Synthesis of Amylose-*block*-polystyrene Rod−Coil Block Copolymers

Katja Loos and Reimund Stadler*

Makromolekulare Chemie II, Universität Bayreuth, Universitätsstrasse 30, 95440 Bayreuth, Germany

Received July 10, 1997
Revised Manuscript Received September 19, 1997

Introduction. In the present communication we demonstrate the synthesis of a hybrid block copolymer based on the combination of a biopolymer (amylose) with a synthetic block (polystyrene). To obtain such materials, amino-functionalized polymers were modified with maltoheptaose moieties that serve as initiators for the enzymatic polymerization with potato phosphorylase (E.C.2.4.1.1). The length of the amylose block can be varied in a broad range.

Similar materials have already been prepared using a water soluble synthetic polymer.[1] It has been speculated that water solubility is of utmost importance to allow the enzymatic polymerization. As will be shown below, polymerization is also possible with end-functionalized synthetic polymers that are not soluble in the polymerization medium (aqueous buffer). This may expand the number of such hybrid materials,[2] which combine the properties of synthetic polymers and of the natural polymer amylose and therefore could allow the preparation of materials showing improved biocompatibility and biodegradibility.

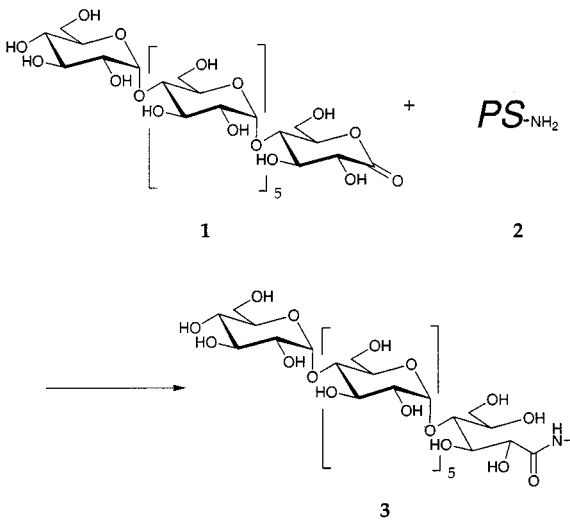
Besides, these synthetic amphiphilic block copolymers might be suitable building blocks for supramolecular assemblies. Supramolecular structures based on block copolymers containing chiral polyisocyanates have already been reported.[3−5] Considering the Kuhn length of amylose (30 nm),[6] the new hybrid materials could also offer some new insights into the behavior of rod−coil systems.

Furthermore, the amylose part of the block copolymers may be functionalized to change the properties of these materials.

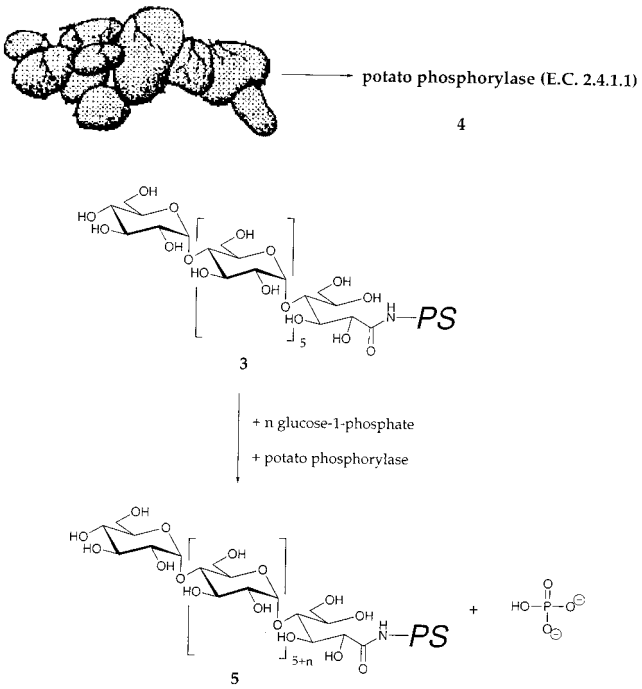
Results and Discussion. Maltoheptaonolactone (**1**) was prepared by acid-catalyzed cleavage of β-cyclodextrin and subsequent oxidation with bromine.[7] Amino-functionalized polystyrene (**2**) (obtained from BASF) was reacted in DMF with maltoheptaonolactone at room temperature (Scheme 1).

The resulting polymer was slowly precipitated into water to give a fine dispersion. As a result, the hydrophilic maltoheptaose residues stick into the aqueous phase. The dried powder was redispersed in aquous buffer and subsequent enzymatic polymerization with potato phosphorylase (**4**) was used to extend the maltoheptaose primer to give amylose-*block*-polystyrene block copolymers (**5**) (Scheme 2). The amylose block obtained by enzymatic polymerization has a very narrow polydispersity that can be proven by GPC analysis. Figure 1 compares GPC eluograms of the amino-functionalized polystyrene ($M_w/M_n = 1.05$), the maltoheptaose-functionalized polystyrene ($M_w/M_n = 1.05$), and one of the amylose-*block*-polystyrene block copolymers ($M_w/M_n = 1.05$; $DP_{amylose\ block} = 70$). It is obvious that the polydispersities of the samples do not change. This means that the amylose block has a polydispersity near 1. The polystyrene sample was prepared via anionic polymerization and termination with dimethylchlorosilane and subsequent hydrosilylation with allylamine.[8] The high molecular weight shoulder observed in the GPC trace resulted from coupling of the allylamine with two dimethylchlorosilane-modified polystyrenes.

Scheme 1



Scheme 2



The conversion during enzymatic polymerization was monitored by the quantitative determination of cleaved phosphate and by GPC analysis. Even though quantitative analysis of GPC data is highly questionable for such composite materials,[9] it proved to be a surprisingly valuable method to follow the enzymatic polymerization. As demonstrated in Figure 2, the number-average degrees of polymerization (DP) calculated on the basis of released phosphate and from the decrease of the GPC elution volume using PS calibration do not differ very strongly.

According to the amount of cleaved phosphate, the weight fraction of amylose residues in the block copolymer varied between 2% and 40%.

The resulting block copolymers have been characterized by IR spectroscopy. Figure 3 compares the IR

* To whom all correspondence should be addressed.

S0024-9297(97)01022-X CCC: $14.00

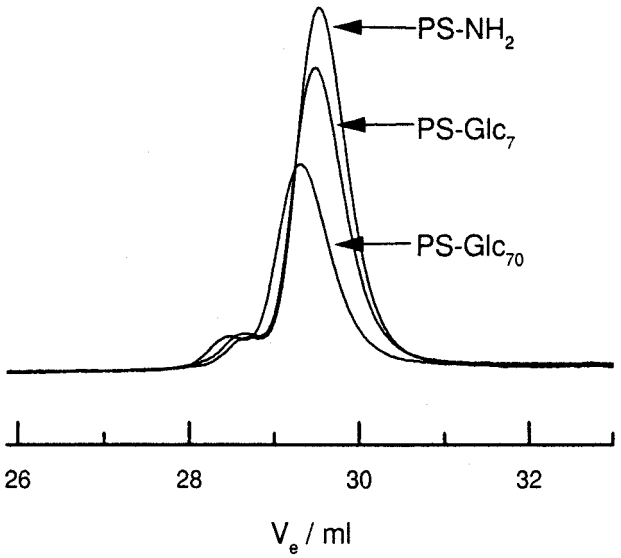


Figure 1. GPC eluograms of monoamino-functionalized polystyrene (PS-NH_2/M_n = 6300), maltoheptaose-functionalized polystyrene (PS-Glc_7), and amylose-*block*-polystyrene (PS-Glc_{70}).

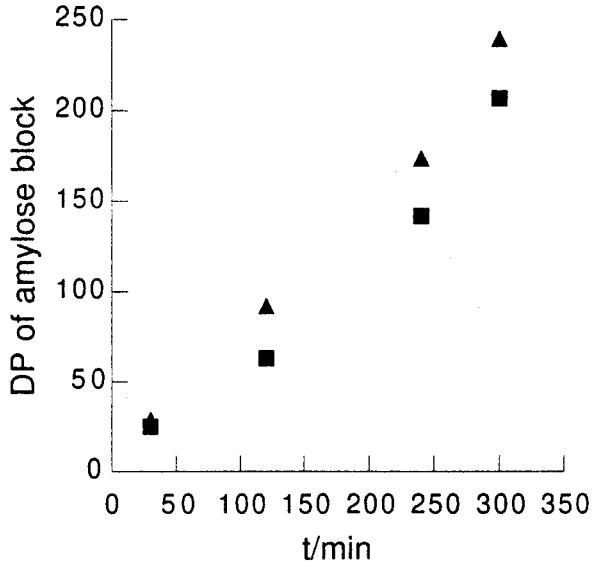


Figure 2. Kinetic data of enzymatic polymerization: (▲) obtained by the amount of cleaved phosphate; (■) obtained by GPC (for a polystyrene block with M_n = 63 000).

spectra of polystyrene, amylose, and an amylose-*block*-polystyrene block copolymer.

As expected, the block copolymer spectrum corresponds to a superposition of the component spectra.

Experimental Part. All solvents were purified by conventional methods.

β-Cyclodextrin (Fluka), and α-D-glucose 1-phosphate dipotassium salt dihydrate (Fluka) were used without further purification.

Monoamino-functionalized polystyrene (**2**) was kindly provided by Dr. A. Gottschalk (BASF AG) and was reprecipitated before use.

Potatoes (*Solanum tuberosum L. var. Christa*) were bought from a local farmer and should not be treated chemically or by irradiation in any way.

Infrared (IR) spectra were recorded on a Bruker spectrometer IFS-48.

Size-exclusion chromatography (SEC) was performed using THF as eluent on a Waters GPC. A differential refractometer and an ultraviolet (UV) spectrometer (254 nm) were used as detectors connected in series. Four cross-linked polystyrene columns (PSS, Mainz, Germany) of gel pore size 10^5, 10^4, 10^3, and 100 Å were used. The molecular weights were determined via calibration with respect to polystyrene standards.

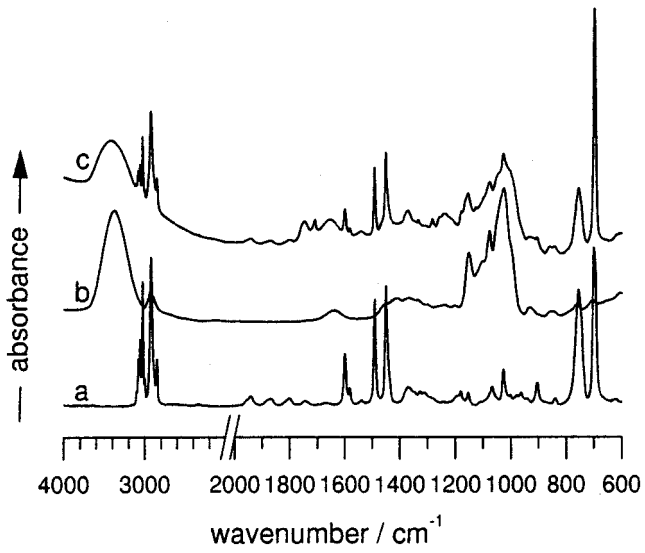


Figure 3. IR spectra of (a) polystyrene, (b) amylose, and (c) amylose-*block*-polystyrene (PS-Glc_{70}).

The synthesis of maltoheptaonolactone (**1**)[5] and potato phosphorylase (E.C.2.4.1.1) (**4**)[10] were performed as described elsewhere.

Maltoheptaose-Functionalized Polymers (3). To 100 mg of monoamino-functionalized polymer samples (**2**) in 20 mL of DMF is added maltoheptaonolactone (**1**) (100% excess with regard to the amino groups). The solution is stirred for 5 h at 80 °C. The product is then precipitated in cold water, filtered off, and washed with a large excess of cold water. The product is dried for several days *in vacuo*.

IR (KBr): 3428 (s), ν-(OH) amylose; 3052 (m) and 3030 (s), ν-(CH) aromatic PS; 2926 (s) and 2864 (m), ν-(CH) aliphatic PS + amylose; 1648 (w), C-1 amide amylose; 1604 (m), 1494 (s), and 1450 (s), in plane bond stretching phenyl rings; 1156 (w) and 1025 (s) ν-(CO); 754 (s), out of plane hydrogen deformation; 698 (vs), out of plane phenyl ring deformation.

Enzymatic Polymerization. To 100 mg of maltoheptaose-functionalized polymers (**3**) and α-D-glucose-1-phosphate dipotassium salt dihydrate (200 times the amount of attached primer) is added 0.3 units of potato phosphorylase (E.C.2.4.1.1) (**4**) per mmol primer, and then the mixture is filled with citrate buffer (pH = 6.2; 0.05 M) to a total volume of 10 mL. Then the suspension is incubated at 37 °C during the polymerization. The polymerization can be monitored by the quantitative photometric measurement of liberated phosphate. The polymerization is stopped by heating the suspension to reflux for 30 s or by adding ethanol. The coagulated protein is scooped out of the solution, and after this, the product is filtered off and washed with water. The product is dried for several days *in vacuo*.

The amount of liberated phosphate can be quantitatively determined by photometric measurements of molybdato phosphate complexes.[11]

IR (KBr): 3428 (s), ν-(OH) amylose; 3052 (m) and 3030 (s), ν-(CH) aromatic PS; 2926 (s) and 2864 (m), ν-(CH) aliphatic PS + amylose; 1648 (w), C-1 amide amylose; 1604 (m), 1494 (s), and 1450 (s), in plane bond stretching phenyl rings; 1156 (w) and 1025 (s), ν-(CO);

754 (s), out of plane hydrogen deformation; 698 (vs), out of plane phenyl ring deformation.

References and Notes

(1) Ziegast, G.; Pfannemüller B. *Makromol. Chem.* **1984**, *185*, 1855.
(2) Loos, K.; Stadler, R. *Makromol. Chem., Rapid Commun.*, in press.
(3) Hoff, S. M.; Novak, B. M. *Macromolecules* **1993**, *26*, 4067.
(4) Siegel, J. S. In *Supramolecular Stereochemistry*; Van Esch, J. H., Sommerdijk, N. A. J. M., Hafkamp, R. J. H., Feiters, M. C., Nolte, R. J. M., Eds.; Nato ASI Series; Kluwer Academic Publisher: Dordrecht/Boston/London, 1995; p 3.
(5) Chen, J. T.; Thomas, E. L.; Ober, C. K.; Mao, G.-P. *Science* **1996**, *273*, 343.
(6) Pfannemüller, B.; Schmidt, M.; Ziegast, G.; Matsuo, K. *Macromolecules* **1984**, *17*, 710.
(7) von Braunmühl, V.; Stadler, R. *Macromol. Symp.* **1996**, *103*, 141.
(8) Weis, C.; Friedrich, C.; Mülhaupt, R.; Frey, H. *Macromolecules* **1995**, *28*, 403.
(9) Dubin, P. L.; Principi, J. M. *Macromolecules* **1989**, *22*, 1891.
(10) Pfannemüller, B.; Burchard, W. *Makromol. Chem.* **1969**, *121*, 1.
(11) Fiske, C. H.; Subbarow, Y. J. *J. Biol. Chem.* **1925**, *66*, 375.

MA971022H