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and Ring Opening Metathesis Polymerization.
Synthesis, Self-Assembly, Thermodynamics and Dynamics**

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Macromolecular Brushes by Combination of Ring Opening,
and Ring Opening Metathesis Polymerization.
Synthesis, Self-Assembly, Thermodynamics and Dynamics

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ABSTRACT

Statistical and block copolymerization of poly(L-lactide) (PLLA) and poly(ϵ -caprolactone) (PCL) macromonomers having an end-norbornenyl group was performed via ring opening metathesis polymerization, ROMP, to produce the corresponding statistical and block brush copolymers consisting of PLLA and PCL side chains on a polynorbornene, PNBE, backbone. The molecular characteristics of the macromolecular brushes were determined by ¹H-NMR spectroscopy and Size Exclusion Chromatography equipped with various detectors. These complex topologies allow addressing important questions on the physics of semicrystalline polymers. These include the role of (i) a doubly grafted PCL or PLLA chain on

a NBE moiety (in the macromonomers), and the role of (ii) brush architecture on the crystallization behavior and dynamics of block and statistical copolymers. Significant differences were found between the macromonomers and the corresponding brush copolymers at the crystalline lamellar and spherulitic superstructure levels. In the symmetric brush copolymers, two discrete crystalline lamellae corresponding to PLLA and PCL crystals were formed with that of PNBE-PLLA being thicker as compared to PNBE-PCL. Crystallization of the minority component (PCL) was totally suppressed in the brush copolymers (statistical and block) with asymmetric composition (PLLA-PCL 80-20). These results suggest strong restrictions in the crystallization of the block with the lower crystallization temperature (PCL) as well as confinement effects in the double macromonomers resulting in lower crystallization and melting temperatures. At the level of spherulitic superstructure, NBE-PCL and NBE-(PCL)₂ form the usual spherulites with growth rates that are dominated by the segmental dynamics. On the other hand, NBE-PLLA forms normal spherulites at low temperatures that transform to banded spherulites at higher temperatures. NBE-(PLLA)₂ forms banded spherulites over the whole temperature range. A common feature of PLLA macromonomers being the nearly temperature independent growth rates in a range of 30 K reflecting a property of the segmental dynamics. In the brush copolymers with symmetric composition both PLLA (in banded spherulites) and PCL could crystallize. PCL crystallization initiated at the same nucleation sites that crystallized PLLA at higher temperatures.

KEYWORDS: Ring Opening Polymerization (ROP); Ring Opening Metathesis Polymerization (ROMP); norbornene; macromonomers; molecular brushes; copolymerization.

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1. INTRODUCTION

During the last decades there has been a great effort in the synthesis of complex macromolecular architectures, since architectural tailoring is known to result in unanticipated properties.¹⁻³ Recent developments in polymer chemistry have allowed the synthesis of novel macromolecular structures with excellent control over the topology, microstructure and composition.⁴⁻¹² The application of fast and quantitative organic chemistry reactions for the transformation of the macromolecular chains along with the synthesis of new initiators, linking and transfer agents, provided valuable tools for the synthesis of complex macromolecular architectures.^{13,14}

Branched polymers are among the most interesting polymeric structures both from a theoretical and applications point of view.^{15,16} They are composed of a main chain polymer, the backbone, on which one or more side chains, the branches, are chemically connected through covalent bonds.¹⁷⁻²⁰ The synthesis of randomly branched graft copolymers can be accomplished through three general methods: 1) the “grafting onto”, 2) the “grafting from”, and 3) the macromonomer method (or “grafting through”). The “grafting onto” method involves the use of a backbone chain containing functional reactive groups, X, randomly distributed along the chain and branches having reactive chain ends, Y. The coupling reaction between the functional backbone and the chain-end reactive branches lead to the formation of graft copolymers. In the “grafting from” method, active sites are generated randomly along the backbone. These sites are capable of initiating the polymerization of a second monomer, leading to graft copolymers. However, the most commonly used method for the synthesis of graft copolymers is the macromonomer method. Macromonomers are oligomeric or polymeric chains bearing a polymerizable end group.^{21,22} Copolymerization of preformed macromonomers with another monomer produces graft copolymers. Homopolymerization of the macromonomers leads to densely grafted structures, called polymacromonomers or polymer brushes. Polymacromonomers have attracted considerable attention in

recent years as a result of their unique properties originating from their large molecular size, high rigidity and shape-persistence properties.²³⁻²⁵ The latter approach toward brush copolymers is highly desirable, because (1) it does not require orthogonal, noninterfering chemistry for grafting different side chains; (2) the side chain and the graft polymer can be well characterized; and (3) it is the only approach that guarantees complete grafting on every repeating unit. However, the macromonomer approach is exceedingly challenging due to steric hindrance at the propagating polymacromonomer chain-end.

In this work, we report on the synthesis of norbornene-functionalized poly(L-lactide), PLLA (NBE-PLLA), and poly(ϵ -caprolactone), PCL (NBE-PCL), macromonomers from stannous octoate-catalysed ring-opening polymerization, ROP, in the presence of a mono- or di-hydroxylated norbornene derivative as initiator. Subsequent Ring-opening Metathesis Polymerization, ROMP, of these PLLA and PCL macromonomers using the 1st generation ruthenium-based Grubbs catalyst afforded narrowly dispersed brush copolymers with different side chains. ROMP is an efficient method to polymerize macromonomers bearing norbornenyl end groups leading to brush polymers.²⁶⁻²⁹ Moreover, due to the high activity of Ru-based olefin metathesis catalysts, high tolerance of the catalyst to functional groups, and its living characteristics, ROMP displays advantages and conveniences toward preparing block brush copolymers. It allows fast polymerization with high macromonomer conversion, facile incorporation of a variety of functional polymers into molecular brush frameworks, and precise control over the macromolecular architecture, by controlling the lengths and structures of backbones and side chains independently.^{30,31}

Scheme I: Synthesis of graft copolymers

PCL and PLLA macromonomers bearing norbornene end groups have been prepared in the past either using norbornenyl based functional initiators or by conducting suitable post-polymerization reactions to introduce end-norbornenyl groups. Conventional ROP reactions based on stannous or aluminum catalysts, organocatalytic and coordination polymerization based on half-titanocene complexes were employed for this purpose. These macromonomers were efficiently homopolymerized or copolymerized with norbornene to afford polymacromonomers or graft copolymers, respectively. In the present study, PLLA and PCL macromonomers are combined in order to prepare two different series of brushes including brush block and brush statistical copolymers (Scheme I).³²⁻³⁹ Both block and statistical graft copolymers are composed of two semicrystalline polymers with very different crystallization/melting temperatures and rates of crystallization.^{40,41} Although a lower degree of crystallinity is generally anticipated in these complex

architectures, there exist several important issues regarding the crystallization behavior. In particular, how double grafting at the macromonomer level with PCL and PLLA chains affect the crystallization behavior at the lamellar and spherulitic length scales? Are PCL and PLLA both able to crystallize in brush block copolymers and brush statistical copolymers, and if so, what is the mechanism? How the segmental dynamics are influenced by the topology in relation to the corresponding homopolymers? Addressing these issues requires an investigation over different relevant length and time scales. Therefore, we employ a combination of structural, thermodynamic, and dynamic probes: X-ray diffraction, polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and temperature modulated DSC with dielectric spectroscopy (DS). While DSC and X-ray diffraction provide with the thermodynamic and structural transformations associated with crystallization, DS provides with the segmental dynamics, *i.e.*, the local friction, pertinent to the nucleation and growth of crystals.

2. EXPERIMENTAL SECTION

Materials. All manipulations were performed using high vacuum and/or Schlenk techniques.⁴²⁻⁴⁵ ϵ -caprolactone was dried and vacuum distilled from calcium hydride twice, prior to use. L-lactide was recrystallized in acetone and subsequently dried overnight under vacuum and stored in the glovebox. Stannous octoate [Sn(Oct)₂], [RuCl₂(=CHPh)(PCy₃)₂] (first-generation Grubbs catalyst) and 5-norbornene-2-methanol 98% (mixture of *endo* and *exo*) were purchased from Aldrich and used as received. Toluene was dried over calcium hydride, degassed and distilled to calibrated cylinder containing oligostyryllithium. Dichloromethane was distilled from calcium hydride, dried over molecular sieves (3 Å or 4 Å) and distilled prior to use. Ethyl vinyl ether and methanol were used as received.

Characterization techniques. SEC experiments were carried out using a modular instrument consisting of a Waters Model 510 pump, a Waters Model U6K sample injector, a Waters Model 401 differential

refractometer, and a set of three μ -styragel columns with the following porosities: 10^3 Å, 10^4 Å and 10^5 Å, which are suitable for separation of molecular weights from 200 up to 4,000,000. The columns were housed in an oven thermostatted at 40 °C. THF or CHCl_3 was the carrier solvent at a flow rate of 1 mL/min. The instrument was calibrated with polystyrene standards covering the molecular weight range from 3000 up to 600000. In addition, the SEC model Viskotek TDA 305-040 equipped with UV-visible photometer, light scattering and viscometric detectors, two columns T6000M general mixed org 300×7.8 mm was employed as well. The carrier solvent was THF at 35 °C and in a flow rate of 1 mL/min. ^1H NMR spectra were recorded in chloroform- d at 30 °C with a Varian Unity Plus 300/54 NMR spectrometer. Thermogravimetric analysis, TGA, experiments were carried out using a Q50 Model of TA Instruments employing samples of approximately 10 mg. The heating rate was adjusted to 10 °C/min.

Synthesis of NBE-PCL macromonomer. Macromonomers were synthesized via ROP of CL using 5-norbornene-2-methanol (mixture of isomers) as the initiator and $\text{Sn}(\text{Oct})_2$ as the catalyst. In a typical experiment 10 mL of CL (9×10^{-2} mol) were distilled from CaH_2 into a flame dried 100 mL Schlenk flask equipped with a magnetic stirring bar and degassed via three freeze-pump-thaw cycles. 30 mL of toluene were added under argon atmosphere to the Schlenk flask using a syringe in order to dissolve the monomer. Then, the initiator (0.25 mL, 2×10^{-3} mol) and the catalyst $\text{Sn}(\text{Oct})_2$ (0.2 mL, 6×10^{-4} mol) were introduced to the monomer solution under argon atmosphere, the reaction flask was immersed in a thermostated oil bath at 120 °C and stirred for 24 h. After cooling to room temperature, the crude product precipitated into cold methanol (400 mL). The precipitate was isolated by filtration, washed with methanol and dried in a vacuum oven overnight.

^1H NMR (CDCl_3): δ (ppm) 6.14-5.94 (2H, olefinic protons on the norbornene ring) 4.07-4.05 (m, CH_2OCO on PCL) 3.69-3.62 (m, PCL- CH_2OH) 2.83 (m, CH on the norbornene ring) 2.68 (m, CH on the norbornene

ring) 2.32-2.28 (m, OCOCH₂ on PCL) 1.67-1.60 (m, CH₂ on PCL) 1.42-1.32 (m, CH₂ on PCL) 0.56 (CH₂ on the norbornene ring)

Synthesis of NBE-(PCL)₂ double macromonomer. A similar approach was adopted as previously, except that 5-norbornene-2,3-dimethanol was used as initiator instead of 5-norbornene-2-methanol. Typical quantities for the synthesis are the following: 5-norbornene-2,3-dimethanol 0.32 g, CL 10 ml (9×10^{-2} mol), Sn(Oct)₂ 0.2 mL (6×10^{-4} mol) and toluene 30 mL.

Synthesis of NBE-PLLA macromonomer. An oven dried 100 mL Schlenk flask equipped with a magnetic stir bar was charged with 10 g of recrystallized LLA. The flask was thoroughly degassed to remove traces of water and acetone from the monomer. The desired amount of degassed anhydrous toluene (50 mL) was added via syringe under argon atmosphere to dissolve the monomer. Then, the initiator (0.25 mL, 2×10^{-3} mol) and Sn(Oct)₂ (0.2 mL, 6×10^{-4} mol) were injected to the monomer solution under argon atmosphere and the reaction flask was immersed in a thermostated oil bath at 120 °C. After 24 h, the content was cooled to room temperature and the polymer was precipitated into methanol. The macromonomer was isolated by filtration, washed with methanol and dried in a vacuum oven overnight.

¹H NMR (CDCl₃): δ(ppm) 6.16-5.92 (2H, olefinic protons on the norbornene ring) 5.20-5.13 (m, CH on PLA) 4.39-4.32 (m, -CH₂OC(O)- of NBE group) 2.83 (s, 1H, allylic proton of NBE group) 2.66 (s, 1H, allylic proton of NBE group) 1.60-1.44 (br, -CH₃ of PLA backbone) 1.37-1.24 (m, -CH< and >CHCH₂CH< of NBE group)

Synthesis of NBE-(PLLA)₂ double macromonomer. A similar approach was adopted as previously, except that 5-norbornene-2,3-dimethanol was used as initiator instead of 5-norbornene-2-methanol. Typical quantities for the synthesis are the following: 5-norbornene-2,3-dimethanol 0.2 g, LLA 5.5 g, Sn(Oct)₂ 0.2 mL and toluene 40 mL.

Synthesis of brush block copolymers via ROMP of macromonomers. An oven-dried schlenk flask was charged with the desired amount of macromonomer for the first block and a stir bar. The schlenk was evacuated and backfilled with argon three times. The desired amount of degassed anhydrous dichloromethane (5 mL) was added via a syringe under argon atmosphere to dissolve the macromonomer. A stock solution of Ru catalyst (20 mg, 2.4×10^{-5} mol) in degassed anhydrous CH_2Cl_2 (10 mL) was prepared in a separate Schlenk flask. The macromonomer solution was injected into the catalyst solution. The reaction was allowed to run at room temperature for 4 h. After the first polymerization was completed, the desired amount of second macromonomer was added as a solution in CH_2Cl_2 (5 mL). After 24 h the polymerization was terminated by addition of 1 mL of ethyl vinyl ether and stirred for additional 30 min. The reaction mixture was then poured into excess cold methanol with stirring and the precipitates were isolated by filtration, washed with methanol and dried in a vacuum oven overnight to yield a white solid.

^1H NMR (CDCl_3): δ (ppm) 6.38-5.32 (norbornenyl alkenyl protons) 5.20-5.13 (CH on PLA) 4.35 ($\text{CH}_2\text{OC}(\text{O})$ of NBE group) 4.07-4.05 (CH_2OCO on PCL) 3.64 (CH_2OH) 2.68 (CH of NBE group) 2.32-2.28 (OCOCH_2 on PCL) 1.66-1.33 (CH_3 on PLA and CH_2 on PCL and CH_2 on NBE).

Synthesis of brush statistical copolymers via ROMP of macromonomers. The statistical copolymers, were synthesized using a similar procedure to the block copolymers except that two types of macromonomers were added simultaneously in the same Schlenk flask and stirred to ensure homogeneous mixing before injected into the catalyst solution.

Differential Scanning Calorimetry (DSC). A Q2000 (TA Instruments) was used for thermal analysis with a cooling/heating rate of 5, 10 and 20 K/min at a temperature range from 233 K to 433 K. The instrument was calibrated for best performance at the specific temperature range and heating/cooling rate. The calibration sequence included a baseline calibration for the determination of the time constants and capacitances of the sample and reference sensor using a sapphire standard, an enthalpy and temperature

calibration for the correction of thermal resistance using indium as standard ($\Delta H=28.71$ J/g, $T_m=428.8$ K), and a heat capacity calibration with sapphire standard. Temperature modulated DSC (TMDSC) was made with an amplitude of 1 V and for periods in the range from 20 to 200 s with corresponding heating rates from 10 to 1 K/min.

Polarizing Optical Microscopy (POM). A Zeiss Axioskop 40, equipped with a video camera and a fast frame grabber was used to follow the structural changes of the samples. The samples were prepared between two Linkam glass microscopy slides with a distance of 25 μm maintained by Teflon spacers. A Linkam temperature control unit (THMS600), equipped with a TMS94 temperature programmer, was employed for the temperature-dependent studies. Images were recorded following slow cooling (1 K/min) from the melt. In a second experiment the kinetics of superstructure formation were investigated by performing T-jumps from high temperatures (melting temperature of each sample) to different final crystallization temperatures where the growth of crystals was followed. Subsequently, the system was heated with 1 K/min and the apparent melting temperature of the superstructure was recorded.

X-ray Scattering. Wide angle X-ray (WAXS) measurements were made using Cu $K\alpha$ radiation from a Rigaku MikroMax 007 X-ray generator using Osmic Confocal Max-Flux curved multilayer optics. Diffraction patterns were recorded on a 2D-detector (Mar345 Image Plate) at a sample to detector distance of 35 cm. Samples in the form of fibers were prepared by a mini extruder. Temperature-dependent WAXS measurements were performed by inserting the fibers into glass capillaries (1 nm diameter). The patterns were recorded with a vertical orientation of the filament axis and the beam perpendicular to the filament. The recorded intensity distributions were integrated along the equatorial and meridional axes and are presented as function of the modulus of the scattering vector, $q=(4\pi/\lambda)\sin(2\theta/2)$, where λ (=1.54184 nm) is the wavelength, 2θ is the scattering angle. Scattering data was taken within the temperature range from 303

K to 403 K in 10 K steps using 1800 s equilibration time and 1800 s measurement time for each temperature step.

Dielectric Spectroscopy (DS). The sample cell consisted of two electrodes, 20 mm in diameter and a thickness of 50 μm . Dielectric measurements were made at different temperatures in the range 223 K to 443 K, at atmospheric pressure, and for frequencies in the range from 1×10^{-2} to 1×10^6 Hz using a Novocontrol Alpha frequency analyzer with an active sample head. The complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' is the real and ε'' is the imaginary part, is a function of frequency ω , temperature T , and in general pressure P , $\varepsilon^* = \varepsilon^*(\omega, T, P)$.⁴⁶ In the analysis of the DS spectra we have used the empirical equation of Havriliak and Negami (HN)⁴⁷:

$$\varepsilon_{HN}^*(\omega, T) = \varepsilon_{\infty}(T) + \sum_{k=1}^3 \frac{\Delta\varepsilon_k(T)}{[1 + (i\omega\tau_{HNk}(T))^{m_k}]^{n_k}} + \frac{\sigma_0(T)}{i\varepsilon_f\omega} \quad (1)$$

where $\tau_{HN}(T, P)$ is the characteristic relaxation time, $\Delta\varepsilon(T, P) = \varepsilon_0(T, P) - \varepsilon_{\infty}(T, P)$ is the relaxation strength of the process under investigation, m, n (with limits $0 < m, mn \leq 1$) describe, respectively, the symmetrical and unsymmetrical broadening of the distribution of relaxation times, σ_0 is the dc-conductivity and ε_f is the permittivity of the free space. In the temperature range where two or more relaxation processes contribute to ε^* there are different ways of representing the data. The one followed here, is based on a summation of two (and in some cases there) HN functions ($k=1-3$) and assumes statistical independence in the frequency domain. In the fitting procedure, we have used the ε'' values at every temperature and in some cases the ε' data were also used as a consistency check. From τ_{HN} , the relaxation time at maximum loss, $\tau_{\max}$, is obtained analytically following:

$$\tau_{\max} = \tau_{HN} \cdot \sin^{-1/m} \left(\frac{\pi m}{2(1+n)} \right) \cdot \sin^{1/m} \left(\frac{\pi mn}{2(1+n)} \right) \quad (2)$$

3. RESULTS AND DISCUSSION

Synthesis of single and double macromonomers

α -norbornenyl-PLLA and α -norbornenyl-PCL macromonomers were synthesized by ROP of LLA and CL respectively, employing 5-norbornene-2-methanol as an initiator (Figure 1) in the presence of tin(II) 2-ethylhexanoate, $\text{Sn}(\text{Oct})_2$, as catalyst. $\text{Sn}(\text{Oct})_2$ is one of the most widely used compounds for initiating the ROP of various lactones and lactides.⁴⁸ It is easy to handle and is soluble in common organic solvents. In addition, this catalyst is highly efficient and allows quantitative conversions even at low concentration. Finally, $\text{Sn}(\text{Oct})_2$ has been accepted as a food additive by the U.S. FDA due to its low toxicity. For the double macromonomers 5-norbornene-2,3-dimethanol was used as initiator leading to PCL and PLLA macromolecules, bearing the norbornenyl group at the middle of the polymer chain (Figure 2).

Figure 1. Synthesis of NBE-PLLA and NBE-PCL macromonomers.

Figure 2. Synthesis of NBE-(PLLA)₂ and NBE-(PCL)₂ double macromonomers.

The molecular characteristics of the macromonomers are given in **Table 1**. Products of relatively narrow molecular distribution were obtained in high yields. Deliberately, the reactions were stopped at conversions 80-85% to avoid the unwanted transesterification side reactions, leading to a broadening of the molecular weight distribution and to possible loss of the end-groups. The molecular weight of the macromonomers was determined by NMR spectroscopy comparing the end group signals with those of the main chain. For the PLLA macromonomers the molecular weight was calculated by integration of the methine proton of PLLA (**i**) and the olefinic protons of the norbornene group (a+b) (**Figure S1, Supporting Information Section**). For the PCL macromonomers the methylene protons of PCL (**m**) and the olefinic protons of the norbornene group were used (**Figure S2, Supporting Information Section**). It is obvious that the M_n values by NMR measurements are very close to the stoichiometric values and to the results obtained by SEC. These results provide direct evidence that well-defined low molecular weight macromonomers have been prepared having the desired norbornenyl groups either at the end or at the middle of the polymer chain.

Table 1. Molecular characteristics of a-norbornenyl macromonomers.

Macromonomers	$M_{w,SEC}^b$ (g mol ⁻¹)	M_w/M_n^b	$M_{n,NMR}^c$ (g mol ⁻¹)
NBE-PLLA ^a	5800	1.18	4200
NBE-PCL ^a	11400	1.32	12400
NBE-(PLLA) ₂ ^a	9000	1.17	4270
NBE-(PCL) ₂ ^a	11300	1.13	8500

^a Conditions: $T=120$ °C / solvent: toluene / reaction time: 24 h

^b by SEC in THF, calibrated with linear polystyrene standards

^c by ¹H NMR (300 MHz, solvent: CDCl₃, temperature: 40 °C)

Synthesis of block copolymacromonomers

A series of brush block copolymers with PLLA and PCL side chains and polynorbornene backbone were synthesized by various feed ratios of macromonomers. The ROMP copolymerization was conducted in CH₂Cl₂ solutions at 25 °C via sequential addition of macromonomers (Figure 3). Different copolymers are symbolized by the letter B and the various feed ratios of the macromonomers; for example, sample B20/80 indicates the block copolymacromonomer synthesized using 20% wt of NBE-PLLA and 80% wt of NBE-PCL macromonomers, respectively, as the feed composition.

The synthesis was conducted by the ROMP of the PLLA macromonomers followed by the polymerization of the PCL macromonomers. The order of the macromonomer addition does not seem to play a crucial role in the synthesis of the block brushes, since the reverse order is also efficient. The 1st generation Grubbs catalyst was employed for the polymerization of the norbornene end groups. It is an active, well-defined and rather inexpensive catalyst, suitable for polymerization reactions. The molecular characteristics of the samples are given in Table 2, whereas characteristic SEC traces are shown in Figure 4. It is obvious that both macromonomers are quantitatively consumed during the synthesis. This result indicates that well-defined macromonomers were synthesized, in agreement with the NMR and SEC characterization data, and that the ROMP reaction proceeds in a very well-controlled fashion, free of side events, such as termination or transfer reactions. Samples of relatively narrow molecular weight distribution were obtained in quantitative yields. SEC equipped with multiangle light scattering detector was employed in order to provide real M_w values for the copolymacromonomers. It is evident that the real molecular weight values are higher than those calculated from the conventional SEC using only refractive index detector. This

is reasonable taking into account the hydrodynamic volume of the copolymer brushes as compared to the corresponding linear ones. Furthermore, multiangle light scattering detection revealed the presence of single and symmetric SEC signals of relatively narrow molecular weight distribution, which is an indication that the copolymerization reaction was efficient leading to products of high chemical homogeneity.

The composition of the block copolymers was calculated by ^1H NMR spectroscopy taking into account the integration of signals from methine protons of PLLA at 5.20-5.13 ppm and from the methylene protons of PCL at 4.07-4.05 ppm (Figure 5). The calculated copolymer composition is very close to the stoichiometric one, confirming that the copolymerization proceeds smoothly in a very well-controlled manner. Taking into account the molecular weights of the respective macromonomers and the block copolymacromonomers along with the composition of the final products, the degree of polymerization of the various macromonomers was calculated. It is clear that the degree of polymerization is low, meaning that the final products adopt a star-like structure resembling to miktoarm stars rather than typical elongated cylindrical brushes. This was further verified by AFM measurements showing the presence of more or less spherical structures of small sizes (**Figs. S3, Supporting Information Section**).

Figure 3. Synthesis of block copolymacromonomers through sequential addition of macromonomers.

Table 2. Molecular characteristics of the block copolymacromonomers^a

Sample	$M_{w,theor}$	$M_{w,SEC}^b$	M_w/M_n^b	%w/w PLLA ^c	%w/w PCL ^c	$M_{w,SEC}^d$	M_w/M_n^d
B20/80	95000	51300	1.13	30	70	104250	1.33
B40/60	60000	46800	1.12	55	45	59460	1.34
B50/50	55000	52900	1.19	63	37	52000	1.23
B60/40	60000	47000	1.09	72	28	63800	1.72
B80/20	50000	45200	1.12	87	13	48600	1.06

^a Conditions: T= 25°C / solvent:CH₂Cl₂ / reaction time: 24h total

^b by SEC in CHCl₃, calibrated with linear polystyrene standards

^c by ¹ H NMR spectroscopy (300 MHz, solvent: CDCl₃, temperature: 40 °C)

^d by SEC-MALS in THF

Figure 4. SEC traces of the macromonomers and the block copolymacromonomer B40/60 (in CHCl₃, at 40 °C).

Figure 5. ^1H NMR spectrum of the block copolymacromonomer B50/50 (300 MHz, solvent: CDCl_3 , temperature: 40 $^\circ\text{C}$).

Synthesis of statistical copolymacromonomers

The statistical copolymacromonomers were synthesized by the simultaneous copolymerization of PLLA and PCL macromonomers. The ROMP copolymerization was conducted in CH_2Cl_2 solutions at 25 $^\circ\text{C}$ (Figure 6). Different copolymers are symbolized by the letter S and the various feed ratios of the macromonomers; for example, sample S20/80 indicates the statistical copolymacromonomer synthesized using 20% wt of NBE-PLLA and 80% wt of NBE-PCL macromonomers respectively as the feed composition.

The products were characterized by SEC using both conventional refractive index detection and multiangle light scattering detector and NMR spectroscopy. The molecular characteristic of the samples are

displayed in **Table 3**, whereas representative SEC traces are given in Figure 7. A typical ^1H NMR spectrum of a statistical copolymacromonomer is given in Figure 8. It is obvious that, as in the case of the block copolymacromonomers, the consumption of the macromonomers is quantitative, confirming that macromonomers are well-defined and the copolymerization method is efficient to afford the desired products. The real M_w values, by light scattering detection, are slightly higher than the apparent M_w values by the conventional SEC measurements for reasons explained earlier. The molecular weight distribution is fairly narrow even measured by the most sensitive light scattering detection. All these confirm that well-defined products were obtained through this copolymerization procedure. In addition, the number of PLLA and PCL macromonomers in the copolymer brushes is low, as calculated by the combination of the molecular weights of the macromonomers, the copolymacromonomers and the composition by NMR of the final copolymers. Therefore, there is only an architectural difference between the block and the statistical copolymacromonomers, since both adopt a star-like structure. Representative AFM images for the statistical copolymacromonomers are given in **Figure S4, Supporting Information Section** and confirm this conclusion.

Figure 6. Synthesis of statistical copolymacromonomers.**Table 3. Molecular characteristics of the statistical copolymacromonomers^a**

Sample	$M_{w,theor}$	$M_{w,SEC}^b$	M_w/M_n^b	%w/w PLLA ^c	%w/w PCL ^c	$M_{w,SEC}^d$	M_w/M_n^d
S20/80	85000	66300	1.12	32	67	79900	1.21
S40/60	65000	54700	1.14	53	47	61300	1.09
S50/50	65000	56800	1.15	63	37	59800	1.12
S60/40	85000	53400	1.14	77	23	84100	1.19
S80/20	60000	51000	1.12	88	12	53000	1.12

^a Conditions: temperature: 25 °C/ solvent: CH₂Cl₂ / reaction time: 24 h^b by SEC in CHCl₃, calibrated with linear polystyrene standards^c by ¹H NMR spectroscopy (300 MHz, solvent: CDCl₃, temperature: 40 °C).^d by SEC-MALS in THF

Figure 7. SEC traces of the macromonomers and the statistical copolymacromonomer S50/50. (in CHCl₃, at 40 °C).

Figure 8. ¹H NMR spectrum of the statistical copolymacromonomer S50/50 (300 MHz, solvent: CDCl₃, temperature: 40 °C).

Thermal Properties

The thermal stability of the two types of macromonomers was evaluated by TGA measurements, as shown in **Figure S5** and **Table S1** of the Supporting Information Section. Evidently, PCL is more thermally stable than PLLA.⁴⁹ The peak of the decomposition curve of PCL in differential thermogravimetry is located at 319 °C, compared to that of PLLA at 267 °C. A single decomposition curve was obtained for each macromonomer showing that the degradation process is not complex. In addition, similar decomposition patterns were obtained for the single and the double macromonomers confirming that the position of the norbornenyl group either at the end or at the middle of the polymer chain does not affect greatly the thermal decomposition. The results of the thermal stability of the brush block and brush statistical copolymers are given in **Tables S2** and **S3** respectively, whereas representative TGA thermograms are provided in **Figures S6** and **S7**, **Supporting Information Section**.

A similar decomposition process was observed in both types of brush copolymers, indicating that the decomposition process is independent from the copolymer architecture. In addition, all samples showed a first peak at 268-300 °C corresponding to the decomposition of the PLLA side chains, a second peak at 320-340 °C corresponding to the decomposition of the PCL side chains and finally a decomposition at 420-440 °C attributed to the PNBE backbone, in agreement with the previously mentioned results on the thermal decomposition of the respective macromonomers and reported data from the literature.²⁶ As a result, the decomposition pattern of the brush polymers indicates that each different polymer chain is thermally decomposed separately. The thermal decomposition profiles of all the brush copolymers show higher decomposition temperatures compared to the respective PCL and PLLA macromonomers. The brush copolymers possess an enhanced thermal stability compared to the linear macromonomer counterparts, likely due to the covalent attachment of PCL and PLLA side chains to the thermally stable PNBE backbone.

This enables the study of the thermal/thermodynamic behavior over a broad temperature range for the macromonomers (NBE-PCL, NBE-PLLA) and their respective double macromonomers (NBE-(PCL)₂,

NBE-(PLLA)₂) by differential scanning calorimetry with several cooling/heating rates. The DSC traces from the second cooling and heating scans (with a rate of 5 K/min) are shown in Figure 9 and Figure 10 and the results are summarized in **Table 4**. Evidently, the attachment of an additional chain in both macromonomers results in the reduction of crystallization and melting temperatures. Furthermore, TMDSC traces of NBE-PCL and NBE-(PCL)₂ (**Fig. S8, Supporting Information**) indicate that the glass temperature remains practically unchanged (see the discussion below with respect to the dynamics). It is well established that PLLA can form four crystal phases (α , β , γ and α' the latter being the disordered form of α) and the dual melting peaks in NBE-PLLA reflect separate melting of the α' crystal phase (higher melting peak, T_{m2}) and of the α crystal phase (lower peak peak, T_{m1}) that coexist at lower temperatures.^{50,51} In the case of NBE-(PLLA)₂ no exothermic peak can be seen on cooling (revealing slower kinetics of crystallization as compared to NBE-PLLA) whereas on heating an exothermic peak (T_c) due to cold crystallization can be observed prior to the dual melting. The slower kinetics of crystallization in NBE-(PLLA)₂ were confirmed by the POM study (see below). Evidently, dual grafting of PLLA chains at a specified distance by the NBE moiety impedes nucleation and affects the crystallization behavior. Finally, in contrast to NBE-PCL, double grafting increases the glass temperature from 297 K in NBE-PLLA to 310 K in NBE-(PLLA)₂ (see below with respect to the dynamics).

Figure 9. DSC traces of NBE-PCL (solid line) and NBE-(PCL)₂ (dashed line) obtained during cooling (left) and subsequent heating (right). All measurements correspond to the second heating run (rate 5 K/min). Arrows indicate the temperature of phase transformation.

Figure 10. DSC traces of NBE-PLLA (top) and NBE-(PLLA)₂ (bottom) at cooling (left) and heating (right). All measurements correspond to the second heating run (rate 5 K/min). Arrows indicate the temperatures of phase transformation.

As far as the brush statistical (S50-50) and brush block (B50-50) copolymers are concerned, their crystallization and melting behavior bear some similarities (Figures 11). By comparing the DSC traces of the copolymers B50-50, S50-50 with the corresponding macromonomers, we find a reduction in the crystallization and melting temperatures. In addition, in S50-50 different from B50-50, PLLA crystallizes solely on cooling whereas in the latter, PLLA crystallizes via cold crystallization on heating. Strikingly, PLLA crystallization is faster in the statistical copolymer than in the brush block copolymer. We will return to this point later. Hence the heating trace of B50-50 copolymer, has three transitions: (1) a melting peak around 328 K corresponding to the melting of PCL, (2) an exothermic peak at 343 K corresponding to the cold crystallization of PLLA and (3) a single endothermic peak at 413 K corresponding to the melting of

PLLA. The respective comparisons with copolymers of different compositions are presented in **Figs. S9-S12, Supporting Information Section.**

Figure 11. DSC traces at cooling (left) and heating (right) of S50-50 and B50-50 and the corresponding macromonomers. All measurements correspond to the second heating run (rate 5 K/min). The arrows indicate the temperature of phase transformations.

Table 4. Thermodynamics (apparent melting temperature and heat of fusion during melting, ΔH_m , and on cold crystallization, ΔH_{cc}) of NBE-PCL, NBE-(PCL)₂, NBE-PLLA, NBE-(PLLA)₂, B50-50 and S50-50.

	T_{m1} (K)	T_{m2} (K)	T_{cc} (K)	ΔH_{m1} (J/g)	ΔH_{m2} (J/g)	ΔH_{cc} (J/g)
NBE-PCL	325	-	-	72	-	-
NBE-(PCL)₂	321	-	-	70	-	-
NBE-PLLA	413	419	-	23	27	-
NBE-(PLLA)₂	185	398	356	12	18	32
B50-50	325	415	345	30	17	5
S50-50	325	415	-	23	19	-

The results on the degree of crystallinity (obtained from DSC), X_c , of NBE-PCL and NBE-PLLA in the brush block and brush statistical copolymers are depicted in Figure 12 as a function of PLLA composition. The degree of crystallinity is defined as $\Delta H_f/\Delta H_\infty$, where ΔH_f is the heat of fusion and ΔH_∞ the heat of fusion for the ideal crystal (the value 135 J/g was employed for PLLA and 139.5 J/g for PCL, respectively).^{52,53} Two remarks can be made at this point. First, the dependence of X_c on PLLA composition is non-linear. Secondly, at PLLA composition of 80%, PCL is unable to crystallize in both brush block and statistical copolymers. The reason lies in the fact that NBE-PLLA crystallizes at a higher temperature and PLLA crystals restrict the available space for NBE-PCL crystals to grow. This has consequences on the crystallization temperature of PCL in the brush copolymers even with symmetric compositions that is lower

than in the corresponding macromonomer (Fig. 11). Polymer crystallization in confined space is different than in the bulk; the crystallization temperature shifts to lower temperatures. Under severe confinement within nanopores, PCL crystallizes even by a different (homogeneous) nucleation mechanism at higher supercooling ($\Delta T=90$ K).^{54,55}

Figure 12. Dependence of the degree of crystallinity of NBE-PCL (green squares) and NBE-PLLA (red circles) on the block (left) and statistical (right) copolymer composition. The solid lines give the dependence of PLLA (red) and PCL (green) degrees of crystallinity on PLLA content. Dashed lines represent linear dependencies.

Self-assembly

To gain more insight on the effect of restriction/confinement on the crystallization mechanism WAXS and SAXS were performed. Semi-crystalline polymers exhibit order in three length scales: (1) the unit cell (of the order of 1 nm), (2) the lamellar morphology (of the order of 10-50 nm) and (3) the spherulite superstructure (of the order of 1-100 μ m). At the length scale of the unit cell, the structure was examined with WAXS. Bragg reflections of the macromonomers (NBE-PCL, NBE-PLLA) are compared with those

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3 of the double macromonomer (NBE-(PCL)₂) in Figure 13. Both NBE-PLLA and NBE-PCL
4 macromonomers crystallize in orthorhombic unit cells with respective parameters $a=1.05$ nm, $b=0.51$ nm
5 and $c=2.36$ nm, and $a=0.74$ nm, $b=0.49$ nm and $c=1.69$ nm. Secondly, the double macromonomer NBE-
6 (PCL)₂ crystallizes in the same unit cell as NBE-PCL and with parameters that are identical to that of NBE-
7 PCL. Evidently, anchoring two PCL chains on the norbornene moiety within a C-C bond does not disrupt
8 the required spacing for a unit cell to form and grow. In Figure 14 a comparison is made between the block
9 and statistical copolymers for different compositions as well as for the respective macromonomers. Two
10 results can be commented at this point: (1) in the case of 50-50 copolymer, PCL and PLLA crystallize in
11 two different unit cells, and (2) a single unit cell is observed in both B80-20 and S80-20 brush copolymers
12 corresponding to the majority component. The inability of the minority phase (PCL) to crystallize in the
13 B80-20 and S80-20 copolymers is in agreement with the DSC result (Fig. 12). The suppressed crystallization
14 of the minority component in the copolymers can be discussed in view of the restriction brought about by
15 spatial confinement. Crystallization of the PLLA units at higher temperatures restrict the available space for
16 PCL crystallization. In contrast, in block and statistical copolymers of B20-80 and S20-80, PCL is still able
17 to crystallize despite the crystallization of PLLA at higher temperatures (**Fig. S9, Supporting**
18 **Information**). The dependence of the orthorhombic unit cell parameters on composition in the brush block
19 and statistical copolymers is provided in **Table 5**.

Figure 13. WAXS patterns of NBE-PLLA (top), NBE-PCL (middle) and NBE-(PCL)₂ (bottom) recorded at 303 K. Dashed lines give the position and (*hkl*) indices of the Bragg reflections corresponding to an orthorhombic lattice.

Figure 14. WAXS patterns comparison of NBE-PLLA (top), NBE-PCL (bottom), B50-50, B80-20 and S80-20 (middle) recorded at 303 K. Dashed lines give the position and (*hkl*) indices of the Bragg reflections corresponding to an orthorhombic lattice.

Table 5. Parameters of the orthorhombic unit cell of NBE-PLLA and NBE-PCL and their dependence on block and statistical copolymer composition.

	PLLA	PCL	B50-50		B80-20	S80-20
			PNBE- PLLA	PNBE- PCL		
<i>a</i> (nm)	1.05	0.74	1.05	0.74	1.06	1.05
<i>b</i> (nm)	0.51	0.49	0.51	0.49	0.52	0.51
<i>c</i> (nm)	2.36	1.69	2.37	1.7	2.37	2.37

Subsequently, we investigate the effect of the complex topology on the lamellar structure with SAXS.

Figure 15 shows SAXS patterns for the S50-50 copolymer as a function of q , for different temperatures. The first curve, at $T=312$ K, was obtained following isothermal crystallization from the melt. The remaining curves were obtained on subsequent slow heating. It should be mentioned that the featureless shape (absence of any peak) of the pattern taken at $T=400$ K (just above the PLLA melting temperature which is lower due to the much slower heating rate in SAXS) suggests that crystallization in the copolymer occurs from a homogeneously mixed amorphous phase in agreement with earlier reports based on PLLA-PCL diblock copolymers.⁵⁶⁻⁶² At $T=312$ K, S50-50 exhibits two peaks, meaning that two discrete lamellae are formed corresponding to NBE-PCL (at higher q) and NBE-PLLA (at lower q , *i.e.*, thicker lamellae) crystalline/amorphous domains. This is explained by noticing that NBE-PLLA is the first component that crystallizes resulting in a restricted available space for NBE-PCL lamellae to grow (templated crystallization for PCL). At higher temperatures, *i.e.*, above the melting point of NBE-PCL ($T_m=322$ K), only one peak due to NBE-PLLA is observed, which gains in intensity and shifts to lower q , indicating that the lamellae of NBE-PLLA thicken with temperature, a feature shared by many semi-crystalline polymers. The temperature dependence of the inverse lamellar thickness – obtained from the Lorentz corrected spectra- of NBE-PLLA within the brush block and statistical copolymers with compositions B50-50, B80-20, B20-80 and S50-50, respectively, is shown for comparison in Figure 15. In the brush block copolymers the figure depicts PLLA

lamellae that are nearly fixed in size with increasing temperature (they do not thicken appreciably) in contrast to the case of the brush statistical copolymer S50-50 where PLLA lamellae thicken on heating. Evidently, the statistical nature of the copolymers is more beneficial for PLLA lamellae to form that at all temperatures are thicker than in the brush block copolymers. The inverse lamellar thickness for the NBE-PCL lamellae are also indicated in the Figure at a single temperature below PCL melting. The long period of the PCL crystalline lamellar is about half the size of the PLLA lamellar. In the brush statistical copolymers both the PLLA and PCL lamellae are thicker as compared to brush block copolymers.

Figure 15. (Left) SAXS patterns of S50-50 recorded at different temperatures. The vertical arrows indicate the position of NBE-PLLA and NBE-PCL peaks at 312 K. (Right) Temperature dependence of the inverse long period of B50-50, S50-50, B20-80 and B80-20. Dashed vertical lines are guides for the eye for the B20-80 (blue) and B50-50 (red) data. Cyan and green triangles give the lamellar thickness of NBE-PCL within B50-50 and S50-50, respectively.

Superstructure formation

POM was employed to follow the self-assembly at the level of the spherulitic superstructure of NBE-PCL, NBE-PLLA and their double macromonomers. The dependence of the radial growth on time was linear and the growth rates were obtained from the slopes. Figure 16 and Figure 17 depict the spherulitic growth rates as a function of the crystallization temperature for NBE-PLLA, NBE-(PLLA)₂ and NBE-PCL, NBE-(PCL)₂, respectively, along with some representative POM images. The crystal growth rate is generally given by the Lauritzen-Hoffman⁶³ equation:

$$G = G_0 \exp\left(\frac{-E}{R(T_c - T_\infty)}\right) \exp\left(\frac{-K_g}{T_c (T_m^0 - T_c) f}\right) \quad (3)$$

where G_0 is the growth rate constant, E is the activation energy for transport of crystallizing units across the crystal-liquid interface, T_m^0 is the equilibrium melting point, T_c is the crystallization temperature, f is a temperature correction factor for the heat of fusion ($=2T_c/(T_m^0 + T_c)$, T_∞ is the “ideal” glass temperature) and K_g is the nucleation rate constant. Figure 16 includes the growth rate of PLLA from literature (dashed line).^{64,65} The main characteristic being the broad maximum with a discontinuity at around 393 K. It is observed that while both NBE-PLLA and NBE-(PLLA)₂ show a nearly T -independent growth rate (within a temperature range of 25 K) that bears similarities to the PLLA homopolymer, the growth rates in NBE-(PLLA)₂ are about an order of magnitude slower than in NBE-PLLA. Strikingly, NBE-PLLA forms normal spherulites (with the maltese cross) at low temperatures that are transformed to banded spherulites at higher temperatures, whereas NBE-(PLLA)₂ forms banded spherulites over the whole temperature range. Banded spherulites⁶⁶⁻⁶⁸ (*i.e.*, a spherulitic crystalline morphology with extinction rings) result from lamellar twisting due to the imbalanced stresses at opposite fold surfaces.

On the other hand, both NBE-PCL and NBE-(PCL)₂ have growth rates that decrease with temperature, *i.e.*, they are diffusion controlled and form normal spherulites over the whole temperature range.

A common feature of both double macromonomers is that they show slower growth rates with respect to their single macromonomers that suggest higher apparent melting temperatures in agreement with results from POM (Fig. S13, Supporting Information). This can be attributed to the restricted mobility induced by the extra chain attached to the norbornene moiety.

Figure 16. Spherulitic growth rates as a function of temperature for NBE-PLLA and NBE-(PLLA)₂ with POM images obtained under isochronal conditions at different temperatures as indicated. The dashed line corresponds to the growth rate of linear PLLA from literature.

Figure 17. Spherulitic growth rates as a function of temperature for NBE-PCL and NBE-(PCL)₂ with POM images obtained under isochronal conditions at different temperatures as indicated. Dashed lines are guides for the eye.

The equilibrium melting temperature of the PCL and PLLA polymacromonomers was extracted based on the Hoffman-Weeks⁶⁹ equation:

$$T_m = \frac{T_c}{\beta} + \left(1 - \frac{1}{\beta}\right) T_m^0 \quad (4)$$

where β is representative of a thickening factor. This involves plotting the apparent melting temperature of the NBE-PCL, NBE-PLLA and their double macromonomers with respect to the crystallization temperature and determine T_m^0 from the intersection with the $T_m = T_c$ line (**Fig. S13, Supporting Information**). Addition of a second chain to the norbornene backbone reduces the equilibrium melting temperature, with the reduction being stronger for NBE-(PLLA)₂ (in agreement with DSC results). This effect can be attributed to crystal imperfections and/or reduced crystal size in the double macromonomers.

In the brush copolymers – despite the presence of both chains and the decreased degree of crystallinity, PLLA is still able to form spherulites with banded structure. This is shown in the POM images of the brush block copolymer B50-50 taken under isothermal conditions at 393 K (where only PLLA can crystallize) as well as for the brush statistical copolymer in Figure 18. In the latter case images were taken on cooling from the melt with 2 K/min. The images depict spherulites of PLLA at 318 K, whose centers are seeds for PCL nucleation at lower temperatures. Hence, in the brush copolymers with the symmetric composition both PLLA (in banded spherulites) and PCL could crystallize at the interior of PLLA spherulites. PCL crystallization initiated at the same nucleation sites that crystallized PLLA at higher temperatures.

Figure 18. (a) POM image of the brush copolymer B50-50 taken under isothermal conditions at 393 K. Scale bar corresponding to 200 μm is shown. (b-d) POM images of the brush statistical copolymer S50-50 taken during cooling from 433 K with a rate of 2 K/min. The images correspond to the following temperatures: 318 K (b); 309 K (c) and 306 K (d). They depict PCL crystallization originating at the same nucleation centers as for PLLA. The scale bar corresponds to 20 μm.

Dielectric behavior and segmental dynamics

In view of the NBE-PLLA and NBE-(PLLA)₂ growth rates being nearly independent of temperature, measurement of the segmental dynamics and of the associated liquid-to-glass temperature, T_g , are necessary to establish the origin of the observed behavior. In general, the form of $G(T)$ can be controlled either by chain diffusion (associated with the segmental dynamics) or by the nucleation barriers as described in Eq. 3. Dielectric spectroscopy is very sensitive to the local dynamics of polymers bearing a dipole moment. In addition, the temperature dependence of the dielectric permittivity provides a sensitive probe of the temperatures of phase transformations and allows for a comparison with results from DSC. The static dielectric permittivity of polar liquids with short-range interactions between molecules has been the subject of a theory by Kirkwood and later by Fröhlich.⁴⁶ Fröhlich considered an infinite continuum of dielectric permittivity, ϵ_s' , and within this a spherical region containing N_0 elementary dipoles that were treated explicitly. On the basis of these assumptions, the dielectric permittivity can be expressed as:

$$\epsilon_s' = \epsilon_\infty + \frac{1}{3\epsilon_0} Fg \frac{\mu^2}{k_B T} \frac{N_0}{V} \quad (5)$$

Here, $F = \epsilon_s'(\epsilon_\infty + 2)^2 / [2(\epsilon_s' + \epsilon_\infty)]$ is the local field, N/V is the number density of dipoles expressed as $(\rho/M)NA$, where ρ is the mass density and M is the molar mass, μ is the dipole moment, and g is the dipole orientation correlation function. **Fig.S14, Supporting Information** provides the dielectric permittivity and its absolute derivative with respect to temperature, obtained on heating at a frequency of 10⁵ Hz, of NBE-PCL, NBE-(PCL)₂, NBE-PLLA, NBE-(PLLA)₂ as well as in the brush copolymers B50-50 and S50-50 (**Fig. S15, Supporting Information**), respectively. For better comparison, DSC and DS were carried out with the same heating rate (5 K/min). Both techniques are sensitive to the crystallization/melting of the macromonomers as evidenced by the peaks in the heat flow and in the derivative of dielectric permittivity with temperature. In addition, a step in dielectric permittivity describing the glass temperature is evident in the case of NBE-

PLLA and NBE-(PLLA)₂, which is shifted to higher temperatures compared to the respective temperature as seen by DSC (because of the much higher frequency in DS). In the case of NBE-(PLLA)₂ (Fig. S14), four consecutive peaks are observed in the derivative representation at 343 K, 358 K, 378 K and 388 K corresponding to glass temperature, cold crystallization and the melting of the two phases, respectively. There is an excellent agreement with the DSC results, and in addition, we obtain the signature of the segmental dynamics at the DS frequency.

Having established the dielectric signatures of the transition temperatures we explore subsequently the local dynamics of NBE-PCL, NBE-PLLA in comparison to their double macromonomers NBE-(PCL)₂ and NBE-(PLLA)₂. The origin of the different dynamic processes can better be discussed with respect to their temperature dependence. The relaxation times of the different processes for the macromonomers are summarized in Figure 19 and Figure 20 for PCL and PLLA, respectively, in the usual Arrhenius representation. The figures depict two dielectrically active processes (α and β) with different temperature dependencies and a single process obtained from TMDSC (structural relaxation). **Fig. S16, Supporting Information** provides the TMDSC traces of NBE-PLLA and NBE-(PLLA)₂, indicating a single structural relaxation at the respective liquid-to-glass temperature. The most intense dielectrically process (α) has relaxation times at maximum loss that conform to the Vogel-Fulcher-Tammann (VFT) equation:

$$\tau = \tau_o \exp\left(\frac{B}{T - T_o}\right) \quad (6)$$

Here, τ_o , is the relaxation time in the limit of very high temperatures, B , is the activation parameter and, T_o , is the “ideal” glass temperature for the processes. The corresponding VFT parameters for the polymers under study are summarized in **Table 6** below. **Figures S17-S18, Supporting Information** depict the temperature dependence of the HN parameters, $T\Delta\epsilon$, m and mn corresponding to the α -process for the

different polymers. On the other hand, the faster β -process, with shape parameters $m=0.4$ and $mn=1$, is located in the glassy state and has an Arrhenius temperature dependence according to:

$$\tau = \tau_0 \exp\left(\frac{E}{RT}\right) \quad (7)$$

where, E , is the activation energy ($\tau_0=6.0 \times 10^{-12}$ s, $E=12.6$ kJ/mol for NBE-PCL and NBE-(PCL)₂). Evidently, double grafting of PCL chains to the norbornene moiety does not produce any effect at the segmental (α) and local (β) dynamics within the crystalline phase. However, a splitting of the α -process is observed in NBE-(PCL)₂ at the melting region. The observed splitting is reminiscent of a liquid crystal behavior.⁷⁰ Nevertheless, the steep temperature dependence of the segmental dynamics suggests that the crystal growth rates obtained in POM (Fig. 17) are controlled by the diffusion of segments to the crystal front.

On the other hand, NBE-(PLLA)₂ shows slower segmental dynamics than NBE-PLLA with a splitting of the α -process at the melting region. In addition, TM-DCS results on the liquid-to-glass temperature revealed a higher T_g in the former unlike with NBE-(PCL)₂. It is remarkable that the segmental dynamics of both NBE-PLLA and NBE-(PLLA)₂ display only a weak temperature dependence over a temperature range of 100 K that is in accordance with the T -independent growth rates in POM (Figure 16). These results on the segmental dynamics of NBE-PLLA can be compared with the segmental dynamics of a PLLA homopolymer^{71,72} that display a steeper T -dependence. Evidently, the NBE moiety at the chain end affects the segmental dynamics of PLLA due to its low molecular weight. Lastly, the relaxation times, τ_0 , obtained by extrapolation to the limit of very high temperatures for all macromonomers investigated (Table 6) are very long and do not conform to the usual times corresponding to lattice vibrations. This finding may reflect segmental dynamics within the restricted amorphous phase (RAF)^{73,74} present in semi-crystalline polymers.

Overall the results from the DS study confirm the thermodynamic results on the phase transformation temperatures and provide further insight into the dynamics within the amorphous and RAF of the PCL and PLLA single and double macromonomers. The nearly temperature independent spherulitic growth rates obtained in POM for NBE-PLLA (Fig. 16) reflect the weak temperature dependence of the segmental process.

Figure 19. Arrhenius relaxation map of the dynamic processes for NBE-PCL (red) and NBE-(PCL)₂ (black) obtained during cooling. The different processes are as follows: (rhombi): β -process from DS; (circles) α process from DS; (stars) α process from TMDSC. The red and black vertical lines indicate temperatures of NBE-PCL and NBE-(PCL)₂ crystallization, respectively.

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Figure 20. Arrhenius relaxation map of the dynamic processes for NBE-PLLA (red) and NBE-(PLLA)₂ (black) obtained during cooling. The different processes are as follows: (rhombi): β -process; (circles) α process; (stars) α process from TM-DSC. The red and black vertical lines indicate crystallization temperatures of NBE-PLLA and NBE-(PLLA)₂, respectively.

Table 6. VFT parameters of the α -process for the NBE-PCL, NBE-(PCL)₂, NBE-PLLA and NBE-(PLLA)₂.

	NBE-PCL	NBE-(PCL) ₂	NBE-PLLA	NBE-(PLLA) ₂
τ_0 (s)	3×10^{-9}	8×10^{-9}	4×10^{-8}	4×10^{-9}
B (K)	1070 ± 70	1020 ± 30	500 ± 50	750 ± 50
T_0 (K)	171 ± 2	169 ± 1	287 ± 2	266 ± 2

4. CONCLUSION

The synthesis of norbornene-functionalized PLLA and PCL macromonomers is reported from stannous octoate-catalysed ring-opening polymerization, in the presence of a mono- or di-hydroxylated norbornene

derivative as initiator. Subsequent ROMP of these PLLA and PCL macromonomers using the 1st generation ruthenium-based Grubbs catalyst resulted to narrowly dispersed brush copolymers with different side chains. In a second study, these macromonomers were efficiently homopolymerized or copolymerized with norbornene to afford polymacromonomers or graft copolymers, respectively. Herein, PLLA and PCL macromonomers were combined to prepare two different series of brushes including brush block copolymers and brush statistical copolymers. With these complex architectures we addressed points relevant to the physics of semicrystalline polymers than include: the role of (i) a doubly grafted PCL or PLLA chain on a NBE moiety (in the macromonomers), and the role of (ii) dense grafting or brush block copolymer architecture on the crystallization behavior and dynamics. Both structural and dynamics probes revealed important differences from linear PCL and PLLA chains at the different length (and time) scales investigated.

Starting from the smallest length scale, all macromonomers (single and doubly grafted) as well as all brush copolymers exhibited identical unit cells with similar unit cell parameters. Two different unit cells were observed in the case of the symmetric (50-50) brush copolymers. However, a single unit cell, corresponding to the majority component, was observed in the more asymmetric brush block and statistical copolymers (B80-20 and S80-20). Significant differences were found between the two macromonomers with the respective dense brush copolymers at the crystalline lamellar level. Specifically, in the case of the symmetric brush copolymers, two discrete crystalline lamellae were formed with that of PNBE-PLLA being thicker as compared to PNBE-PCL. The PLLA lamellae thicken on heating in the case of the brush statistical copolymer but, strikingly, not in the case of the brush block copolymer. Furthermore, crystallization of the minority component was totally suppressed in brush statistical and block copolymer with asymmetric composition (80-20). These results, in accord with results from the thermodynamics, suggest strong restrictions in the crystallization of the block with the lower crystallization temperature (PCL) as well as

confinement effects in the double macromonomers resulting to lower crystallization temperatures. Finally, important differences appear at the level of spherulitic superstructure between the two macromonomers. NBE-PCL and NBE-(PCL)₂ form the usual spherulites with growth rates that are dominated by segmental dynamics. On the other hand, NBE-PLLA form normal spherulites at low temperatures that transform to banded spherulites at higher temperatures, while NBE-(PLLA)₂ forms banded spherulites over the whole temperature range. A common feature of PLLA macromonomers being the nearly temperature independent growth rates in a range of 30 K.

In the brush statistical and block copolymers with the symmetric composition both PLLA (in banded spherulites) and PCL could crystallize. PCL crystallization initiated at the same nucleation sites that crystallized PLLA at higher temperatures.

To trace the origin of the temperature independent growth rates we followed their thermodynamic properties as well as their structural and the local dynamics. A reduction of crystallization and melting temperature in both double macromonomers and brush block and statistical copolymers was observed, whereas their liquid-to-glass temperatures were affected in a different way; NBE-(PCL)₂ exhibited identical T_g to NBE-PCL, but the T_g in NBE-(PLLA)₂ increased by 13 K relative to NBE-PLLA. In addition, segmental relaxation times in the latter system were nearly independent of temperature over a wide temperature range. This finding is held responsible for the weak temperature dependence of the spherulitic growth rates of NBE-PLLA and NBE-(PLLA)₂.

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SUPPORTING INFORMATION

NMR spectra, AFM images, TGA results together with synthetic details, results from temperature modulated DSC, normal DSC traces, apparent melting temperatures as well as results from Dielectric spectroscopy are provided in the supporting information section.

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TOC Graphic

**Macromolecular Brushes by Combination of Ring Opening and Ring Opening Metathesis
Polymerization. Synthesis, Self-Assembly, Thermodynamics and Dynamics**

Christiana Nikovia, Lazaros Theodoridis, Stelios Alexandris, Panayiotis Bilalis, Nikos Hadjichristidis,

George Floudas, Marinos Pitsikalis