TEMPO Containing Polynorbornene Block Copolymers Prepared via ROMP and Their use as Scaffolds in Sol/Gel-Process

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Summary: Block copolymers ($\mathbf{B_{50}T_{30}}$ and $\mathbf{B_{21}T_{30}}$) containing free nitroxide-radicals with two different chain lengths derived from the monomers (+/−) *endo*,*exo*-bicyclo[2,2,1]-hept-5-ene-2,3-dicarboxylic acid-bis-O-*tert*.-butyl ester (***monomer B***) and (+/−)*endo*,*exo*-bicyclo[2,2,1]-hept-5-ene-2,3-dicarboxylic acid-bis-O-2,2,6,6-piperidinoxyl-ester (***monomer T***) were polymerized via ring opening metathesis polymerization (ROMP). The ter.-butyl-moiety in block B could then be hydrolyzed to obtain amphiphilic block copolymers which were used as scaffolds in subsequent sol/gel-process. The resulting block copolymers were analyzed via small angle X-Ray scattering (SAXS) to investigate microphase separation and the sol/gel products were analyzed by X-Ray Diffraction (XRD) to prove the formation of ordered TiO_2 crystals.

Keywords: block copolymers; ROMP; sol/gel; TEMPO; titanium dioxide

Introduction

2,2,6,6-tetramethyl-piperidinyl-1-oxy (TEMPO) is a stable organic radical, which can be incorporated into polymers, used as polymeric stabilizer, oxidants of alcohols[1] and charge-storage materials[2]. Among these applications, charge-storage materials based on TEMPO-carrying polymers have attracted increased interest[3,4]. Ring-opening metathesis polymerization (ROMP)[5–7] of TEMPO-containing monomers generates polymers in a living polymerization with controlled molecular weights and low polydispersities, as demonstrated by Masuda et al.[3]. We here report on the synthesis of TEMPO containing norbornene based block copolymers (BCP) via ROMP with controlled architecture and their use as scaffolds for the hydrolysis of titanium-species via sol/gel-process to generate nanostructured TiO_2 aiming to improve their charge-storage characteristics.

Experimental Part

Materials and Instruments

Monomers (+/−)*endo*,*exo*-bicyclo[2,2,1]-hept-5-ene-2,3-dicarboxylic acid-bis-O-*tert*-butyl ester (***monomer B***)[8] and (+/−)*endo*,*exo*-bicyclo[2,2,1]-hept-5-ene-2,3-dicarboxylic acid-bis-O-2,2,6,6-piperidinoxyl-ester (***monomer T***)[3] were synthesized according to the procedures from elsewhere. Polymerization reactions were carried out using Grubbs' 3rd generation catalyst (**III**). Other chemicals are purchased from Sigma Aldrich and used as received. Dichloromethane (DCM) for polymerization reactions was dried over calcium hydride (CaH_2) by distillation. Molecular weight and the molecular weight distributions of the generated polymers were characterized by gel permeation chromatography (GPC) on a

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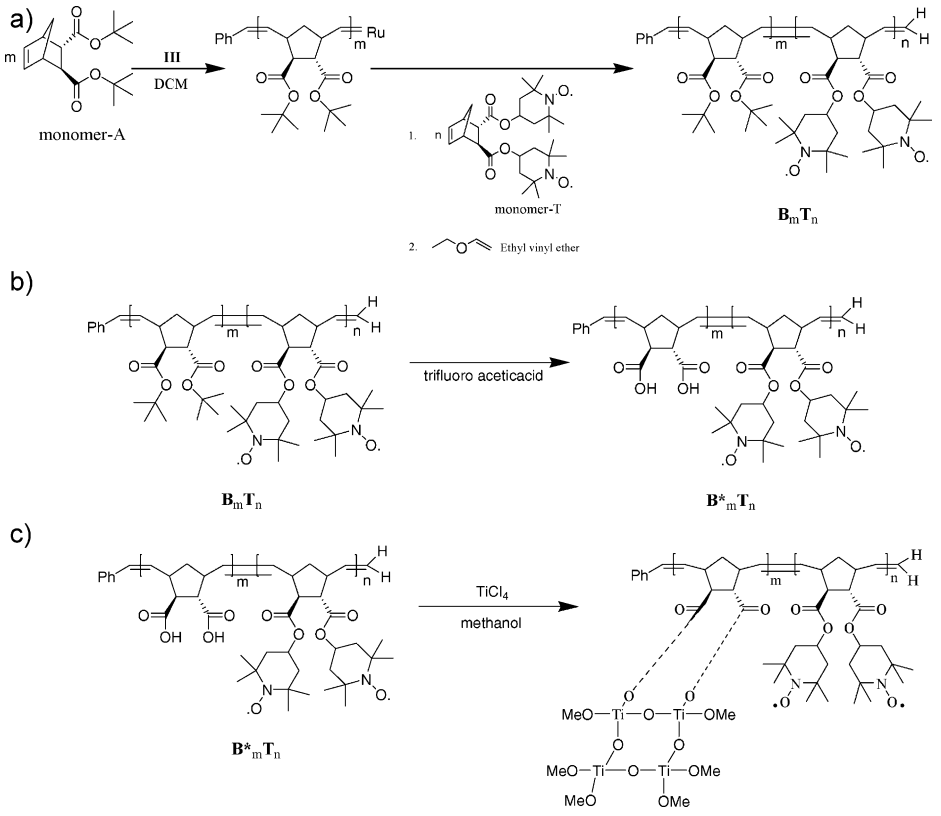
Viskotek GPCMax VE 2001 with THF (stabilizer induced) as solvent and 1.00 ml/min flow rate, column temperature at 35 °C, detector temperature at 35 °C. Calibration was done with polystyrene standards equipped with two TSK-gel columns (H_{HR}-HGuard + GMH_{HR}-N, bead size: 5 μm, Mw(polystyrene) < 4×10^5) and one *ViscoGel HR High Resolution* column (G2500 HR, bead size: 5 μm, Mw(polystyrene) < 20000) with a *TDA 302 Triple Detector Array*.

Polymer Synthesis

The general procedure for polymerization reactions is as followed: A known amount of monomer and initiator were dissolved in 1 ml of freshly distilled DCM separately and injected by a syringe into a vial which was dried and flushed with Argon (Ar) gas and sealed before. The reaction mixture was left to stir in Ar atmosphere during polymerization. After the first monomer was consumed (as monitored via GPC), the second monomer dissolved in DCM was added to the reaction mixture. Polymerization reactions were quenched by adding cold ethyl-vinyl ether (0.5 ml). The synthesized polymers (BCP-$\mathbf{B}_m\mathbf{T}_n$) were isolated via silica column-chromatography (see Scheme 1a).

For the cleavage of the *tert.*-butyl moiety 100 mg of BCP-$\mathbf{B}_m\mathbf{T}_n$ were dissolved in DCM and placed into a round bottom flask which was dried and flushed with Ar before. To the reaction flask trifluoroacetic acid (3 ml) was added and the reaction mixture was left to stir under Ar atmosphere for 24 hours. The reaction mixture was poured into toluene and all solvents were evapo-



Scheme 1.

a) Synthetic pathway to the block copolymer $\mathbf{B}_m\mathbf{T}_n$; b) cleavage and c) sol/gel reaction (III: Grubbs' 3rd generation catalyst).

Table 1.
Result of polymerization reactions.

entry	block copolymer	$M_{n\ calc.}$ (g/mol)	$M_{n\ GPC}$ (g/mol)	PDI[a]	yield (%)
1	BCP-$\mathbf{B}_{50}\mathbf{T}_{30}$	29200	25600	1.3	92
2	BCP- $\mathbf{B}_{21}\mathbf{T}_{30}$	20874	16400	1.3	89
3	BCP- $\mathbf{B}^*_{50}\mathbf{T}_{30}$	—	—	—	94[b]
4	BCP- $\mathbf{B}^*_{21}\mathbf{T}_{30}$	—	—	—	97[b]

[a]determined via GPC with THF as eluent,
[b]yield of isolated polymer after cleavage.

rated using rotary vapor. The crude product was dissolved in a small amount of THF, and the pure product (BCP-$\mathbf{B}^*_m\mathbf{T}_n$) was obtained by precipitating into cold pentane (see Scheme 1b).

Sol/gel reactions were carried out according to the procedure adopted from the literature[9] as followed: BCP-$\mathbf{B}_m\mathbf{T}_n$ type block copolymer or BCP-$\mathbf{B}^*_m\mathbf{T}_n$ type block copolymer was dissolved in methanol (100 eq.) and $TiCl_4$ (1 eq.) was added to the solution. The reaction mixture was left to stir for at least 3 days in order to form the gel. After gelation, the excess of solvent and HCl were evaporated under reduced pressure via a rotary evaporator. The resulting product was heated at 150 °C overnight in order to promote the formation of TiO_2 crystals (see Scheme 1c).

Results and Discussion

The results of the polymerization reactions are shown in Table 1. The polymers were obtained with the projected molecular weight and a narrow molecular weight distribution. As the BCP-$\mathbf{B}^*_m\mathbf{T}_n$ type block copolymers were not directly synthesized they do not have GPC measurements as it is seen in the entries 3 and 4.

Block copolymers were analyzed via SAXS to investigate the microphase structure (see Figure 1). For BCP-$\mathbf{B}_{50}\mathbf{T}_{30}$ a lamellar structure with a domain size of 20 nm was observed. BCP-$\mathbf{B}_{21}\mathbf{T}_{30}$, did not show a regular structure due to the absence of a second order scattering peak, however, a domain size of 15.3 nm was calculated. Due to the absence of scattering peaks in the hydrolyzed block copolymers (BCP-$\mathbf{B}^*_m\mathbf{T}_n$ type) we were unable to determine the microphase structures.

Sol/gel reactions with the block copolymers as scaffolds were conducted in methanol as solvent and $TiCl_4$ as titania precursor in a ratio of 1:100:1 and left to stir for at least three days. After gelation excess solvent and HCl were removed and the product was heated at 150 °C overnight in order to induce the crystallization of TiO_2 particles and also retain the organic component. The resulting samples were analyzed via XRD to prove the presence of

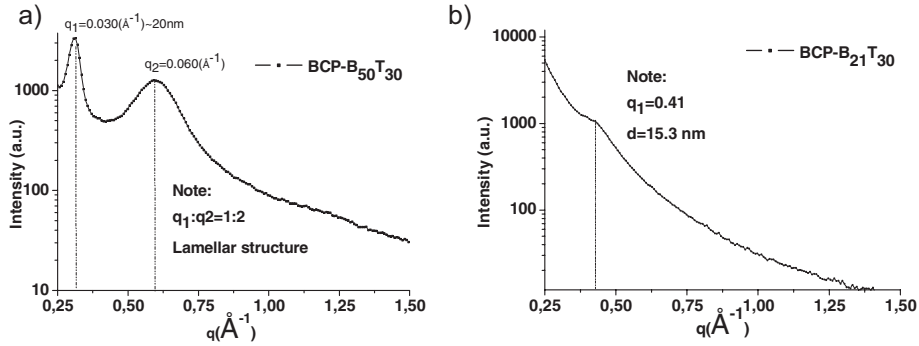


Figure 1.
SAXS results of block copolymers a) BCP-$\mathbf{B}_{50}\mathbf{T}_{30}$ and b) BCP-$\mathbf{B}_{21}\mathbf{T}_{30}$.

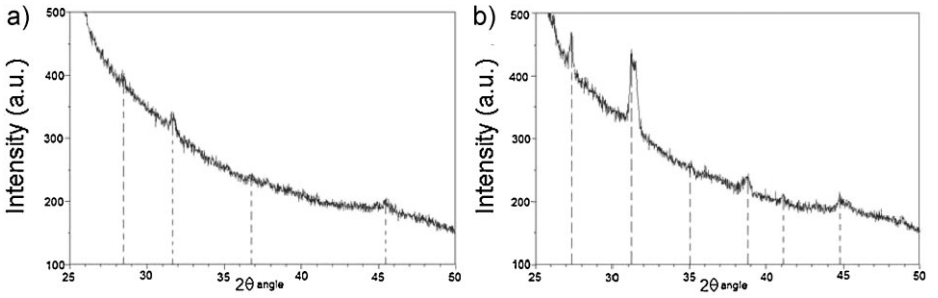


Figure 2.
XRD results of sol/gel products of block copolymers a) BCP-$\mathbf{B}_{50}\mathbf{T}_{30}$ and b) BCP-$\mathbf{B}^{*}{}_{21}\mathbf{T}_{30}$.

TiO_2 crystals. The analysis showed that only BCP-$\mathbf{B}_{50}\mathbf{T}_{30}$ and BCP-$\mathbf{B}^{*}{}_{21}\mathbf{T}_{30}$ had generated TiO_2 crystals (see Figure 2). As the obtained compounds still contained organic component within the sol-gel products an accurate determination of the exact nature of the crystals was not possible. However the XRD graph of BCP-$\mathbf{B}^{*}{}_{21}\mathbf{T}_{30}$ displayed a resemblance to anatase phase TiO_2 according to the literature[9].

Conclusion

We were able to synthesize TEMPO containing norbornene based block copolymers via ROMP with the achievement of projected molecular weight and a low polydispersity by use of Grubbs 3rd-generation catalyst. The resulting block copolymers were analyzed via SAXS displaying a lamellar structure with a domain size of 20 nm for BCP-$\mathbf{B}_{50}\mathbf{T}_{30}$. Furthermore, the synthesized block copolymers were used as scaffolds in a sol/gel reaction generating TiO_2 particles under formation of ordered TiO_2 crystals.

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