolecular polymers **BC1** and **BC2**, whereas mixing of **1a**, **1b** with the 2,6-diaminotriazine-substituted PIB (**3**) generated the supramolecular pseudo-BCPs **BC3** and **BC4**. Calorimetric investigations revealed only minor changes in the crystallization behavior of **BC1**–**BC4**, with Avrami exponents close to three, indicative of an unrestricted crystal growth. The presented pseudo-BCPs **BC3** and **BC4** represent the first of their kind, demonstrating that for the modest molecular weights synthesized up to now, the incompatability between the blocks is small and crystallization only weakly affected. As both blocks are small, a partial mixing of the PIB and PCL polymers is assumed, which also can be deducted from the rheological data. Similar to effects in covalent, weakly microphase separating BCPs, where the region of templated and even confined crystallization are reached by increases in the Flory–Huggins interaction parameter (χN), current future work is focussed on chain elongation of the respective PCL and PIB-blocks as well as the increase in the strength of the used hydrogen-bond.

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