

Layered Morphology of Poly(phenylene)s in Thin Films Induced by Substitution of Well-Defined Poly(ϵ -caprolactone) Side Chains

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ABSTRACT: Poly(ϵ -caprolactone) (PCL)-based macromonomers and the corresponding substituted polyphenylene polymers have been synthesized in various chemical structures. The effect of chemical structure and the crystallization of PCL on the resulting morphology in thin films have been investigated. PCL macromonomers containing the central 2,5-dibromo-1,4-phenylene moiety were synthesized by ring-opening polymerization (ROP). Poly(phenylene) polymers were then synthesized by cross-coupling of the PCL macromonomers in Yamamoto polycondensation reactions. Thin films of macromonomers and polymers were prepared by spin-coating on silicon substrates, and the resulting morphology in thin films was characterized by atomic force microscopy (AFM). Substitution of semicrystalline PCL side chains to the rigid poly(phenylene) backbone induced layered morphology in thin films. Our results indicate that increasing backbone rigidity causes grafted PCL side blocks to crystallize in better-defined layered structures parallel to the underlying substrate. Such layering was not observed when polystyrene (PSt) or poly(2-methyloxazoline) (POx) polymers were grafted to the rigid poly(phenylene) backbone. Hindering PCL crystallization by attaching PSt or POx to the end of PCL also prevented the formation of layered structures.

Introduction

Backbone conformation, side-chain ordering, and the resulting morphology affect various properties of the polymeric materials, such as mechanical strength and electronic properties. Electronic structure of conjugated polymers is closely related to the backbone conformation. The planarity of chains has been reported to increase conductivity.¹ The observed color changes in thiophenes as a function of temperature and solvent quality were interpreted in terms of torsion in the conjugated chain.²

Polyphenylene (PP) is a typical conjugated polymer with excellent mechanical properties and thermal and thermooxidative stability. Other interesting and important properties that PPs exhibit include liquid crystallinity³ and photo- and electroluminescence.⁴ Since the discovery that polyphenylene (PP) conducts electricity when doped with oxidizing or reducing agents,⁵ a great deal of research has gone into the study of this material and its derivatives.^{6–8} The effect of side-chain chemistry and side-chain length on the planarity of PP backbones has been extensively investigated by various groups.⁹ The necessity to generate a well-defined macroscopic architecture¹⁰ for improved material properties has been the interdisciplinary connection between synthesis and material science.

The key structural factor in describing the supramolecular ordering of PP is their anisotropic shape, which follows from a rodlike architecture that differentiates them from flexible polymers.¹¹ Unfortunately, PPs are insoluble in many organic solvents, which limit their processability. Therefore, attachment of conformationally mobile alkyl side chains to the backbone has been

important because it has allowed the controlled synthesis of soluble and processable PPs with high molecular weight. In view of the expected large persistence length of the main chain and of the flexibility of the side chains, such molecules have been termed "hairy-rod" polymers.¹² On combining a stiff, insoluble, rodlike polymer such as PP with a soft coil, for example polystyrene, it is possible to form a new polymer with novel and interesting properties.¹³ Current methodologies for the direct synthesis of derivatized PP are primarily based upon nickel- and palladium-mediated cross-coupling reactions due largely to their preservation of regiochemistry and nearly quantitative yields.^{3,4,8,14}

Poly(ϵ -caprolactone) (PCL) is a nonpolar aliphatic polyester having a melting temperature T_m of 63 °C and a glass transition temperature T_g of -70 °C. PCL can form useful polymer blends with other polymers to be used in a variety of applications.¹⁵ PCL is immiscible with high molecular weight polystyrene (PSt).¹⁶ Miscibility of PSt and PCL oligomers at low T and the existence of upper critical solution temperature (UCST) behavior were predicted¹⁷ in accordance with experiments.^{18,19} PCL is highly crystallizable. The crystallized form of PCL, as in other semicrystalline polymers, consists of alternating amorphous and folded chain crystalline lamellae. In very thin films of crystalline polymers, the geometrical confinement effect of the solid substrate causes these lamellae to orient parallel to the substrate.²⁰ To take advantage of this property of PCL lamellae to align parallel to the substrate in obtaining planarity of rigid PP backbones, we synthesized various chemical structures containing homo-PCL and grafted PCL and investigated the morphology of these molecules in thin films.

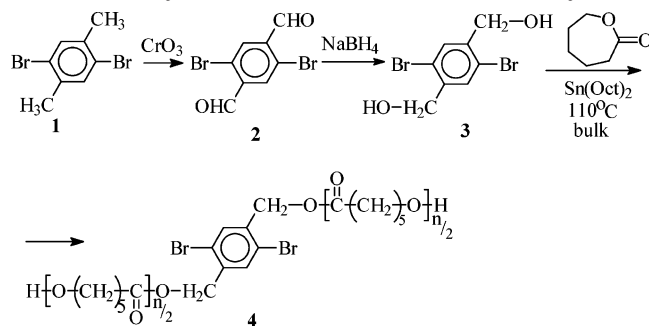
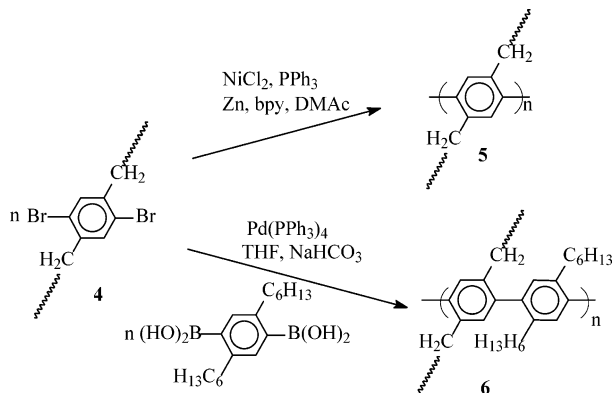
Living polymerizations are chain growth reactions that proceed in the absence of irreversible chain transfer and chain termination. The final average molecular weight of the polymer can be adjusted by varying the

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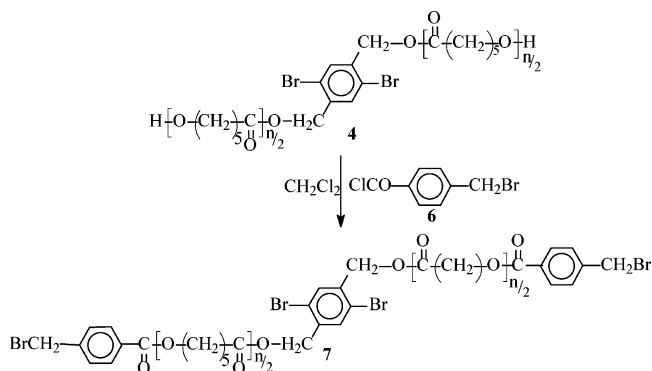
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Scheme 1. Synthesis of PCL Macromonomer by ROP**Scheme 2. Synthesis of PCL Grafted PPP by the Yamamoto (5) or Suzuki (6) Method**

Where is: poly(ϵ -caprolactone)

initial monomer/initiator ratio, while maintaining a narrow molecular weight distribution ($M_w/M_n < 1.5$).²¹ So, polymers can be end-functionalized and block-copolymerized with other monomers. Thus, it has opened new pathways to create many new materials with vastly differing properties by varying the topology of the polymer (comb, star, dendritic, etc.), the architecture of the polymer (random, periodic, graft, etc.), or the functional groups at various sites of the polymer (end, center, side).²² Atom transfer radical polymerization (ATRP), introduced by Matyjaszewski,^{23,24} has been proven to be effective for a wide range of monomers and appears to be a powerful tool for the polymer chemists, providing new possibilities in structural and architectural design and allowing the development of new products with monomers currently available. We have previously reported on the details of the synthesis of PPs having various chemical structures and side groups. PPs with PSt side chains starting from ATRP initiators as 1,4-dibromo-2,5-bis(bromomethyl)benzene²⁵ or benzene-2,5-dibromomethyl-1,4-bis(boronic acid propanediol diester)²⁶ have been synthesized. The first initiator was also used for the synthesis of PTHF-based macromonomers by cationic ring-opening polymerization (CROP), and PPs with PTHF or with PTHF/PSt alternating side chains were synthesized by the Suzuki or Yamamoto methods.²⁷ When 2,5-dibromo-1,4-(dihydroxymethyl)benzene was used for ROP of ϵ -caprolactone, well-defined PCL-based macromonomers were obtained and used for synthesis of PPs by the same cross-coupling methods (Schemes 1 and 2).²⁸

Other macromonomers and the corresponding PPs were also similarly designed.²⁹ By combining bromine-functionalized PSt-type macromonomers with PCL ones in Yamamoto copolycondensation reactions, PPs with both PSt and PCL side chains were obtained.³⁰ These

Scheme 3. Synthesis of PCL-Based Bifunctional Macroinitiator for ATRP or CROP

materials have interesting properties due to microphase-separated morphology of crystalline (PCL) and amorphous (PSt) side groups. By reacting the final OH groups of **4** with 4-bromomethyl benzoyl chloride, a benzyl bromide-ended PCL was synthesized (Scheme 3) and used as bifunctional macroinitiator for ATRP of styrene³¹ or CROP of 2-methyloxazoline (Scheme 4). The obtained copolymers preserved the same central 2,5-dibromo-1,4-phenylene moiety and provided the possibility to use them further in Suzuki- or Yamamoto-type polymerization reactions.³²

In this study, we investigated the morphology of these macromonomers and polymers in thin films. Our investigations showed that PCL crystallization induced layered structure formation in thin films and increasing backbone rigidity improved the formation of well-defined layers. The tendency of PCL, on either side of the rigid backbone, for the substrate caused planarity of the backbone in well-defined interfaces.

Experimental Section

Materials. PCL homopolymer (Aldrich, $M_w \sim 65\,000$ g/mol, $M_n \sim 42\,500$ g/mol, $T_m = 61$ °C) was used as reference in morphology determination. All other molecules have been synthesized and characterized as described in detail in previous publications.^{28–32}

The synthesis of 2,5-dibromo-1,4-(dihydroxymethyl)benzene (bifunctional initiator for ROP of ϵ -caprolactone) and the corresponding poly(ϵ -caprolactone) macromonomer **4** is seen in Scheme 1.²⁸ For **4** (Chart 1): $M_{n,\text{HNMR}} = 3050$ ($M_{n,\text{GPC}} = 4270$), polydispersity = 1.12. ¹H NMR (**4**) (CDCl_3) (δ , ppm): 7.58–7.48 (**a**), 5.13–5.01 (**b**), 4.10–3.82 (**g**), 3.64–3.48 (**h**), 3.44–3.33 (**j**), 2.43–2.33 (**i**), 2.33–2.07 (**c**), 1.73–1.43 (**d**, **f**), 1.43–1.16 (**e**).

The synthesis of poly(*p*-phenylene)s with PCL side chains by Yamamoto (**5**) or Suzuki (**6**) methods is seen in Scheme 2.²⁸

For **5** (Chart 1): $M_{n,\text{GPC}} = 27\,150$, polydispersity = 1.41. ¹H NMR (CDCl_3) (δ , ppm): 7.30–7.27 (**a**), 5.1–5.02 (**b**), 4.10–3.90 (**g**), 3.61–3.59 (**h**, **j**), 2.34–2.12 (**c**, **i**), 1.78–1.45 (**d**, **f**), 1.40–1.20 (**e**).

For **6** (Chart 1): $M_{n,\text{GPC}} = 38\,700$, polydispersity = 1.7. ¹H NMR (CDCl_3) (δ , ppm): 7.53–7.30 (**a**), 7.19–6.98 (**k**), 5.10–4.85 (**b**), 4.28–3.76 (**g**), 3.69–3.53 (**h**, **j**), 2.62–1.99 (**c**, **i**, **l**), 1.97–1.45 (**d**, **f**, **m**), 1.45–1.21 (**e**, **n**), 1.21–0.99 (**o**, **p**), 0.94–0.61 (**q**).

4-Bromomethyl benzyl chloride (Scheme 3) was synthesized from α -bromo-*p*-toluic acid according to a previously reported procedure;³² mp (DSC): 33–34 °C. ¹H NMR (CDCl_3) (δ , ppm): 8.12–8.11 (d, 2H, Ar *ortho* to CO), 8.09–8.06 (d, 2H, Ar *ortho* to CH₂), 4.63 (s, 2H, CH₂Br).

The synthesis of PCL with benzyl bromine end groups (polymer **7**, Chart 1, Scheme 3) was performed by esterification of final OH groups of **4** with **6**.³¹ $\text{DP}_{n,\text{PCL}} = 24.6$, $M_{n,\text{HNMR}} = 3300$ ($M_{n,\text{GPC}} = 5300$), polydispersity = 1.11. ¹H NMR (**7**) (CDCl_3)

Scheme 4. Synthesis of Block Copolymers PSt–PCL–PSt (8) and POx–PCL–POx (9) by ATRP and CROP of the Respective Monomers, Using as Bifunctional Macroinitiator the Modified PCL (7)

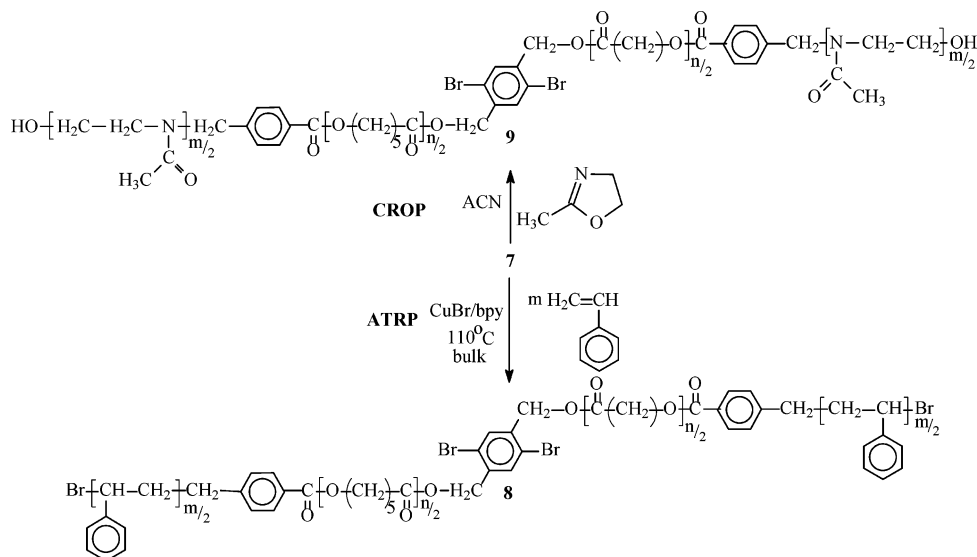
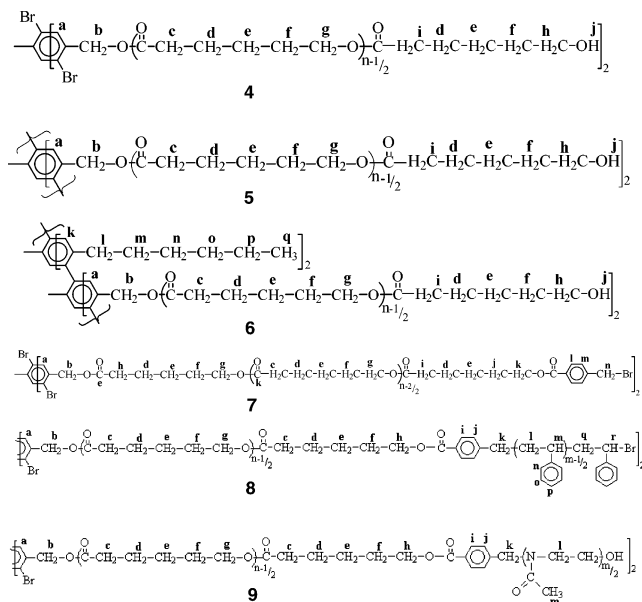


Chart 1



(δ , ppm): 8.13–7.91 (l), 7.55–7.34 (m), 7.51 (a), 5.09–5.02 (b), 4.60–4.52 (n), 4.30–4.22 (k), 4.08–3.85 (g), 2.41–2.32 (i), 2.32–2.12 (c), 2.12–2.06 (h), 1.79, 1.47 (j, d, f), 1.47–1.16 (e).

Synthesis of Block Copolymer PSt–PCL–PSt (8) in Scheme 4) by ATRP. A round-bottom flask equipped with a magnetic stirrer and a lateral neck with tap was used. The system was vacuumed and backfilled with dry nitrogen several times. Catalyst (CuBr , 0.0631 g, 0.44 mmol), ligand bipyridine (bpy, 0.2061 g, 1.32 mmol), initiator (7, 0.726 g, 0.22 mmol), and styrene (St, 2 mL) were introduced under an inert atmosphere. The flask was placed in an oil bath warmed at 110°C and stirred at that temperature. After 40 min, the mixture was diluted with THF and poured into 10-fold methanol. The solid was collected after filtration and drying at 40°C in a vacuum overnight. The polymer was purified by passing through a silica gel column using THF as eluent and reprecipitated into methanol. $\text{DP}_{n,\text{CL}} = 25$ and $\text{DP}_{m,\text{St}} = 19$, $M_{n,\text{HNMR}} = 5200$ ($M_{n,\text{GPC}} = 11\,500$), polydispersity = 1.07.³¹ ^1H NMR (8, Chart 1) (CDCl_3) (δ , ppm): 8.06–7.7 (i), 7.61–7.52 (a), 7.51–6.27 (j, o, p, n), 5.21–5.08 (b), 4.65–4.56 (r), 4.40–4.19 (h), 4.19–3.79 (g), 2.59–2.08 (c, k, q), 2.11–1.02 (d, e, f, l, m).

Synthesis of Block Copolymer POx–PCL–POx (9) in Scheme 4) by CROP. A solution of 2-methyl-2-oxazoline (8

mmol, 0.68 g) and 7 (0.23 mmol, 0.779 g) in 6 mL of dry acetonitrile was heated at 80°C for 10 h under nitrogen. After this time, a 2.5 mL solution of 0.2 N methanolic KOH was added to end the reaction, and the reaction was stirred 0.5 h more than cooled at room temperature. The polymer was precipitated in diethyl ether. Further purification was achieved by reprecipitation of the polymer in diethyl ether, using chloroform as solvent. $\text{DP}_{n,\text{CL}} = 25$ and $\text{DP}_{n,\text{Ox}} = 34.5$, $M_{n,\text{HNMR}} = 6350$. ^1H NMR (9, Chart 1) (CDCl_3) (δ , ppm): 8.08–7.98 (i), 7.68–7.61 (a), 7.39–7.16 (j + CDCl_3), 5.18–5.07 (b), 4.4–4.18 (h, k), 4.18–3.82 (g), 3.68–3.19 (l), 2.38–2.21 (c), 2.21–1.89 (m), 1.44–1.29 (d, f), 1.29–1.17 (e).

^1H NMR spectra of PCL-based polymers 7–9 are seen in Figure 1.

Methods. ^1H NMR spectra were recorded on a Bruker 250 MHz spectrometer using CDCl_3 as solvent and tetramethylsilane as the internal standard. GPC measurements were performed with an Agilent1100 RI apparatus equipped with three Waters Styragel columns HR series (4, 3, 2 narrow bore) at a flow rate of 0.3 mL/min, the temperature of the refractive index detector of 30°C , and THF as eluent. Molecular weights were calculated using polystyrene standards.

Thin films were prepared by spin-coating at 2000 rpm for 1 min from solutions in chloroform on oxidized silicon substrates. The concentration of the solutions was less than 1 wt %, resulting in films of thicknesses less than 50 nm. Film thicknesses were measured by a Microphotonic ELX-01R ellipsometer using 632.8 nm laser light at 70° angle. Silicon substrates were kept in UV-ozone plasma for 15 min prior to spin-coating to ensure hydrophilicity of the surface. A water drop spread homogeneously on UV-ozone-treated substrates. Spin-coated films were kept in a vacuum oven at low temperatures for solvent evaporation and later annealed at various temperatures depending on the chemical structure and composition. Morphology of polymers in thin films was characterized by NT-MDT Solver P47 AFM in tapping mode.

Results and Discussion

When semicrystalline polymer PCL is crystallized in the bulk, spherulites are observed. In each spherulitic domain, alternating amorphous and crystalline lamellae grow out from the crystal nucleus while branching to fill the volume. In thin films of PCL on solid substrates, the orientation of the amorphous/crystalline lamellae is affected by the geometrical confinement of the substrate. The lamellae can be perpendicular to the substrate surface (edge-on lamellae) or parallel to it (flat-on lamellae). It is known for semicrystalline polymers

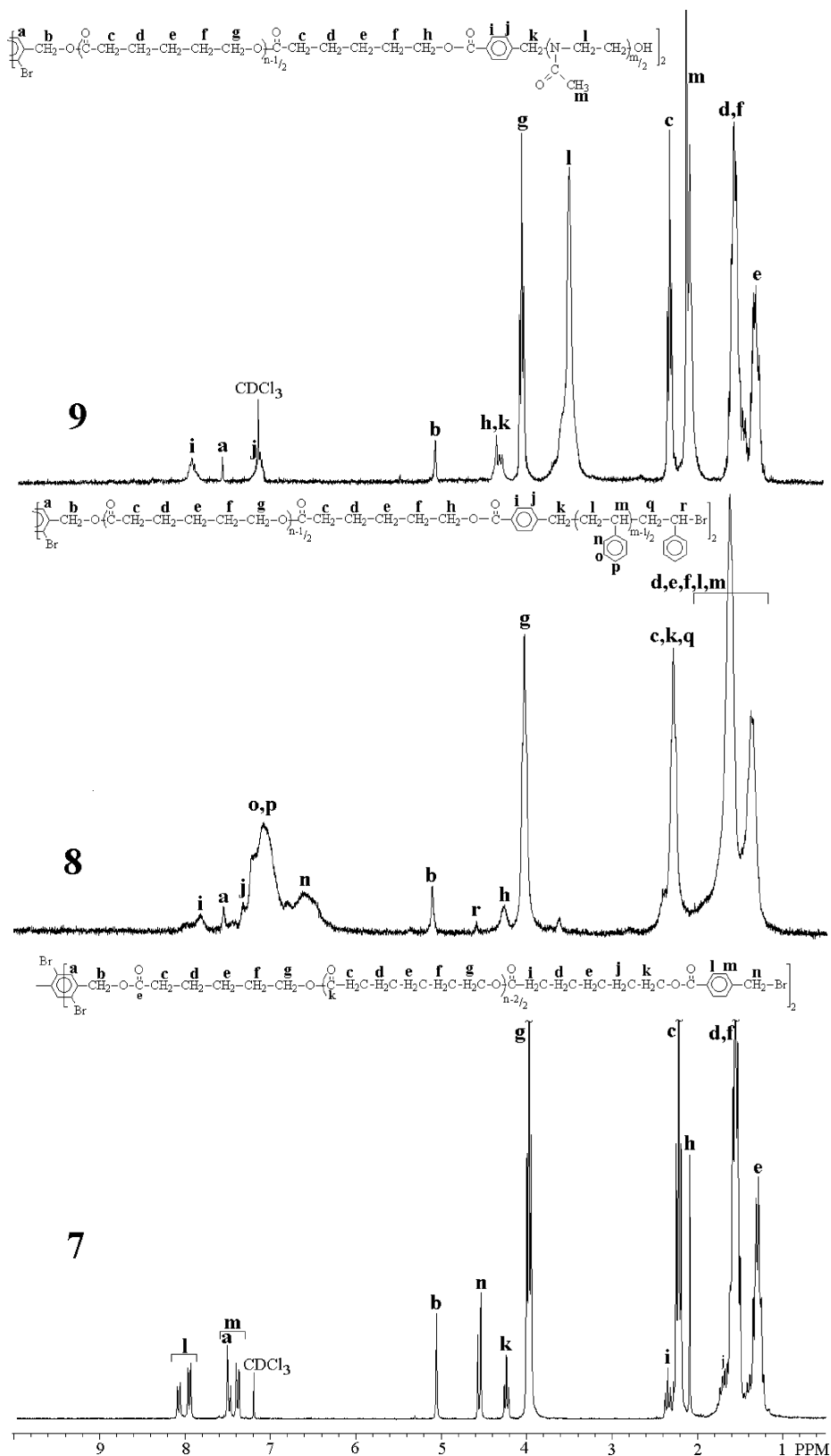


Figure 1. ^1H NMR spectra of PCL-based polymers **7** (Scheme 3), **8**, and **9** (Scheme 4).

that the lamellae switch from edge-on to flat-on as the film thickness decreases below ~ 500 nm.²⁰

Figure 2 shows the AFM phase picture of 110 nm thick PCL homopolymer (Aldrich, $M_w \sim 65\,000$ g/mol, $M_n \sim 42\,500$ g/mol, $T_m = 61$ °C) on SiO_2 immediately after spin-coating. The edge-on lamellae were clearly observed. The brighter thin lines correspond to the crystalline layers and are seen to branch occasionally.

The darker regions between the thin lines are the amorphous layers. The width of the crystalline layers is equal to the fold length of the polymer chain. In the figure, the width was measured to be 8–10 nm, consistent with previous measurements and the theories. When this film was melted, kept at 75 °C for 15 min, and recrystallized at 45 °C (undercooling (= $T_m - T_c$) of 16 °C), large areas of flat-on lamellae were observed

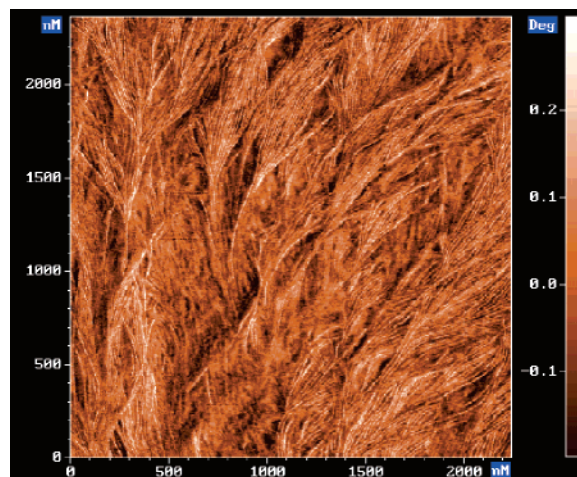


Figure 2. AFM phase picture of 110 nm thick commercial PCL homopolymer (Aldrich, $M_w \sim 65\,000$ g/mol, $M_n \sim 42\,500$ g/mol) on SiO_2 immediately after spin-coating.

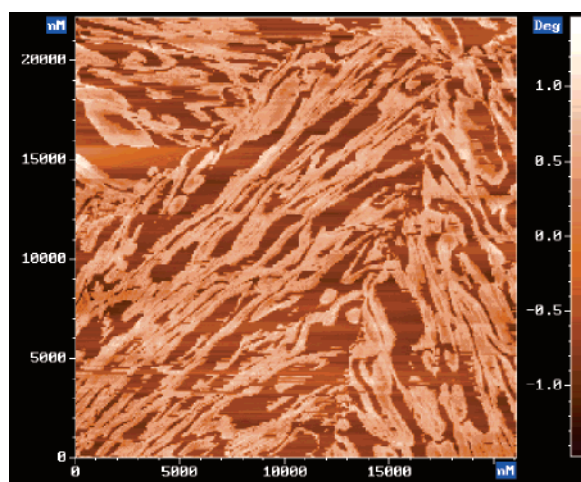


Figure 3. Film of Figure 2 after melting and recrystallization. $20\ \mu\text{m} \times 20\ \mu\text{m}$ area of the film surface where four domains consisting flat-on lamellae meet at the upper right corner.

as seen in the AFM phase picture of Figure 3. The figure shows a $20\ \mu\text{m} \times 20\ \mu\text{m}$ area of the film surface where four domains consisting of flat-on lamellae meet at the upper right corner. Within the domains, the bright crystalline regions are oriented in the same direction. In the largest domain of the figure the crystalline

regions go from lower left to upper right corner. The darker areas are the amorphous layers. The crystalline regions cannot be edge-on lamellae because the width of these regions is ~ 500 nm, much larger than the typical fold length of ~ 10 nm. The evidence for the flat-on lamellae comes from the height of these regions: the height is ~ 10 nm, consistent with the expected fold length and indicating that the crystalline layer is parallel to the surface (the polymer chain axis is perpendicular to the surface).

When PCL is attached to 1–4 points of a phenyl ring (polymer 4, Scheme 1), the spherulitic crystalline domains of PCL were also observed in thin films, but the microstructure within the domains was significantly different. After spin-coating polymer 4 on SiO_2 substrates, edge-on lamellae were observed in AFM phase pictures as seen in Figure 4a. Alternating crystalline and amorphous layers were seen to extend regularly over a region of 500 nm. This regularity is expected to originate from the ordering effect of the planar phenyl ring. This effect was more significant and better observed for flat-on lamellae. Keeping this film at $70\ ^\circ\text{C}$ for 1 h and quenching down to $30\ ^\circ\text{C}$ (undercooling ($= T_m - T_c$) of $17\ ^\circ\text{C}$) resulted in flat-on lamellae as seen in Figure 4b. Here the widths of the flat-on domains were 70–80 nm. Few edge-on lamellae having width of ~ 10 nm were also observed. The area covered by flat-on lamellae was much larger than that of edge-on lamellae.

We took advantage of the $-\text{OH}$ groups at the ends of PCL to enhance flat-on lamellae formation and to investigate microstructure in more detail. SiO_2 substrates were kept in UV-ozone plasma prior to spin-coating and made completely hydrophilic (a water drop wets such substrates homogeneously). The strong interaction of the $-\text{OH}$ group of PCL polymer 4 with the substrate induced flat-on lamellae even after spin-coating, without any melting and recrystallization. The flat-on lamellae and the resulting layered structure after spin-coating were clearly observed as seen in Figure 5a (AFM height picture) and 5b (AFM phase picture). The height of the layers was found to be 10 nm, as expected.

Melting this film at $75\ ^\circ\text{C}$ and recrystallizing at $30\ ^\circ\text{C}$ improved the layered structure. Figure 6a shows AFM height picture of this film. Three layers were clearly observed in the picture. The layer height was ~ 8 nm between the bottom layer and middle layer and

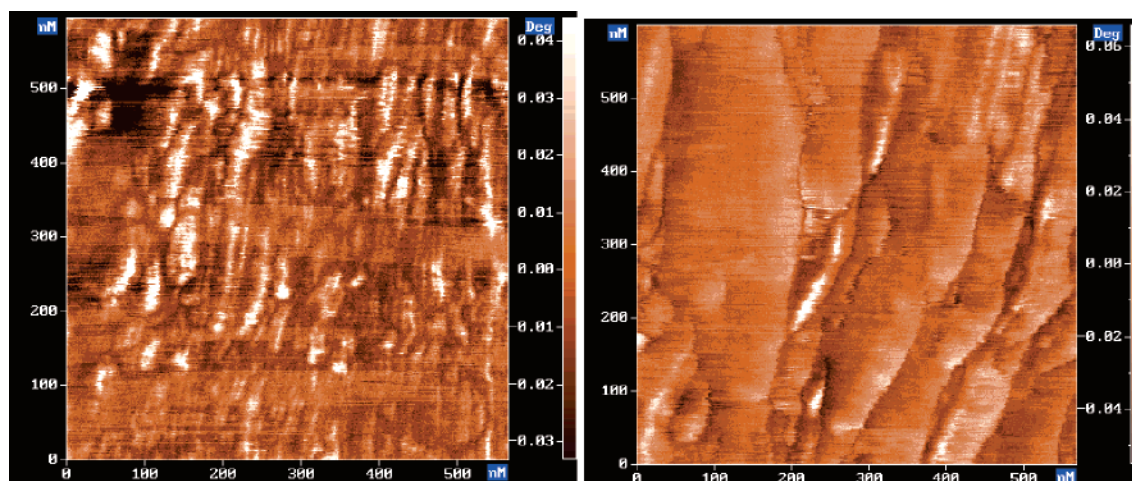


Figure 4. (a, left) AFM phase picture of edge-on lamellae in polymer 4 films on SiO_2 substrates after spin-coating. (b, right) AFM phase picture of flat-on lamellae in polymer 4 films after melting and recrystallization.

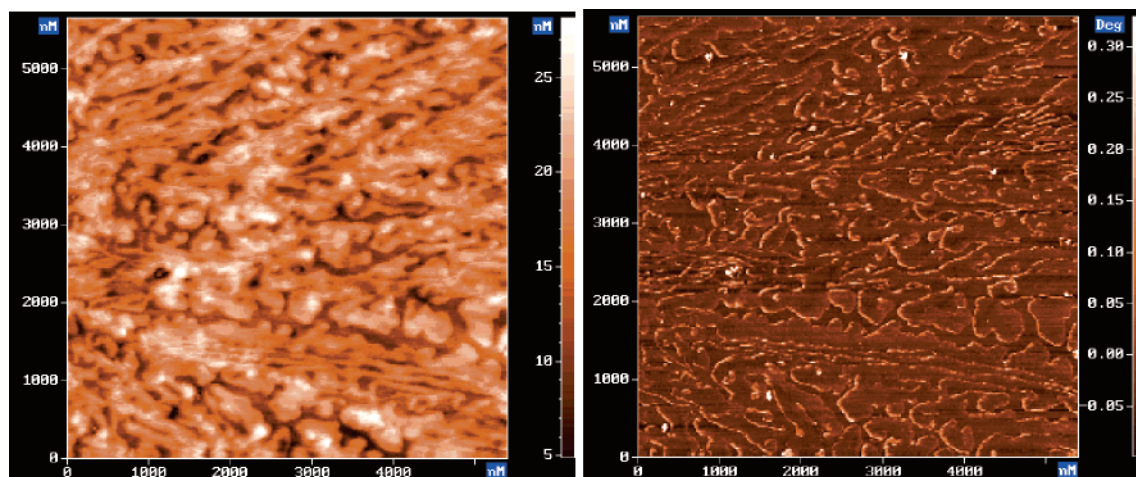


Figure 5. (a, left) AFM height picture of film of macromonomer **4** on UV-ozone-treated SiO₂ substrates. The strong interaction of the -OH group of PCL with the substrate induced flat-on lamellae right after spin-coating, without any melting and recrystallization. (b, right) AFM phase picture of the same film.

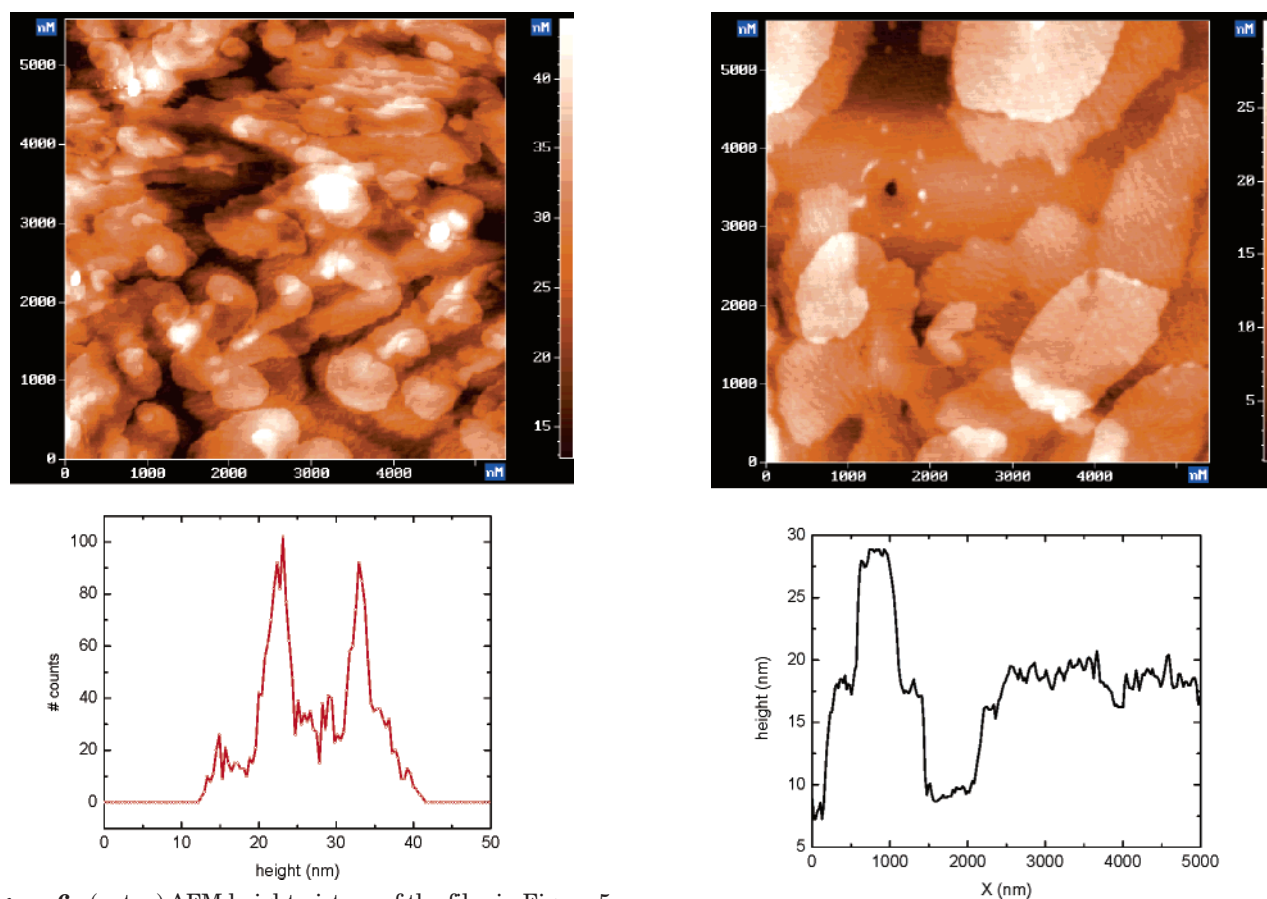


Figure 6. (a, top) AFM height picture of the film in Figure 5 after melting and recrystallization. (b, bottom) The histogram of heights of (a) showing the layering.

~10 nm between the middle layer and top layer. The histogram of heights in Figure 6b clearly shows this layering.

Poly(*p*-phenylene) polymer having PCL side groups (polymer **5**, Scheme 2) was obtained by polymerization of macromonomer **4**. Similar to commercial PCL homopolymer and macromonomer **4**, thin films of **5** on hydroxylated SiO₂ substrates also showed spherulitic crystalline domains with flat-on lamellae. The layered structure in the films was more regular as compared to films of macromonomer **4**, and different microstructures were clearly observed in different layers. Figure 7a

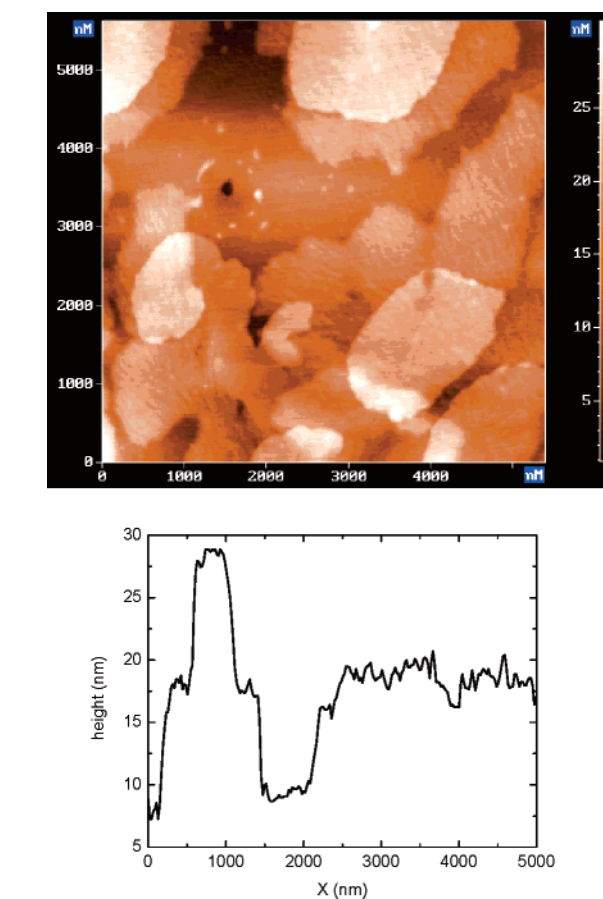


Figure 7. (a, top) AFM height picture of 5 μm × 5 μm area of a 34 nm thick polymer **5** film after melting and recrystallization. (b, bottom) Variation of height along a 5 μm horizontal distance. Two different layers having layer height of ~10 nm were clearly seen on top of the bottom layer.

shows an AFM height picture of a 5 μm × 5 μm area of a 34 nm thick film after keeping at 75 °C for 1 h and recrystallizing at 30 °C. Figure 7b shows the variation of height along a 5 μm horizontal distance. Two different layers having layer height of ~10 nm were clearly seen on top of the bottom layer. The depth of the hole, ~10 nm, in the upper left corner gives the thickness of the bottom layer which we will call layer 1. The observed microstructure of the bottom layer (layer 1) and the top layer (layer 3) were relatively smooth while middle layer

(layer 2) showed rough features within the layer. The alternating smooth and rough microstructure within the layers was due to whether the layer finished with PCL side blocks (rough microstructure) or with the rigid polyphenylene backbones (smooth microstructure). The $-OH$ groups at the end of PCL side blocks prefer to be on the hydroxylated substrate. The segregation of PCL side blocks on either side of the phenyl ring toward the substrate causes rigid polyphenylene backbones to stay on the top surface of layer 1 in a plane parallel to the surface in which all phenyl rings of the backbone lie flat. The aggregation of the backbones and the planarity of the phenyl rings create a relatively smooth top layer for layer 1. In layer 2, the rigid polyphenylene backbones go on top of polyphenylene backbones of layer 1, exposing the PCL side blocks on top and creating a rougher microstructure because of fold irregularities and chain ends. In layer 3, PCL side blocks go on top of layer 2 because $-OH$ end groups prefer to be together. The orientation then looks same as in layer 1, and a smooth microstructure was observed on top. This alternation is expected to continue as the film gets thicker. Our investigations of the extent of this alternation have been continuing.

The enhancement of layering with increasing rigidity of the backbone is determined by thermodynamics of the system rather than kinetics. The enhanced layering reflects the tendency of the film to have the lowest energy morphology by crystallizing PCL side blocks on the substrate and ordering the rigid backbones on top of it. It is not expected to be due to differences in crystallization kinetics of polymers **4** and **5**. In the bulk and at the same undercooling, polymer **5** crystallizes faster than polymer **4** because of much larger nucleation density of crystallites compared to polymer **4**. An improvement in order in thin films of polymer **5** can thus not be attributed to the slowing down of crystallization rate.

Decreasing the density of PCL side blocks 50% prevented the formation of layered structure. When polyphenylenes with alternating side groups of PCL and hexyl (polymer **6**, Scheme 2) were spin-coated on hydroxylated SiO_2 substrates, smooth films were obtained initially, but these films dewetted easily when temperature reached the melting temperature of the PCL blocks (44.8 °C). The dewetted areas show either a smooth ~ 12 nm thick interfacial layer on the substrate or ~ 10 nm height spheres. The smooth interfacial layer is expected to be the first layer of molecules whose PCL side groups face the substrate and hexyl side groups face the air. The observed tiny spheres must be the surface micelles formed when this single molecular layer was ruptured. The film on top of the smooth interfacial layer was not stable and showed auto-dewetting. These observations suggest that the density of layers is also critical in the stability of the layered structures.

We tried to hinder the crystallization of PCL side groups and the formation of layered structures in macromonomer **4** films by attaching either a hydrophobic amorphous polymer, PSt (polymer **8**, Scheme 4) or a hydrophilic amorphous polymer, POX (polymer **9**, Scheme 4), to the ends of the PCL groups. Films of polymer **8** were stable and did not show any sign of dewetting when annealed above glass transition temperature of PSt up to 130 °C for 20 h. The top surface was smooth without any features, indicating that lower surface energy PSt was at the top surface. Any indication of layering could not be observed.

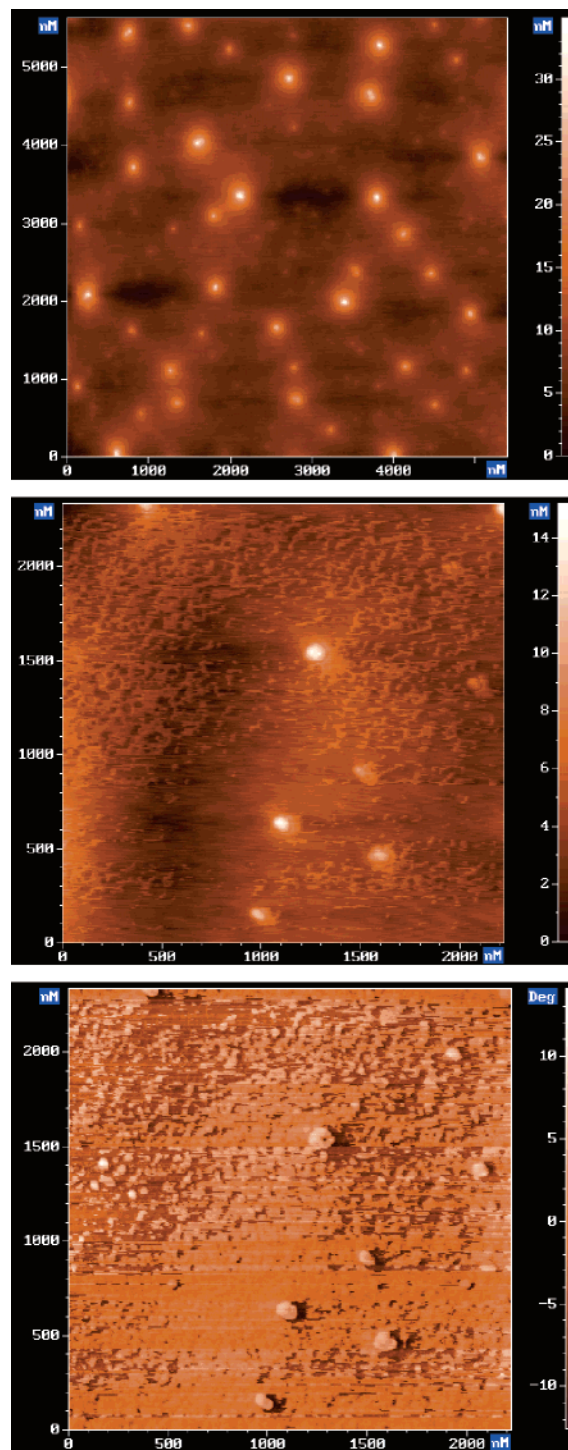


Figure 8. (a, top) AFM height picture of a 40 nm thick film of polymer **9** on hydroxylated SiO_2 substrate after spin-coating. The height of aggregates vary between 10 and 20 nm. (b, middle) AFM height picture of the film after annealing the film at 120 °C for 18 h. (c, bottom) AFM phase picture of the film in (b).

The AFM height picture of a 40 nm thick film of polymer **9** on hydroxylated SiO_2 substrate is seen in Figure 8a after spin-coating. The surface is smooth with some aggregates whose height vary between 10 and 20 nm. These aggregates are the PCL blocks sticking out to the air because of their hydrophobicity and much lower surface energy compared to POX. The evidence for this comes from the AFM height and phase pictures taken after annealing the film at 120 °C and quenching down to room temperature fast. 120 °C is above the

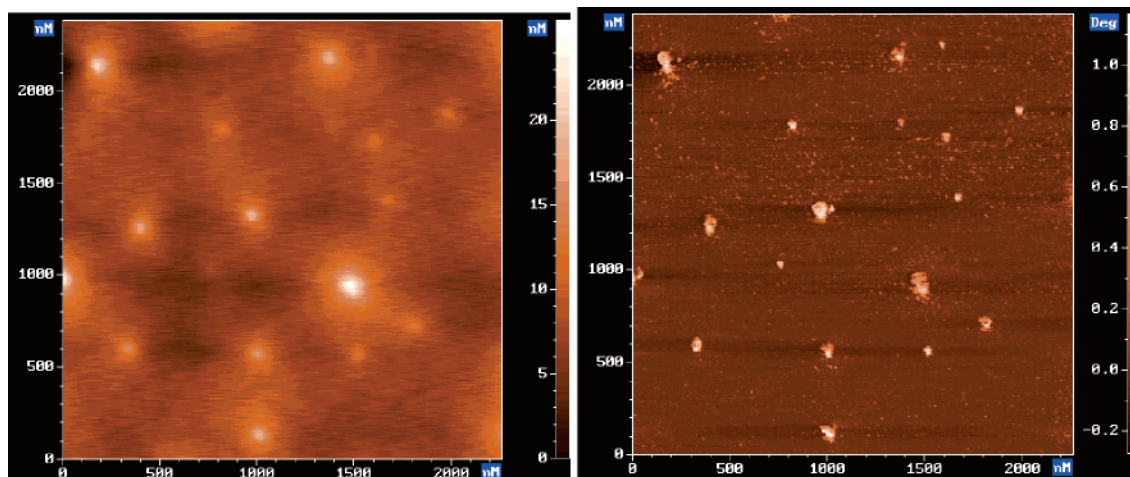


Figure 9. (a, left) AFM height picture of the film in Figure 8a after annealing further at 150 °C. (b, right) AFM phase picture of the film in (a).

melting temperature of PCL and the glass transition temperature of POx. Figure 8b shows the AFM height picture and Figure 8c the phase picture after annealing for 18 h. A ~ 2 nm thick layer was seen to spread from the aggregates onto the top surface. These regions have darker phase contrast, indicating relative softness with respect to the other parts of the top surface. The reproducibility of the AFM pictures was confirmed by taking several pictures in the same area. Spreading of PCL was favored on top of POx because of lower surface energy of PCL compared to POx which minimized the overall interfacial energy of the film. When the film was further annealed at 150 °C, a smooth film having smaller and rounded aggregates were observed as seen in AFM height and phase pictures of parts a and b of Figure 9, respectively. From the chemical structure of the molecule (Scheme 4), the 2 nm thick top PCL layer must have PCL loops sticking out. The expected thickness of such loops for about 3000 g/mol PCL blocks is consistent with the measured value of 2 nm. Because PCL crystallization is hindered in such loops, the top layer is an amorphous PCL layer and has darker phase contrast. Only the larger PCL aggregates show bright phase contrast, an indication of crystallinity in aggregates. As expected, for molecules terminated with amorphous polymers of PSt (polymer 8) or POx (polymer 9), PCL crystallization was hindered and the formation of layered structures was prevented.

Conclusions

Poly(*p*-phenylenes) having grafted PCL side groups show well-defined layered morphologies in thin films. Such layered morphology is formed because of the tendency of semicrystalline PCL in thin films to crystallize such that alternating amorphous/crystal layers orient parallel to the solid substrate. To obtain such morphology, we took advantage of not only the effect of confinement (film thickness) on orientation (flat-on lamellae) but also the strong interaction of $-OH$ groups at the end of PCL blocks with the hydroxylated SiO_2 substrate. These strong interactions also ensure the stability of the resulting morphology. Alternating layers of flat-on PCL lamellae and rigid poly(*p*-phenylene) backbones have been identified for polymer 5 (Scheme 2) by differences in the microstructures of the layers. The smoothness of the layers containing poly(*p*-phenylene) backbones indicates the planarity of the phenyl

rings of the backbone. This observation is important because electronic structure of conjugated polymers is closely related to the backbone conformation, and the planarity of chains has been reported to increase conductivity. Such layering was not observed when amorphous polymers (PSt or POx) were grafted to the rigid poly(phenylene) backbone. When PCL crystallization was hindered by attaching PS or POx to the end of PCL, the layered morphology was also not formed. These observations clearly show that crystallization of the side groups in well-defined layers induces planarity of the phenyl rings in the backbone and a layered morphology in thin films.

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