Stereocomplex Formation of Densely Grafted Brush Polymers

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 Supporting Information

ABSTRACT: In this report, we explore the capability of macromolecules to interdigitate into densely grafted molecular brush copolymers. We demonstrate that by using the tendency for stereocomplexation between poly(L-lactide) and poly(D-lactide) as a driving force complementary linear polymers and brush copolymers can form a stereocomplex. However, stereocomplex formation between complementary brush copolymers is restricted and only partially observed when the side chains are of a critical molecular weight.


T_m=129-150°C
Stereocomplex Formation

T_m=137-141°C

T_m=137-141°C

T_m=183-212°C

T_{m1}=136-139°C
T_{m2}=191-200°C
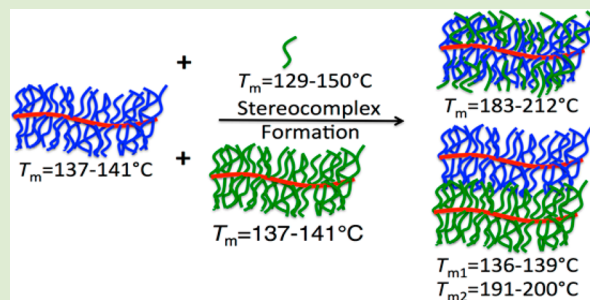
Molecular brush copolymers are constructed from polymeric side chains that are covalently linked to a common polymer backbone.[1−3] The steric interactions of the side chains play an important role in their physical properties, often enforcing a rigid and extended backbone[4] with a low capability for chain entanglement.[5] The minimal degree of chain entanglement enables their ability to self-assemble very rapidly compared to their linear analogues.[6] These properties have inspired potential applications for these polymers such as photonic paint,[7−10] drug delivery systems,[11,12] and for various nanostructures.[13−15]

We have been interested in the synthesis of molecular brush copolymers using a grafting-through approach that ensures quantitative grafting density along the polymer main chain. Because of the high density of the grafted polymers, they have shown to restrict the diffusion of polymers to their backbone while being permeable for small molecules.[16] This resistance to allowing macromolecules to diffuse through them has, to the best of our knowledge, only been studied when there was not a strong driving force for the polymer to interact with the brush polymer side chains.

The stereoisomers poly-L-lactide (PLLA) and poly-D-lactide (PDLA) have been reported to show a strong tendency to interact with each other to form stereocomplexes,[17,18] even with certain topological restraints such as in cyclic polymers.[19] Stereocomplexes made from polylactides have a variety of uses including biodegradable films,[20] fibers,[21,22] hydrogels,[23,24] and nucleation agents.[25,26] Sparsely grafted polymers have also shown stereocomplex formation,[27] as well as graft polymers with oligomeric side chains.[28] In this report, we investigated if the propensity for stereocomplexation between PLLA and PDLA could act as an adequately strong driving force to allow macromolecules, both linear and brush, to diffuse through densely grafted brush side chains of various sizes to form the stereocomplexes.

We utilized the macromonomer (MM) approach for the synthesis of the brush polymers, which ensures quantitative grafting density.[3,29−31] The MMs, PLLA and PDLA, were synthesized through modified literature procedures by ring-opening polymerization from a norbornene-based alcohol initiator catalyzed by an N-heterocyclic carbene (Scheme 1).[19,32,33] To study the side-chain size effect on stereocomplex formation, four pairs of PLLA and PDLA MMs were synthesized, with molecular weights ranging from 5.9 to 17.4 × 10^3 g/mol (Table 1). Brush copolymers were subsequently synthesized from each of the MMs via ring-opening metathesis

Scheme 1. General Reaction Scheme for the Synthesis of the Macromonomers (C) from a Norbornene Initiator (A) and Lactide (B) (top) and for the Synthesis of the Brush Copolymer (D) from the Macromonomer (C) (bottom)
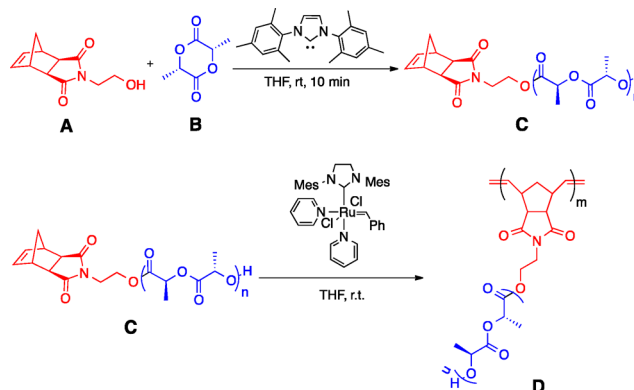
Table 1. Results for the Macromonomers and Brush Copolymers

sample	M_n $(10^3$ g/mol$)^a$	PDI $(M_w/M_n)^b$	(yield)/conversion $(\%)^b$	$[\alpha]^c$	T_m $(°C)^d$	ΔH_m $(J/g)^d$
$_L$MM-1	5.9	1.18	(63)	−133	129	16
$_L$MM-2	8.6	1.16	(72)	−140	148	34
$_L$MM-3	11.7	1.24	(46)	−140	150	31
$_L$MM-4	13.0	1.11	(63)	−132	144	42
$_D$MM-1	6.6	1.17	(49)	+126	128	20
$_D$MM-2	8.6	1.15	(82)	+142	149	36
$_D$MM-3	10.6	1.08	(63)	+139	149	32
$_D$MM-4	17.4	1.05	(27)	+153	149	43
$_L$Br-1	1.07×10^3	1.02	100	−139	-	-
$_L$Br-2	1.22×10^3	1.06	91	−146	139	24
$_L$Br-3	1.53×10^3	1.03	92	−147	141	13
$_L$Br-4	2.15×10^3	1.05	77	−135	137	14
$_D$Br-1	1.19×10^3	1.03	100	+121	-	-
$_D$Br-2	1.18×10^3	1.04	94	+143	138	23
$_D$Br-3	1.07×10^3	1.16	89	+140	139	25
$_D$Br-4	2.55×10^3	1.03	78	+156	139	18

^{a}Measured by NMR for MMs and GPC for brush polymers. ^{b}Measured by GPC. ^{c}Measured with a polarimeter ($c = 3$ mg/mL, CHCl$_3$). ^{d}Measured by DSC.

polymerization (ROMP) using a Ruthenium-based third-generation initiator (Scheme 1). The brush polymers were synthesized with a degree of polymerization through the main chain from 100 to 200 MM units, yielding brush copolymers with molecular weights ranging from 1.07 to 2.55×10^6 g/mol (Table 1).

Organocatalyzed polymerization of the enantiomeric lactide monomers produces polylactide MMs that are highly isotactic.[19,34,35] The brush copolymers derived from these MMs exhibit optical rotations similar to their respective MMs, while showing consistently lower melting temperatures and heats of melting than their corresponding MMs (Table 1). In fact, differential scanning calorimetry (DSC) analysis did not reveal a melting transition temperature for the brush polymers with the shortest side chains. We attribute this to the confinement of the side chains by the brush copolymer architecture, which inhibits their mobility and capability for crystallization.

Blends of the MMs were formed by pairing similar molecular weight stereoisomers in equal weight ratios. The mixtures were dissolved in dichloromethane, and stereocomplexation was achieved via controlled evaporation. Blends of the MMs with their complementary brush polymer as well as blends of brush/brush copolymers were prepared in an analogous manner (Table 2). After annealing, the samples were dried under vacuum and analyzed by DSC.

As expected, the MM blends (**A1**−**A4**) formed distinct stereocomplexes, evidenced by the DSC analysis that showed higher melting temperatures (192−213 °C) and heats of melting (37−46 J/g) (Table 2) than their pristine counterparts. The MM/brush copolymer blends (**B1**−**B8**) also formed distinct stereocomplexes with melting temperatures similar to the corresponding MM blends, albeit with lower heats of melting. Therefore, we infer that the MMs are able to sufficiently diffuse into the brush copolymer to interact with the side chains to form a stereocomplex. Interestingly, although the highest molecular weight MM/brush blends (**B4**, **B8**) showed stereocomplex formation, they also showed a smaller peak corresponding to the nonstereocomplexed polylactides, suggesting nonquantitative stereocomplex formation.

Table 2. DSC Results for the Polymer Blends

blend	P$_L$LA	P$_D$LA	T_m $(°C)^a$	ΔH_m $(J/g)^a$
A1	$_L$MM-1	$_D$MM-1	192	37
A2	$_L$MM-2	$_D$MM-2	212	46
A3	$_L$MM-3	$_D$MM-3	213	39
A4	$_L$MM-4	$_D$MM-4	202	43
B1	$_L$MM-1	$_D$Br-1	183	25
B2	$_L$MM-2	$_D$Br-2	211	31
B3	$_L$MM-3	$_D$Br-3	212	27
B4	$_L$MM-4	$_D$Br-4	205, 141	24, 1.9
B5	$_L$Br-1	$_D$MM-1	192	29
B6	$_L$Br-2	$_D$MM-2	210	27
B7	$_L$Br-3	$_D$MM-3	212	17
B8	$_L$Br-4	$_D$MM-4	204, 143	21, 5.8
C1	$_L$Br-1	$_D$Br-1	-	-
C2	$_L$Br-2	$_D$Br-2	137	4.3
C3	$_L$Br-3	$_D$Br-3	138	6.0
C4	$_L$Br-4	$_D$Br-4	139, 192	12, 6.5
D1^b	$_L$Br-2	$_D$Br-2	136, 200	18, 5.1
D2^b	$_L$Br-3	$_D$Br-3	136, 196	18, 5.9
D3^b	$_L$Br-4	$_D$Br-4	138, 191	23, 5.5

^{a}Measured by DSC. ^{b}Blends heated at 150 °C for 4 days after controlled evaporation.

The brush/brush polymer blends (**C1**−**C4**) showed varied properties. The blend with the shortest side chains (**C1**) did not show any transition peak in its DSC traces, like its parent brush polymers, while the two brush blends with the intermediate length side chains (**C2**−**C3**) showed melting temperatures close to their parent brushes but with lower heats of melting. The brush blend with the longest side chains (**C4**) showed two transition peaks, corresponding to a major melting transition temperature (138.5 °C) and a weaker melting transition temperature at 191.8 °C, indicative of some stereocomplex formation. We believe that longer side chains provide more conformational freedom, as the longer side chains can extend further from the sterically congested core brush off the main chain (Figure 1a). This may allow for some interaction between brush copolymers at the chain end of the side chains, enabling some stereocomplex formation (Figure
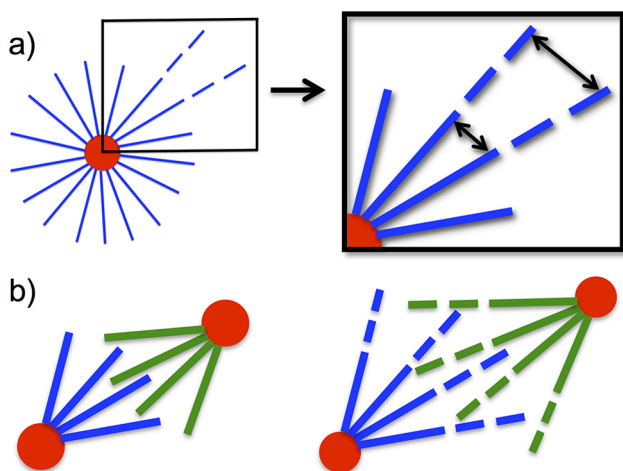
Figure 1. Schematics showing that (a) longer side chains (where dashed lines represent extended side chain lengths) will have more conformational freedom further from the brush copolymer core which can result in (b) a potentially bigger overlap of side chains to enable stereocomplex formation.

1b). As previously noted, the brush polymers tend to have lower melting transition temperature than their corresponding MMs or blends involving MMs (both MM/MM and MM/brush blends). This leads us to conjecture that this is a result from true brush/brush interactions.

To investigate if we could thermally induce stereocomplexation, we thermally annealed the three biggest blends under vacuum at 150 °C for 4 days after controlled evaporation (**D1**−**D3**, Table 2). The sample with the longest side chain (**D3**) did not show an increase in stereocomplexation, but instead the ratio between the heats of melting from before and after thermal annealing became skewed toward the nonstereocomplexed transition temperature. Meanwhile, the other two samples (**D1**−**D2**) started revealing evidence of some stereocomplex formation. This suggests that with heating the benefit of the stereocomplex forming interactions can overcome the tendency of these brush copolymers to evade entangling, although only to a limited extent.

A brush statistical copolymer sample was also synthesized via ROMP by polymerizing a mixture of the lowest molecular weight MM pair in DCM yielding a polymer with M_n of 4.87×10^5 g/mol (PDI = 1.09). This polymer exhibited a melting transition temperature (175.8 °C) and heat of melting (12 J/g) that suggested a weak stereocomplex formation, while the analogous brush/brush blend (**C1**) had not shown any stereocomplex formation. Since the other brush/brush blends did not show much stereocomplex formation either, we hypothesize that the intramolecular interactions between the PLLA and PDLA side chains, in the brush statistical copolymer, must play an important role in the stereocomplex properties of the brush statistical copolymer sample.

In conclusion, we have showed that when there is an adequately strong driving force brush polymers can allow for diffusion of macromolecules into their side chains and have found that at sufficient distance from the brush polymer main chain some entanglement may begin to take place at the edges of the side chains. These results add to the intriguing properties of brush polymers and may aid in extending the scope of applications for these macromolecules.

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Notes

The authors declare no competing financial interest.

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