Enhanced Melt Stability of Star-Shaped Stereocomplexes As Compared with Linear Stereocomplexes

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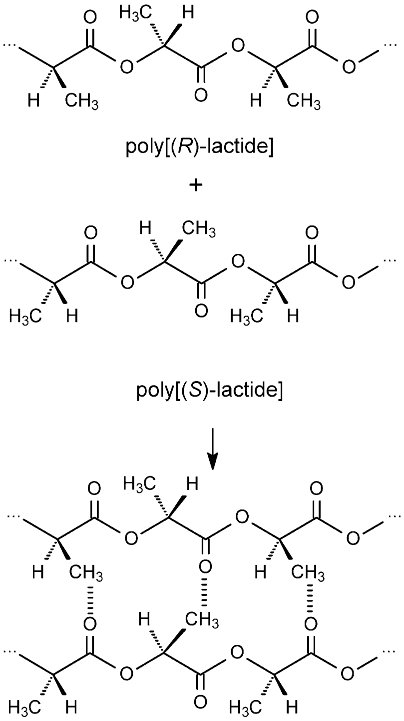
Introduction. Macromolecules composed of repeating units with complementary attracting sites can form intermolecular complexes. Typical examples are provided by natural macromolecules such as polysaccharides, polypeptides, or nucleic acids. Synthetic polymer chemistry taking a lesson from biology developed a variety of macro- or supramolecular systems in which complementary interactions give rise to hierarchical structural order, resulting in macromolecular materials very often with new, exceptional properties.[1−8] Macromolecules of identical chemical composition but different stereochemical configuration of repeating units, either enantiomeric or diastereomeric, are also able to form intermolecular complexes—called stereocomplexes.[9] Macromolecular stereocomplexes usually form in the solid state crystalline structures melting at higher temperature (T_m) than that of the homochiral components alone. This is also the case of the poly[(*R*)-lactide]/poly[(*S*)-lactide] stereocomplex.[10−24] Unfortunately, for linear high molar mass ($M_n \geq 10^5$) polylactides neither is there enough memory preserved in preformed stereocomplexes to survive melting nor is there enough specificity in formation of stereocomplexes in the poly[(*R*)-lactide]/poly[(*S*)-lactide] melt. Eventually, a mixture composed of homochiral crystallites and stereocomplex crystallites is formed. Here we show that in the instance of star-shaped high molar mass ($M_n \geq 10^5$) enantiomeric polylactides formation or re-formation of the poly[(*R*)-lactide]/poly[(*S*)-lactide] stereocomplex in the melt is complete and perfectly reversible due to the hardlock-type interactions.

Results and Discussion. Polylactides, (bio)degradable and biocompatible polymers prepared from renewable resources, have recently become an industrial reality.[25,26] One of their deficiencies is a relatively low melting temperature. Indeed, T_m of the high molar mass linear poly[(*R*)-lactide] ((*R*)-PLA) or poly[(*S*)-lactide] ((*S*)-PLA) is only ≤180 °C, whereas (*R*)-PLA/(*S*)-PLA stereocomplexes have T_m reaching 230 °C.[10−14]

Thus, successful preparation of higher melting, stable polymeric stereocomplexes based on the high molar mass polylactides is of self-explanatory importance. The stereocomplexes of linear, high molar masses (*R*)-PLA and (*S*)-PLA are known, not to be able to re-form back from the melt in any reasonable time.[14] The ability of restoring stereocomplexes decreases with increasing molar mass. It has particularly been observed that for macromolecules with a molar mass (M_n) above ≈10^4 crystallites of homochiral components coexist with crystallites of the stereocomplex when pure stereocomplexes are melted and then crystallized once again,[14] although for macromolecules with M_n below 10^4 the homochiral crystallites may be absent. The actual proportions of both crystalline structures depend on the experimental conditions of the melting−cooling runs and on further annealing. Nevertheless, for the higher molar mass stereocomplexes, according to the existing reports and in agreement with our own experience, there is "always" present (at least for any time of annealing used until now) a certain portion of the lower melting homochiral crystallites.

Scheme 1. Stereocomplex Formation from the Linear Poly[(*R*)-lactide] and Poly[(*S*)-lactide][a]



[a] The attracting, complementary interactions result from a weak hydrogen bonding.[19]

For the present study linear (*R*)-PLA and (*S*)-PLA were prepared by separate polymerizations of the corresponding (*R*,*R*)- and (*S*,*S*)-lactide monomers [(*R*,*R*)-LA and (*S*,*S*)-LA] with a tin(II) 2-ethylhexanoate/1-butanol catalytic/initiating system.[27] The ^{1}H NMR homonuclear decoupled spectra[21,22,24] recorded for these polymers confirmed their enatiomeric purity. Indeed, only one perfectly symmetrical singlet was observed from $-[C(O)C\mathbf{H}(CH_3)O]_n-$ protons at 5.16 ppm δ ($CDCl_3$ solvent, 25 °C), indicating homochirality in both (*R*)-PLA and (*S*)-PLA. Stereocomplexes were prepared from equimolar mixtures of (*R*)-PLA and (*S*)-PLA of similar number-average molar masses. Solutions of the enantiomeric polymers in CH_2Cl_2 solvent were mixed, and stereocomplexes were carefully precipitated into methanol. Separated, washed with methanol, and dried stereocomplexes were analyzed by differential scanning calorimetry (DSC). Parts a and b of Figure 2 show DSC traces of stereocomplexes formed from linear macromolecules with M_n ≈10^4 and ≈10^5, respectively. Both featured only one endothermic peak in the first run at 226 and 228 °C, respectively. However, after being melted for 2 min at 240 °C, i.e., 12−14 °C above T_m, the second runs have shown that the original samples, consisting exclusively of stereocomplexes, retain stereocomplexes after second melting only when M_n ≈10^4. The sample with M_n ≈10^5 shows, however, in the second thermal run two peaks, one at 180 °C and the second at 220 °C, indicating formation of a certain fraction of homochiral, lower melting crystallites. However, it is known that in order to obtain

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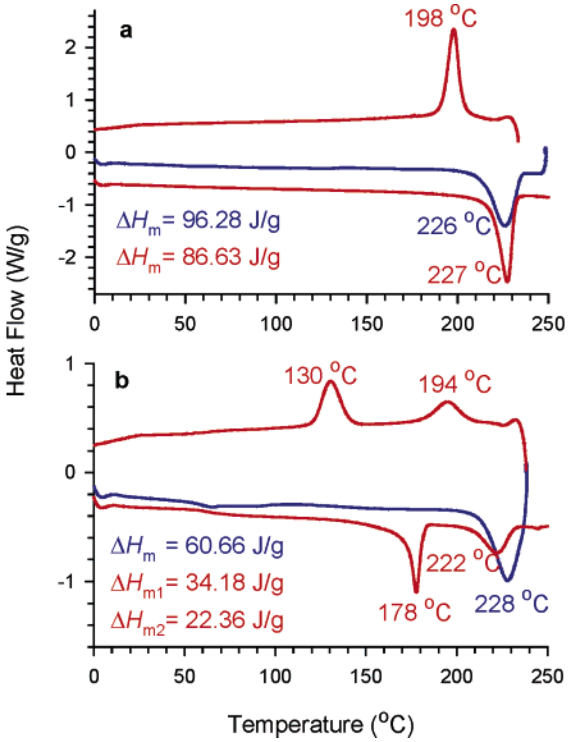


Figure 1. DSC thermograms of stereocomplexes prepared from equimolar solutions of linear (*R*)-PLA and (*S*)-PLA: (a) enantiomeric polymers with $M_n = 9700$ ($M_w/M_n = 1.15$) and $M_n = 10\,300$ ($M_w/M_n = 1.13$); (b) enantiomeric polymers with $M_n = 81\,000$ ($M_w/M_n = 1.31$) and $M_n = 85\,000$ ($M_w/M_n = 1.34$). After the first runs (dark blue traces) samples were melted for 2 min at 240 °C, and after cooling down heating was applied again (red traces). Rates of heating and cooling were equal to 10 °C min^{-1}.

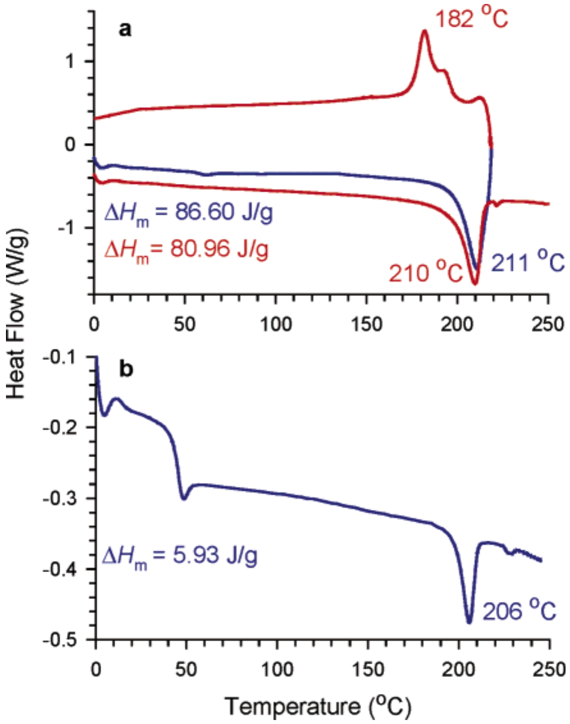


Figure 2. DSC thermograms of stereocomplexes prepared from equimolar mixtures of star-shaped 13-arms (*R*)-PLA and (*S*)-PLA with $M_n = 125\,000$ ($M_w/M_n = 1.21$). (a) By precipitation from solution. After first run (dark blue trace) samples were melted for 2 min at 220 °C (10 °C above T_m), and after cooling down heating was applied again (red traces). (b) By melting. Melted and blended at 220 °C for 30 min and then annealed at 180 °C for 24 h. Rates of heating and cooling were equal to 10 °C min^{-1}.

materials with useful physical properties the M_n of polylactides at least equal to 5×10^4 is required.[15]

When we attempted forming stereocomplexes directly by melting together of linear (*R*)-PLA and (*S*)-PLA with $M_n \approx 10^5$, then after thorough mixing of the melt of a sample with $M_n \approx 10^5$ two peaks were observed in DSC already in the first run, indicating again that, besides crystalline stereocomplexes, crystallites of homochiral macromolecules are present. It has occurred to us that if in place of linear macromolecules star-shaped and/or highly branched macromolecules are used, then the interaction of *R*- and *S*-macromolecules in the melt could be enhanced. Thus, corresponding 6-, ≈13-, 24-, and 32-arm star-shaped macromolecules were prepared separately from (*R*,*R*)-LA and (*S*,*S*)-LA monomers as described by us elsewhere.[28−30] The multichain star-shaped macromolecules have been prepared with the corresponding tin(II) 2-ethylhexanoate/multifunctional initiating system. The following multihydroxyl initiators were used: dipentaerythitol (6-OH), product of cationic polymerization of 3-hydroxymethyl-3-ethyloxetane containing on average 13-OH groups, dendrimeric polyester on base of trimethylolpropane (TMP) and 2,2-bis(hydroxymethyl)propionic acid—generation 3.0 (24-OH)—and DAB-Am-32, polypropylenimine dotriacontaamine dendrimer—generation 4.0 (32-NH_2).

First we attempted to prepare stereocomplexes by mixing these stars with linear macromolecules of opposite chirality. None of the mixture of stars (having $M_n \geq 10^5$) with linear macromolecules with similar M_n and opposite chirality gave stereocomplexes surviving melting. However, stereocomplexes of star-shaped (*R*)-PLA and (*S*)-PLA macromolecules based on 13 and higher number of −OH or −NH_2 group initiators survived melting, although similar stereocomplexes of stars with smaller number of arms were not stable enough and contained after crystallization from the melt a certain proportion of homochiral crystallites.

The stability of stereocomplexes of 13-, 24-, and 32-arm star-shaped macromolecules in the melt was documented by DSC thermograms. For example, thermograms of 13-arm PLA are shown in Figure 2a, where DSC traces of stereocomplexes based on 13-arm stars, prepared by precipitation from solution are given. In the first run stereocomplexes show only one peak (T_m = 211 °C). Then, after melting at 220 °C the recrystallized sample gave again only one endothermic peak at T_m = 210 °C, indicating the exclusive presence of stereocomplexes. Almost identical thermal behavior was observed for 24- and 32-arm star-shaped polylactide stereocomplexes. In Figure 3 the DSC thermograms for the corresponding stars are compared with that for the 6-arm star sample with similar M_n. The following procedure was used for all samples: after the first run in DSC samples of stereocomplexes were kept at 250 °C for 2 min and then cooled to room temperature for a few seconds, and the DSC traces were recorded again. In all instances except the 6-arm macromolecules, exclusively two peaks appeared in the thermograms: cold crystallization exothermic peak approximately at 75−85 °C and melting peak at 200−205 °C, i.e., in the temperature range characteristic for the stereocomplex. On the other hand, for the 6-arm star-shaped PLA the melting peak of homochiral crystallites additionally appeared at 171 °C. It is important that stereocomplexes made by a direct mixing in the melt at 220 °C, i.e., 50 °C above T_m for (*R*)-PLA and (*S*)-PLA components with the number of PLA arms equal to and higher than 13 show in DSC only one peak of melting, above 200 °C (Figure 2b). The observed T_m of these stereocomplexes of star-shaped macromolecules is lower by ∼20 °C than T_m of similar

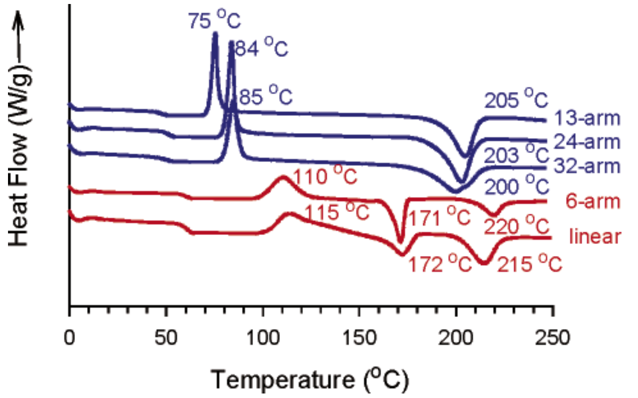


Figure 3. DSC thermograms of stereocomplexes prepared from equimolar mixture of linear and star-shaped 6-, 13-, 24-, and 32-arm (*R*)-PLA and (*S*)-PLA melted at 250 °C and then rapidly quenched to room temperature in order to preserve an amorphous structure. Rate of heating was equal to 10 °C min^{-1}. Molar masses and enthalpies of fusion (ΔH_m) are collected in Table 1.

Table 1. Molar Masses (M_n), Molar Mass Distributions (M_w/M_n), and Enthalpies of Fusion (ΔH_m)

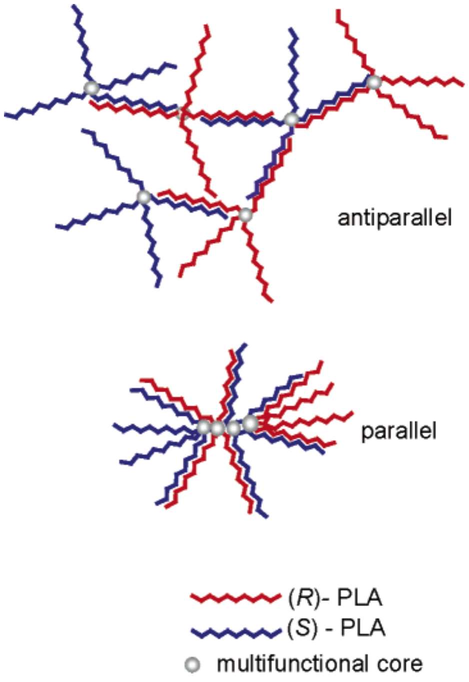
entry	$M_n \times 10^{-3}$ (MALLS)	M_w/M_n	$\Delta H_m{}^a$/J g^{-1}
linear (*S*)	81	1.31	46.9
linear (*R*)	85	1.34	46.2
linear sc	*b*	*b*	30.4; 22.0
6-arm (*S*)	88	1.12	39.7
6-arm (*R*)	86	1.11	35.8
6-arm sc	*b*	*b*	29.7; 18.4
~13-arm (*S*)	125	1.21	38.4
~13-arm (*R*)	125	1.21	36.9
~13-arm sc	*b*	*b*	55.0
24-arm (*S*)	259	1.52	39.6
24-arm (*R*)	224	1.51	39.5
24-arm sc	*b*	*b*	51.2
32-arm (*S*)	377	1.20	47.4
32-arm (*R*)	356	1.21	46.9
32-arm sc	*b*	*b*	47.9

[a] Second run after fast cooling to room temperature from melt (annealed 2 min at 250 °C, 10 °C min^{-1}) linear and star-shaped PLA's and their stereocomplexes (sc). [b] Because of insolubility of the stereocomplexes in common solvents, the molar mass measurements were carried out for their starting, homochiral components only.

stereocomplexes based on linear macromolecules although the thermal conditions have not yet been optimized.The reason for the enhanced stability of the stereocomplexes formed from star-shaped macromolecules is not yet clear to us. At least two explanations could be given. The first comes from an existence of a particular geometry of interaction of branches in star-shaped macromolecules. This interaction may differ from interaction of linear macromolecules. In star-shaped macromolecules arms forming stereocomplexes may predominantly interact in the antiparallel (antisense) manner because of the fixation of the symmetry of PLA arms in the star structure. Parallel interaction of arms of star-shaped structures is more difficult because of the steric hindrance (crowding). This is shown in the simplified picture in Scheme 2.

On the other hand, linear (*R*)- and (*S*)-PLA macromolecules may form both parallel and antiparallel complexes with geometrically equal probability. Thus, the enhanced stability of the stereocomplexes may result from the exclusively antiparallel packing, provided that antiparallelism gives enhancement of stability. Cantow et al. calculated the interaction energies (E_{int}) between the PLA chains (helices) in the unit cell.[16] The result of this calculation gave for the parallelly oriented helices $E_{int} = -119$ kcal mol^{-1} and for the antiparallelly oriented $E_{int} = -111$ kcal mol^{-1}. These data indicate that for both modes of packing the interaction energy is higher than for the enantiomeric crystals (composed of homochiral macromolecules), for which $E_{int} = -96$ kcal mol^{-1}. However, the parallel helices according to these calculations interact stronger than the antiparallel ones, in contrast to what is needed to explain stronger interaction of stars. These calculations, giving a difference of only a few percent between two linear structures, may however not fully apply to the star structures.

Scheme 2. Schematic Structure of Parallel and Antiparallel Stereocomplexes of the Star-Shaped Macromolecules



Another possibility is related to the differences in the way the stereocomplexes are broken down to individual macromolecules in the melt. If we assume that linear stereocomplexes are dismantled starting from one end—like the double helix of DNA—then the further process could proceed by unzipping. One stereocomplex, composed of two macromolecules packed together in either a parallel or an antiparallel manner is not helped by an "entourage" in any way. The two individual helices or their fragments may then combine with their neighbors—individual macromolecules—of the same or opposite helical turn. When, however, a part of a given pair in the stereocomplex is already unzipped, then the unzipped fragments are not having as much freedom as they would have in the linear stereocomplex. Some may form back stereocomplexes with a nearby arms of the opposite chirality Apparently, a certain "density" (i.e., number of arms in the star-shaped macromolecule) is needed for this behavior. This particular "neighboring participation", resembling to a certain extent the mechanism of hardlock fruits linking when put together, which could be more quantitatively described in entropic terms, may thus also or alternatively be responsive for enhanced stability of stereocomplexes made by star-shaped macromolecules.

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Supporting Information Available: Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

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