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Self-association of bis-(α,β-D-glucopyranosyl)-polyisobutylene

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Abstract—In this paper, we report the structure and apparent molecular weights of bis-(α,β-D-glucopyranosyl)-polyisobutylene (Gluc-PIB-Gluc) aggregates in $CDCl_3$ by NMR spectroscopy. Analysis of DOSY (diffusion-ordered NMR spectroscopy) experiments of a solution of Gluc-PIB-Gluc showed the presence of aggregates that were corroborated with dynamic light scattering. The structure of the aggregates was also studied by correlation spectroscopy (COSY) and nuclear Overhauser effect spectroscopy (NOESY) experiments.

Keywords: ^{1}H, ^{13}C NMR; Diffusion-ordered NMR; Self-assembly; Glucose; Polyisobutylene

1. Introduction

It is known that several types of block copolymers form micelle-like aggregates when dissolved in a block-selective solvent.[1–5] Amphiphilic block copolymers, that is, block copolymers possessing hydrophilic and hydrophobic chains are interesting from both academic and practical points of view.[6–15] The self-assembly of amphiphilic block copolymers into various types of polymer aggregates, for example, micelles, vesicules, or rod-like associates can be expected when dissolving them in water (preferred for the hydrophilic blocks) or in organic solvents (preferred for the hydrophobic blocks).[6–15] Similar association phenomenon can also be expected when the hydrophilic blocks are replaced with a relatively large hydrophilic molecules, for example, glucose.[16] In one of our previous papers bis-(α,β-D-glucopyranosyl)-polyisobutylene (Gluc-PIB-Gluc) was synthesized; in this structure the PIB block and the glucose units represented hydrophobic and hydrophilic segments, respectively.[16] A dynamic light scattering study of the solutions of Gluc-PIB-Gluc in water and in tetrahydrofuran revealed the presence of aggregates (average molecular sizes are 280 and 180 nm, respectively). However, similar to other amphiphilic molecules, the aggregation behavior of Gluc-PIB-Gluc is highly dependent on the block-selective solvent used. Although DLS gives information on micellar parameters such as average particle size and particle size distribution, it does not provide any particular information about the structure of the polymer aggregates. Modern NMR methods, such as NOESY and DOSY are able to provide information not only about average particle size but also about the structure of the polymer aggregates formed. Application of DOSY for the determination of sugar size or the molecular weights of the aggregates has also been reported.[17,18] In this article, we report the investigation of the polymer aggregates formed from Gluc-PIB-Gluc in $CDCl_3$, the preferred solvent for the PIB segment, but not the Gluc-portion. The structure of Gluc-PIB-Gluc is shown in Scheme 1.

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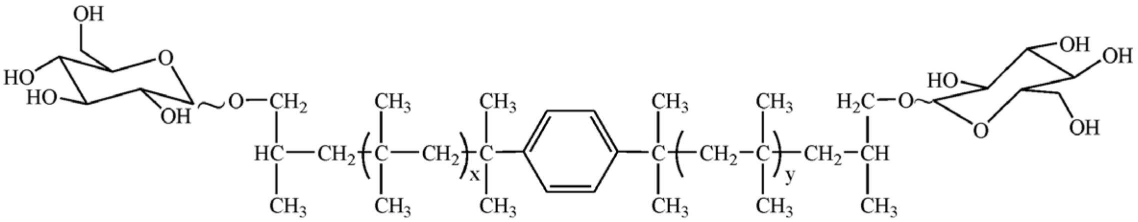

Scheme 1. Structure of bis-(α,β-D-glucopyranosyl)-polyisobutylene (Gluc-PIB-Gluc).

2. Results and discussion

The partial COSY spectrum of Gluc-PIB-Gluc with assignments of the resonances are shown in Figure 1. The unlabelled peaks in Figure 1 belong to the methylene protons of the polyisobutylene chain-ends. In addition, the glucopyranose skeleton protons of the α anomer are of much weaker intensities.

The aggregates formed from Gluc-PIB-Gluc in $CDCl_3$ were studied by NOESY spectroscopy (Fig. 2). The signals due to intra-sugar, through-space interactions are of like phase with respect to the diagonal. This fact indicates that the glucopyranosyl rings lack the mobility expected for the terminal parts of the molecules. Most probably, reverse micelle-formation is responsible for this inflexibility because of the vicinity of the intermolecular glucopyranosyl end-groups. Possible hydrogen bonding and other intermolecular interactions may hinder internal motions within the aggregates. In β-D-glucopyranosides the 1,2-*trans*-diaxial NOE interaction is generally weak (because of the large intra-ring distance) but in case of Gluc-PIB-Gluc the anomeric hydrogen (H1 in Fig. 1) showed a strong interaction with H2, which is probably due to reverse micelle generation. The 1,2-*trans*-diaxial interaction was observed in the NOESY spectrum even at 3.3 mg/mL concentration.

Three NOESY cross peaks are clearly observed for the α anomeric proton in Figure 2. The strongest cross peak at 3.58 ppm is assigned to H2 of the α anomer and the two unassigned cross peaks of lower intensity may arise from inter-ring NOEs. These peaks cannot be unambiguously assigned because of spectral overlap but they must arise from inter-residue effects because of the probable $^4C_1$ conformation of the α anomer. Even in the case of the improbable alternative chair conformation of the α anomer, we would have only two intra-unit NOEs (H1–H2, H1–H5), which are not observed.

Not surprisingly, the β anomeric proton has more NOE cross peaks because it has intra-unit H1–H3 and H1–H5 NOE cross peaks, in addition to inter-ring NOEs. Based on the NOESY spectrum (Fig. 2), it has been proven that the polymer molecules having α-linked glucopyranose units are also aggregated. Furthermore, all carbohydrate–carbohydrate NOE cross peaks in the

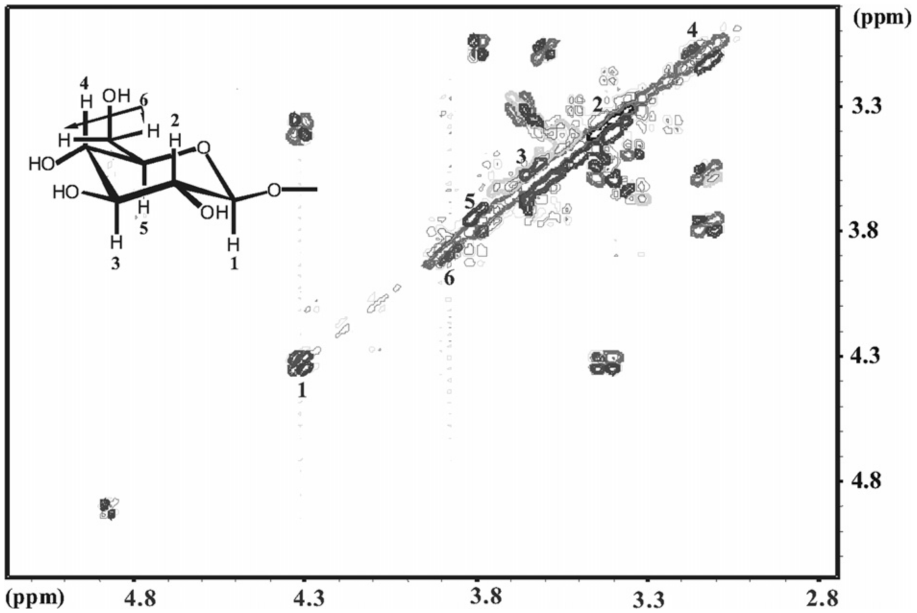

Figure 1. Partial COSY spectrum of bis-(α,β-D-glucopyranosyl)-polyisobutylene with assignments.