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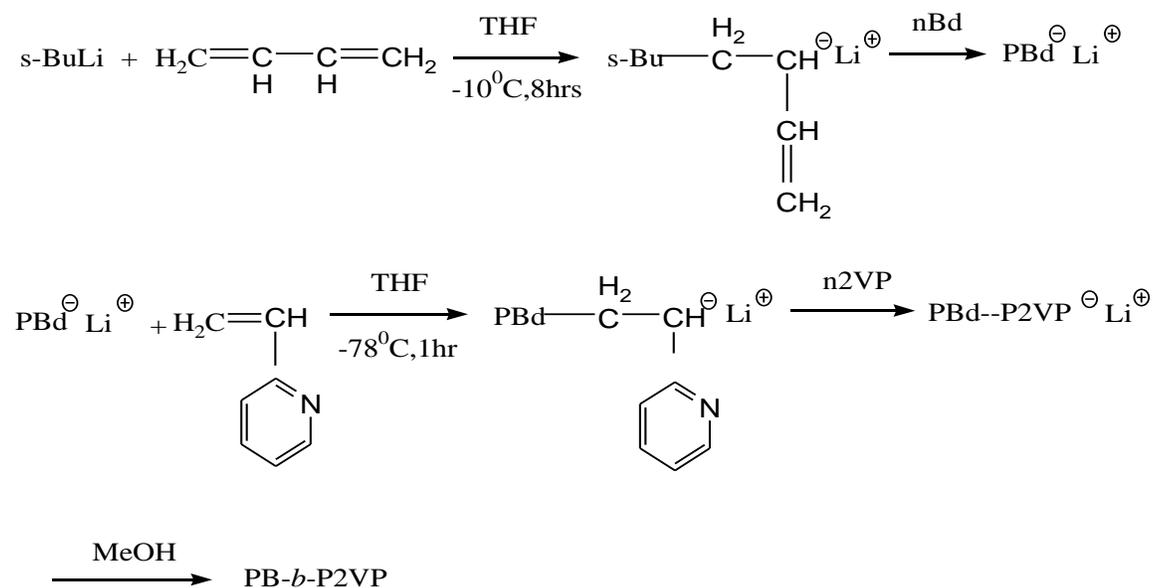
Hierarchical Structures in Lamellar Hydrogen Bonded LC Side Chain Diblock Copolymers

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SYNTHESIS OF PBd-P2VP

PBd-P2VP was synthesized according to the procedure described in Scheme S 1. For the synthesis, THF was purified by *s*-BuLi. A polar solvent (such as THF) can cause side reactions in polymerizations where the 1,2 addition of dienes is required, or when using polar monomers.



Scheme S 1. Synthesis of PBd-P2VP.

The optimal conditions for the synthesis of the PBd-b-P2VP copolymers include, first of all, the polymerization of the Bd monomer in THF solvent in low temperature (-20 °C) for 12 hours. For the successful polymerization of the polar monomer of 2VP, polar THF solvent is needed in order to avoid termination phenomena. Even a minor increase of temperature above -78°C, results in the formation of gel, which is a result of the macromolecules with large molecular weight.

The synthesis is divided into three days. During the first day of the synthesis, a flask of THF, which includes aloe (a mixture of metallic K and Na in a ratio of 3:1), is connected to a high vacuum line. The solvent is then frozen with the aid of liquid sodium and degassed. A 500 ml flask is connected to a nearby position in the high vacuum line for a crack check. After the second flask has been degassed, 10 ml of *s*-BuLi is introduced through septum using a syringe. The septum is then removed from the flask by flame cut and THF distillation is initiated from the first flask to the second one.

After the desired amount of solvent has been distilled, the flask is degassed and the solution is defrosted by an isopropanol bath (liquid sodium at -40 °C). The solvent is then stirred for two hours in order for all the reactions between THF and *s*-BuLi to take place (*s*-BuLi produces alkoxides, which stabilize the living PBd). After the stirring is over, the isopropanol bath is removed and the solution is stirred for additional 24 hours in room temperature.

The butadiene monomer polymerization takes place during the second day of the synthesis. The first step is the purification of pyridine. The final pyridine break seal is attached to the polymerization apparatus (Figure S) and is maintained at -78 °C by using a bath of isopropanol and dry ice. The apparatus is then attached to the high vacuum line, checked for holes or cracks and then degassed. Through the septum ~8 ml of normal *n*-BuLi and ~4 ml diphenylethylenium (DPE) are inserted in the apparatus forming the 1,1 diphenylhexyl lithium (DPHL), which is red colored. The septum is removed by flame cut at point B and the desired amount of THF is distilled in the purified apparatus.

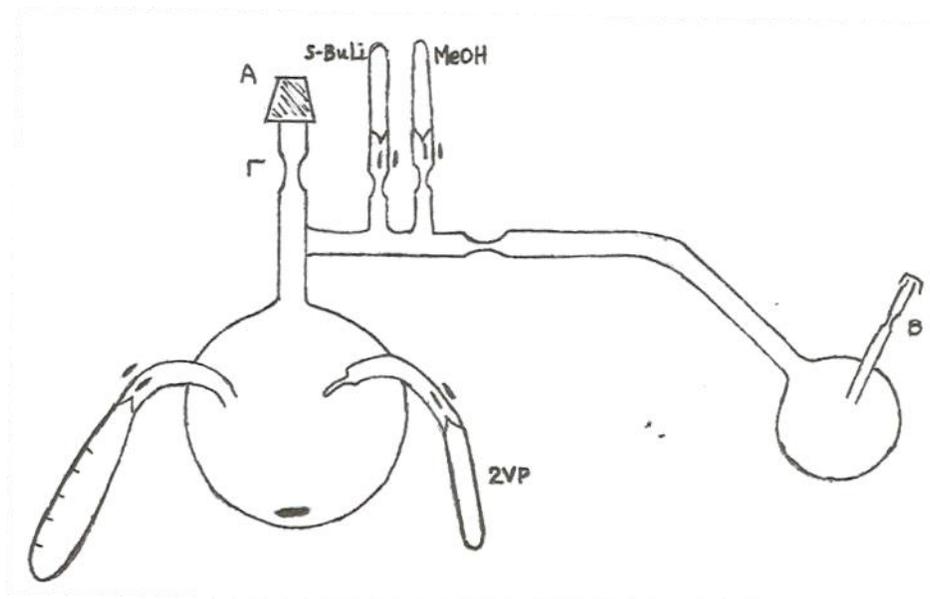


Figure S 1. Apparatus for PBd-P2VP synthesis.

DPHL is used for the apparatus purification instead of the *n*-BuLi because the latter reacts with THF. After the distillation is completed the apparatus is removed from the high vacuum line by fusion at point Γ (see Figure S). Every time when THF is the solvent, prior to any flame cut the solution must be well frozen with liquid nitrogen (-196 °C) and maintained at this temperature until the flame cut point reaches room temperature (25 °C). By cooling the flame cut point the pyrolysis of THF, which would lead to undesired byproducts, is being avoided.

The apparatus is then purified 4-5 times with the DPHL solution and purified through distillation and condensation of the solvent at every point of the apparatus (~1 h 30 min or ~20 times). The solvent from the purification section is then distilled to the main reactor of the apparatus by sinking the first part of the apparatus in a bath of 30 °C and the second one in icy water. As soon as the distillation is over the purge section is removed by flame cut.

The main reactor, where the THF has been distilled, is then placed in an isopropanol with dry ice bath (-78 °C) under stirring for 5 min until it has reached the same temperature. The fragile part of the *s*-BuLi break seal is then broken and after that the same happens to the break seal of the butadiene monomer, which is being distilled to the main reactor of the polymerization. After the distillation the apparatus is left in the fridge at -20 °C for 14 hours until the end of the butadiene polymerization.

During the third and final day of the polymerization procedure, after the Bd polymerization is over, the main reactor is placed in an isopropanol-dry ice bath (-78 °C) under stirring for 5 min until it has reached the same temperature. The fragile part of the 2-vinylpyridine (2VP) break seal is broken initiating its distillation. The 2VP polymerization lasts about 1 hour and it has to be at -78 °C strictly. After the 2VP polymerization is over the fragile part of the methanol break seal is broken so that it is inserted to the polymerization solution in order to deactivate the active centers and end the polymerization. This is visible through the decrease of the solution viscosity. The copolymer precipitates in excess of acetone.

CHARACTERIZATION OF PBd-P2VP

By following the above synthesis procedure the copolymer PBd-P2VP characteristics match the molecular characteristics of ideal polymers. The molecular weight distributions are very narrow, which is a typical behavior of the anionic polymerization ($PID < 1.1$). It is important to mention that within the final product there was no terminated PBd.

Table S 1 shows the Kind numbers and corresponding ^1H NMR chemical shifts of the polymers in question. The ^1H NMR spectrum is shown in Figure S .

Size exclusion chromatograph is shown in Figure S . PDI of the PBd-P2VP is 1.03 according to the data.

Table S 1. Kind-number of protons and chemical shift for PB-P2VP.

Polymer	Kind-Number of Protons	Addition	Chemical Shift (ppm)
PBd	olefin (2)	1,4	5.35
	olefin (1)	1,2	5.6
	olefin (2)	1,4	4.95
P2VP	aromatic (1)	--	8.5

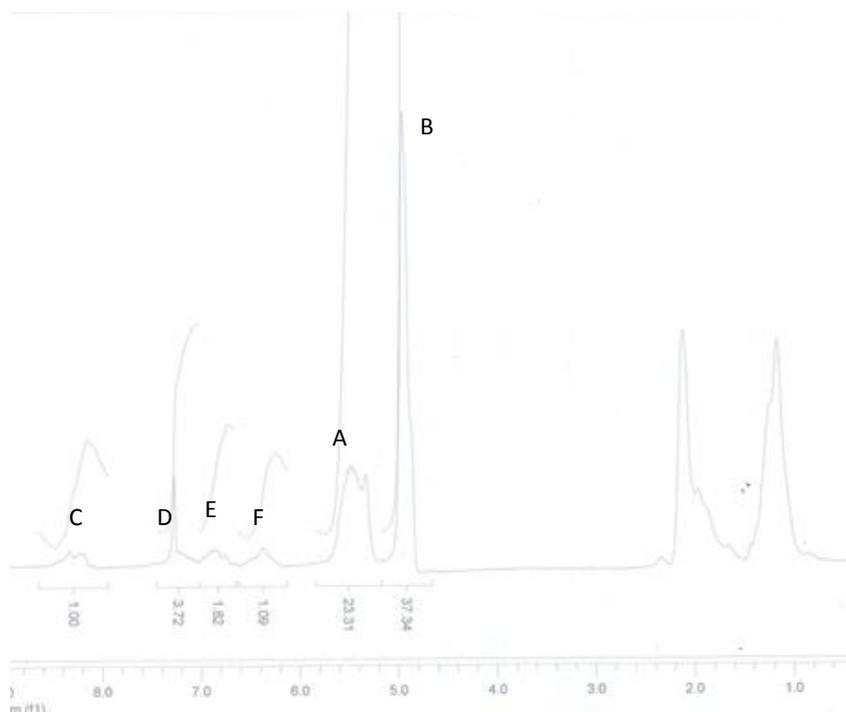
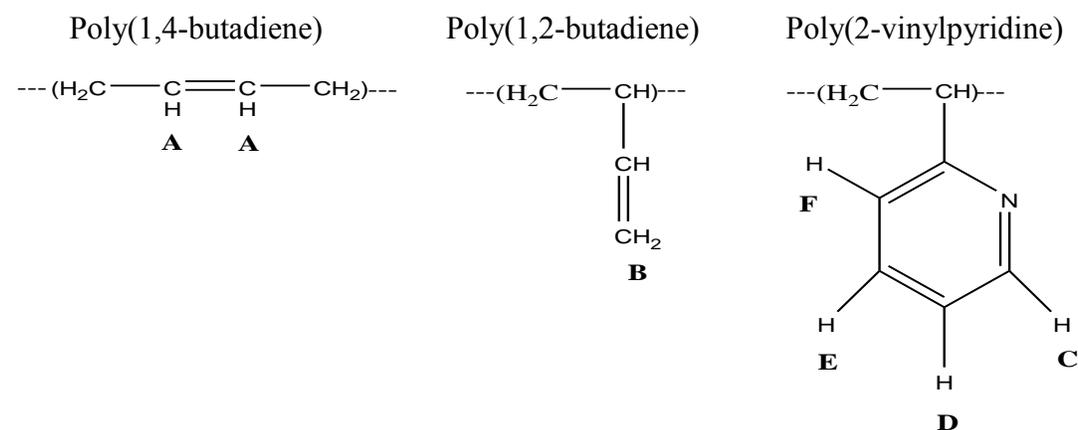


Figure S 2. ¹H NMR spectrum of PB-P2VP.

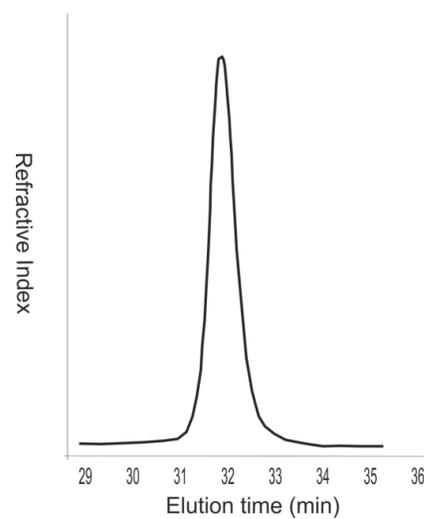


Figure S 3. SEC of PBd-P2VP.