

Self-organization of stack-up block copolymers into polymeric supramolecules

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Abstract Polyethylene oxide *-b-* polypropylene oxide *-b-* polyethylene oxide (EO₁₀₆PO₇₀EO₁₀₆) block copolymer self-organizes into polymeric supramolecules, characterized by NMR as phase transition from the isotropic stack-up block structure to the ordered cubic polymeric supramolecular structure. Its dependence on both temperature and copolymer concentration is clearly shown by the changes in line shape and chemical shift of the PO₇₀ block β , γ resonances.

Keywords Self-assembly · Block co-polymer · NMR

Self-assembly of polymeric supramolecules is a powerful tool for producing functional materials that combine several properties [1]. Potential applications include: information storage, magnetic fluid, medical diagnosis, catalysis, ceramics, sensors, separations and reactions involving large molecules, chromatographic media, proton conducting materials, controlled release of agrochemicals, hosts for supramolecular assembly, and pigments/solubilising agent in paints and cosmetics [2].

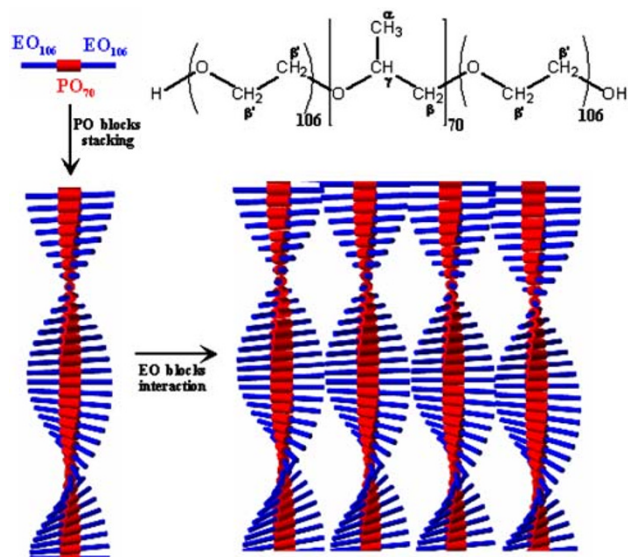
Commercially available non-ionic Pluronic[®] or Synperonics triblock copolymers [3] (polyethylene oxide–polypropylene oxide–polyethylene oxide, EO_mPO_nEO_m) are superior polymeric templates, which produce material of a wide pore diameter and wall thickness [4, 5]. The concept of stacking triblock

copolymers [4] was proposed to produce very long-range linear nanostructures, due to extension more or less indefinitely in both directions. The synthesized conical molecules, which are shaped like a badminton shuttlecock, were reported to stack together in a directed manner [6]. The specific shapes open up the huge potential for directionalities of alignment, causing by hydrogen-bonding and/or weak van der Waals interactions.

Pluronic[®] F127 is the subject of interest for this study. It has the formula of EO₁₀₆PO₇₀EO₁₀₆. As illustrated in Scheme 1, this triblock compound consists of a hydrophobic PO₇₀ block sandwiched by two hydrophilic EO₁₀₆ blocks. For simplicity, there are two different modes of interaction for self-assembled block copolymer, namely hydrophobic PO₇₀ and hydrophilic EO₁₀₆ packing segments. In both cases, the packing of large molecules, i.e., EO₁₀₆PO₇₀EO₁₀₆, means that only a fraction of molecules will be in direct contact due to hydrogen-bonding, polar or van der Waals forces. Because of the unique amphiphilic property, the material self-assembles into stacking structures. Hydrogen-bonding among the PO₇₀ units are expected to drive the triblock molecules to assemble into linear-rotating cylinder structures [4]. Its phase behavior is temperature and concentration dependent, which relies on the level of dehydration of EO₁₀₆ and PO₇₀ block. An additional self-assembly process pushes the corona-surrounded domains into unusual anisotropic interactions, which was suggested to be a cubic phase [7].

NMR (nuclear magnetic resonance) for studying liquid crystalline systems was discussed, [8] to elucidate thermotropic and lyotropic phase transitions. The studies of the ¹³C NMR of EO₆₁PO₄₁EO₆₁ (F87) at

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Scheme 1. Self-organization of stack-up $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ into polymeric supramolecules

low concentration less than 1% (w/w) have been documented previously, [9, 10] even the self-assembly behavior in water of a mixture of $\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}$ (L64) and $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ (P105), was explored [11] by ^2H NMR at 25 °C. However, the experimental application of these techniques and the interpretation of their results are more complicated than in homogeneous systems [7, 12]. To date, no complete NMR study of F127 polymer has been published. This study is focused on the ^1H NMR analysis of F127 in D_2O . All spectra were recorded on samples dissolved in D_2O contained in a 5 mm o.d. NMR tube, on a Varian Unity 500 MHz NMR Spectrometer equipped with a 5 mm inverse probe. Excitation pulse width was approximately $81^\circ(10 \mu\text{s})$, data acquisition time 4.096 s, relaxation delay time 6 s, pulse repeat time approximately 10 s. The residual HDO peak was used as a secondary reference as a function of temperature [13] to calibrate the chemical shifts. Although not ideal, this should remove the gross effects of temperature dependence of the chemical shift.

As shown in Fig. 1, the chemical shifts of both PO_{70} and EO_{106} blocks appear to be temperature-dependent. There is a fine structure (β_{CH_2} or γ_{CH}) at 20 °C, and partial overlap with β'_{CH_2} units of EO_{106} block. The spectra at 40 and 60 °C are similar; the resonances of ^1H (α_{CH_3} , γ_{CH} and β_{CH_2}) of PO_{70} block decrease as temperature increases. At temperatures above the phase transition, [7] the signal is increased, due to an increased relaxation rate of the interacting PO_{70} blocks, with the decrease of segmental mobility [14]. The attachment is proposed through a block of segments (PO_{70}) where the block may be considered

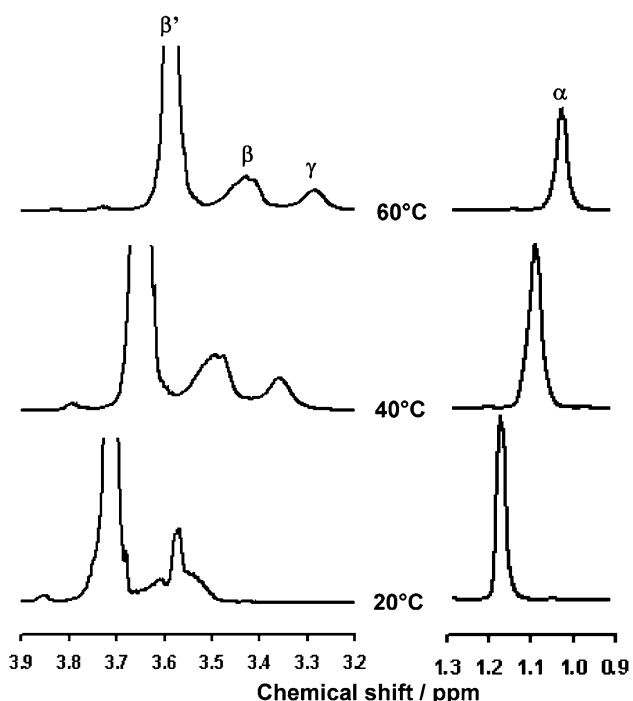
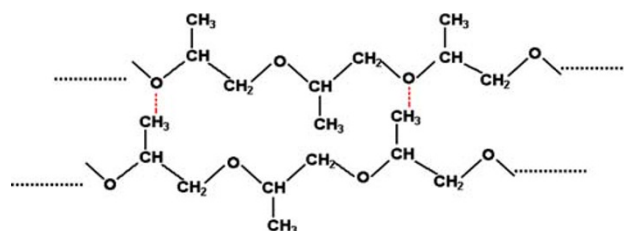


Fig. 1 ^1H NMR spectra of PO_{70} block of $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ in D_2O (1% wt) at various temperatures

to be stacked by hydrogen-bonding among the PO_{70} units as illustrated in Scheme 2.

The $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ self-assembly system is envisaged as a series of central-stacked linear units with a cubic phase. As shown in Fig. 2, the resonances of ^1H (γ_{CH} and β_{CH_2}) of PO_{70} block are also dependent on concentration. Fig. 2 clearly illustrates the phase transition from the isotropic stack-up block structure to the ordered cubic polymeric supramolecular structure. Its dependence on both temperature and copolymer concentration is clearly shown by the changes in line shape and chemical shift of the PO_{70} block β , γ resonances.

Under aqueous conditions, the PO_{70} block is expected to display more hydrophobic interaction over range of 35 to 80 °C, [15] thus increasing the tendency for mesoscopic ordering to occur. The $-\text{CH}_2$ -resonance of EO_{106} blocks is also dependent on temperature and



Scheme 2. PO_{70} block stacking due to hydrogen bonding

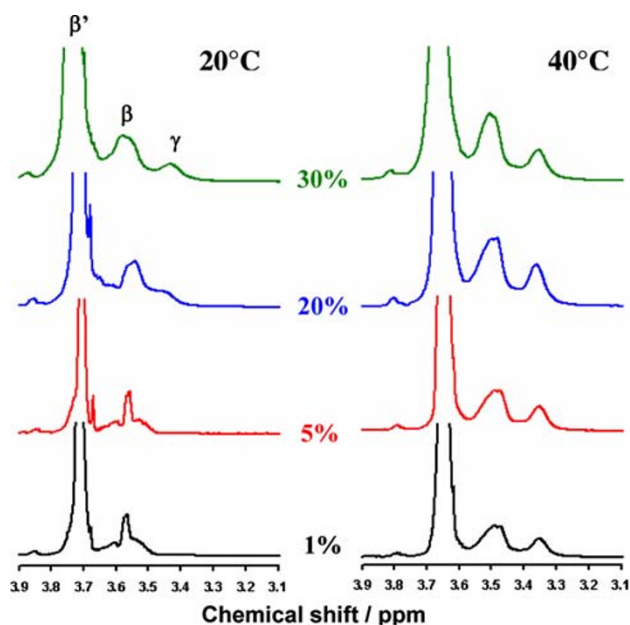


Fig. 2 Effect of temperature and concentration on ^1H NMR spectra of EO_{106} and PO_{70} blocks of $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ in D_2O

concentration. With increasing temperature, the signal is broadened, indicating a transition, which causes a decrease of the amount of mobile polymer segments. In comparison to low concentration, 20 and 30% polymer solutions were placed in an oven at 80°C over night to homogenize the solutions. As indicated in Fig. 2, the resonance is broadened as concentration increases. The increased line width of ^1H (β_{CH_2}) can be attributed to an increased relaxation rate of the interacting EO_{106} blocks, and thus reflects a reduced mobility of the segments observed. Also, chemical shifts of ^1H (γ_{CH} and β_{CH_2}) towards high field indicate electron density increased as molecules closely attach due to PO_{70} units assembly, while the chemical shift of ^1H (β_{CH_2}) from the $-\text{CH}_2$ -resonance of EO_{106} blocks remains 3.670 ppm. As shown in Fig. 3, the use of the $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ amphiphile as a template to form silica-based nanostructured materials [4] extends more or less indefinitely in both directions to produce very long-range linear nanostructures.

NMR can be an important source of information on the behavior of self-assembly of block copolymers. The hydrophobic PO_{70} domains self-associate into a core to escape contact with water, pushing the hydrophilic EO_{106} domains into a corona surrounding the core. It can help elucidate the mechanisms of interactions with the building blocks. The concept of stacking interactions has become increasingly important, with isotropic, anisotropic, or hierarchical structures being obtained, depending on the type of template self-organization mechanism employed.

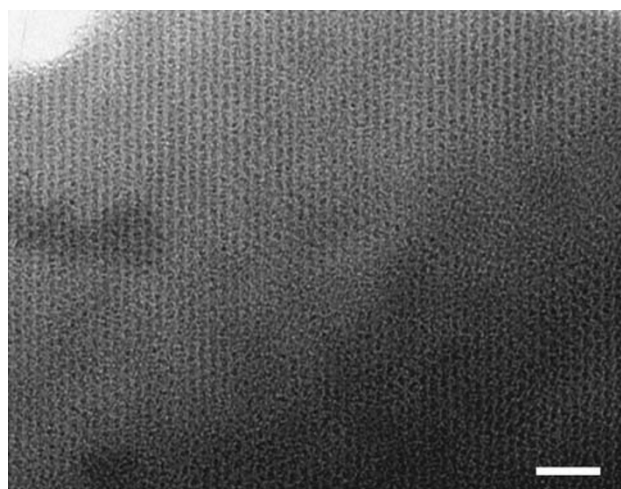


Fig. 3 TEM micrograph of nanostructured silica networks templated by a $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ self-assembly system. The combination of two solutions: 20(wt)% of triblock copolymer dissolved in ethanol (solution I); and 28(wt)% of tetraethoxysilane (TEOS) in ethanol, adjusted to pH 2 with a 0.1 M HCl, and left to equilibrate for 90 min at 70°C (solution II). Solution I and II were mixed and left to age for 3 h at room temperature. Calcination was carried out by heating at 450°C for 16 h under oxygen as described previously. Inserted scale bar: 40 nm

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