

Nanostructure formation in thin films of block copolymers prepared by controlled radical polymerization

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Introduction

A characteristic feature of block copolymer systems is the repulsion between unlike blocks causing microphase separation at mesoscopic length scales.^[1] The size and type of ordering can be controlled varying the molecular weight, chemical structure, molecular architecture and composition of the block copolymers. Understanding and controlling the morphology of a block copolymer is essential for any application and allows for selective surface patterning in thin films.^[2,3]

Here we employ block copolymers based on p-hydroxystyrene. They consist of a block with protected phenolic OH groups and a further block with unprotected phenolic OH groups. The big difference in the polarity of the two blocks causes a strong incompatibility which result in a phase separation even for blocks of low molecular weight. The gradual removal of a protecting group leads to a change of the composition of the block copolymer which should also affect the morphology. This coherence is of great interest especially for phase investigations in thin films (thickness <100 nm). The formation of a defined nanostructure requires usually block copolymers with a very low polydispersity.^[2,3,4] Therefore the synthesis of the block copolymers was carried out applying nitroxide mediated free radical polymerization (NMRP).^[4] Of special interest was the preparation of block copolymers with one Boc protected block since those protecting groups can be removed by simple thermal treatment.

Experimental

Materials. The polymers were prepared via nitroxide mediated controlled radical polymerization as described elsewhere.⁶⁻⁸ The alkoxyamine (Hawker adduct 1) were prepared according to the literature.⁹ Frechet type dendritic azides have been synthesized according the methodology in literature [10,11,12] paper mit Arnulf citieren. Trimethylsilylacetylstyrene (2) was obtain by a Sonogashira reaction following a procedure as described previously [11]. Trimethylsilylacetylstyrene (2) was obtain by a Sonogashira reaction following a procedure as described previously [12]

Instrumentation. Molecular weights and polydispersities of polymer samples were determined by gel permeation chromatography with polystyrene as standard (Polyscience) and chloroform as eluent.

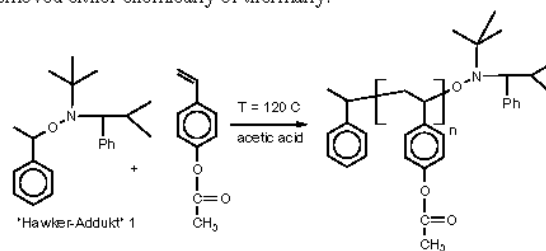
¹H-NMR spectra were measured with a Bruker DRX 500 using 5 mm tubes. As solvent CDCl₃ (99.8 % D) was used.

Synthesis of Poly(4-trimethylsilylacetylstyrene) (3) and its copolymers. Ca. 1 mol-% of initiator and an equimolar amount of nitroxide was added to 4-trimethylsilylacetylstyrene. The solution was degassed by four freeze-pump-thaw cycles, polymerized at 125 °C in nitrogen atmosphere and stopped after different times to obtain kinetic information. Random copolymers of 4-trimethylsilylacetylstyrene and styrene of varying feed compositions were obtained in the same manner. Furthermore, block copolymers were synthesized by sequential monomer addition of 4-trimethylsilylacetylstyrene using poly(4-acetoxystyrene) as macroinitiator and diglyme as a solvent. For the 1,3-dipolar cycloaddition reactions the alkyne group was quantitatively deprotected by adding a twofold excess of tetrabutyl ammonium fluoride. All polymers were purified by repeated precipitation in methanol.

Results and Discussion

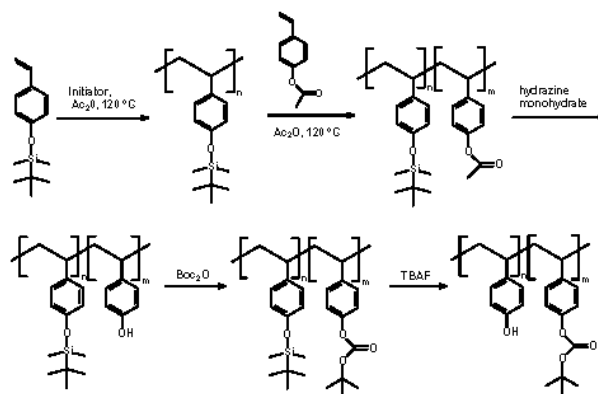
Preparation of BOC protected p-hydroxystyrene block copolymers. Orthogonally protected block copolymers based on p-hydroxystyrene were prepared with high control via NMRP using an alkoxyamine (Hawker-adduct 1) as a unimolecular initiator (Scheme 1). p-Acetoxystyrene (Ac-OSt), p-tert-butoxystyrene (TBU-OSt), p-

tert-butyltrimethylsilyloxystyrene (TBDMs-OSt) and p-tetrahydropyranoxystyrene (THP-OSt) were employed as monomers. The preparation of the block copolymers was accomplished by sequential monomer addition. Selective removal of the acetyl protecting group of the block copolymers via hydrazinolysis resulted in the formation of only partly protected block copolymers. Other protecting groups could be removed either chemically or thermally.



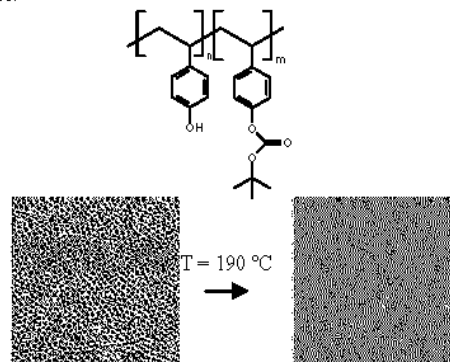
Scheme 1: Synthesis of poly(p-acetoxystyrene) via nitroxide mediated controlled radical polymerization

For the first time, also BOC protected segments could be realized by NMRP using a well defined macroinitiator for subsequent monomer addition. A series of polymer analogous highly selective reactions were necessary to achieve the desired structures without unwanted loss of the BOC protecting groups (Scheme 2). The different block copolymers are phase-separated as indicated by the observation of two T_g 's in DSC measurements.



Scheme 2: Sequence of reactions necessary to achieve BOC containing block copolymers based on p-hydroxystyrene

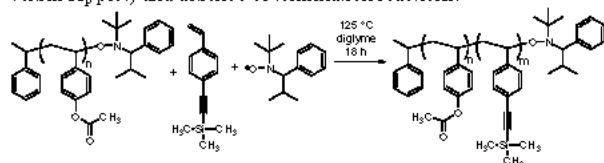
Nanostructured thin film - surface patterning. Thin films of partially protected block copolymer were prepared by spin or dip coating. A well defined nanostructure could be observed as a result of phase separation e.g. cylinders in a matrix oriented perpendicular or parallel to the substrate or particles in a matrix. The nanostructure was controlled by the block copolymer composition, by the film preparation parameters and by the environmental conditions. In the case of the BOC protected segments thermal treatment resulted in a deprotection of the blocked segment and subsequent homopolymer formation with loss of the nanostructure. The nanostructure of the polymeric films determines surface properties e.g. the wetting behavior.



Scheme 3: Loss of nanostructure of BOC containing block copolymer after thermal treatment of a thin film

Poly(4-trimethylsilylacetylstyrene) (3). For further studies, the hydroxystyrene monomers were modified with an alkyne side group giving the chance for further polymer analogous reaction on random and block copolymers. We were able to carry out the nitroxide-mediated radical polymerization keeping high control over molar masses and end groups also with these new monomers.

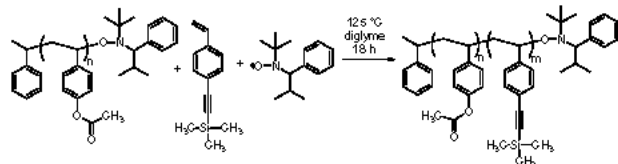
By increasing the amount of trimethylsilylacetylstyrene in random copolymerizations with styrene it was found out that the polydispersity is increasing from 1.17 for polystyrene to 1.86 for poly(4-trimethylsilylacetylstyrene), respectively. Addition of large amounts of nitroxide resulted in a dramatically improvement of polymerization performance with polydispersities ranging from 1.2-1.3. Kinetic experiments of trimethylsilylacetylstyrene in presence of nitroxide (scheme 3) confirmed absence of transfer reactions (M_n versus X_p plot) and absence of termination reactions.



Scheme 4: Polymerization of trimethylsilylacetylstyrene (2) using Hawker-adduct 1

A variety of modification reactions on the resulting polymers was studied using the [2+3] dipolar cycloaddition reactions of alkyne with azides ("click chemistry") which is highly selective and leads to complete conversion at mild reaction conditions.

The synthesis of poly(acetoxystyrene-*b*-trimethylsilylacetylstyrene) as a coil-rod block copolymer precursor was done by using *p*-acetoxystyrene with molecular weight of 13,400 g/mol as macroinitiator and sequential addition of 4-trimethylsilylacetylstyrene in diglyme as a solvent (Scheme 5). The obtained molecular weight and block ratio (1:8 by NMR; 1:5.5 by GPC) was in well agreement with the calculated one (1:6). Surprisingly, the degree of conversion was determined to be very low (25 %). Presumably the rate of polymerization was slowed down by nitroxide addition and the solvent being used (40 wt.-%).



Scheme 5: Synthesis of poly(acetoxystyrene-*b*-trimethylsilylacetylstyrene) as a precursor for coil-rod block copolymers

The deprotection of all kinds of alkyne-containing polymers was most easily and successfully done by tetrabutyl ammonium fluoride (TBAF). After 2 hours stirring at 0°C no residual signals for TMS-group could be detected in $^1\text{H-NMR}$ spectra.

Synthesis of dendronized random copolymers. So far, a [G-1] azide of the Fréchet type could be successfully linked to poly(4-acetylstyrene-*r*-styrene) containing roughly 10 % deprotected alkyne groups. The addition of the dendritic fragment to the polymer backbone has been realized by using the Cu(I)-catalyzed reaction of an azide and the alkyne group. The Click-approach was conducted at room temperature for 48 hours, using 0.1 mol-% $\text{Cu}(\text{PPh}_3)_3\text{Br}$ as catalyst and THF as solvent. The azide moiety was used in twofold excess. The polymer could be efficiently purified by repeated precipitation in a 10:1 mixture of methanol and DMF. The conversion was determined by means of $^1\text{H-NMR}$ to be 89 %.

Conclusions

Orthogonally protected block copolymers of based on *p*-hydroxystyrene were prepared with high control via nitroxide mediated radical polymerization using an alkoxyamine as an unimolecular initiator. Thin films of partially protected block copolymer were prepared by spin or dip coating. A well defined nanostructure could be observed as a result of phase separation e.g. cylinders in a matrix

oriented perpendicular or parallel to the substrate. The nanostructure of the polymeric films can be defined by the block copolymer composition and it determines surface properties and allows further, selective functionalization. The thin films can be designed in a way to allow a patterning based on a thermal or photochemical stimulus.

It could be also shown that trimethylsilylacetylstyrene (2) can be homopolymerized in a controlled manner. Furthermore the synthesis of alkyne-containing block copolymers as coil-rod block copolymer precursors was demonstrated. Subsequent deprotection of alkyne groups was quantitatively achieved by treatment with tetrabutyl ammonium fluoride. Moreover, the Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction gave promising results for the synthesis of dendronized polymers. The phase separation behavior of these products is under investigation.

Acknowledgements

The authors would like to thank the Deutsche Forschungsgemeinschaft (DFG) for financial support.

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