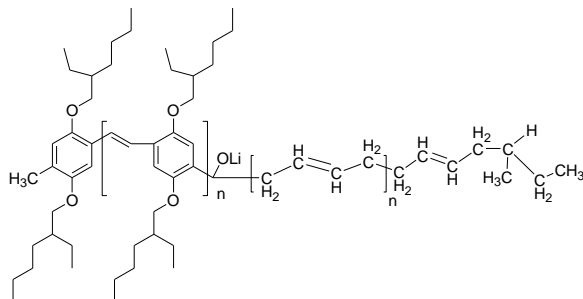


**Poly(2,5-di(2'-ethylhexyloxy)-1,4-phenylenevinylene)-b-Bd (1,4 rich addition)**

**Structure:**



Mn x 10 <sup>3</sup> DEHPPV-b-Bd	PDI
2.0-b-3.5	1.9

Synthesis of such diblock copolymers was carried out in two steps:

1. synthesis DEH-PPV bearing end group of aldehyde:
2. Reaction of Poly butadiene living lithium salt with aldehyde terminated DEH\_PPV. Followed by rigorous fractionation to remove any untreated poly butadiene fractions.
3. Aldehyde end group DEH-PPV is synthesized by polymerization of Seigrst polycondensation under basic condition in DMF, followed by hydrolysis in acidic water. The polymer was then dissolved in chloroform and washed with distilled water until neutral, dried over  $\text{MgSO}_4$  and precipitated into cold methanol.

The reaction scheme shows the synthesis of poly(1,3-butadiene) using a lithium carbanion initiator. The initiator is a lithium carbanion of 2,2,4-trimethylpentane, represented as  $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{Li}$ . This reacts with 1,3-butadiene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ ) in cyclohexane. The reaction proceeds via a living polymerization mechanism, resulting in a poly(1,3-butadiene) chain with a lithium end group. The polymer structure is shown as  $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{Li}-[\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2]_n$ , where the repeating unit is enclosed in brackets with a subscript  $n$ . The lithium end group is shown as  $\text{OLi}$  in the polymer structure.

The molecular weight was obtained by  $^1\text{H}$  NMR by comparing the end aldehyde group at 10.5 ppm to aromatic proton at 7.54 ppm or vinyl proton at 7.26 ppm for the aldehyde end functionalized prepolymer followed by block copolymer.

MEH-PPV-Bd is soluble in THF,  $\text{CHCl}_3$  hexane.

**10**

CCOC(=O)c1ccc(cc1C(=O)OC)C(=O)OC

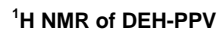
<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound **10**. The spectrum shows peaks at 10.00 (s, 1H), 7.00 (d, 2H), 6.80 (d, 2H), 3.57 (m, 2H), 3.04 (m, 2H), 2.57 (s, 3H), 2.15 (s, 3H), 1.57 (s, 3H), 1.24 (s, 3H), and 0.95 (s, 3H). The chemical structure of **10** is shown above the spectrum.

Cc1cc(O)cc(O)c1 + BrCC(C)CC  $\xrightarrow[80\text{ }^{\circ}\text{C}]{\text{KOH}}$  CC1=CC(OC(C)CC)C(OC(C)CC)=CC1C

CC1=CC(OC(C)CC)C(OC(C)CC)=CC1C + Nc1ccccc1N  $\xrightarrow[\text{POCl}_3]{\text{DMF}}$  CC1=CC(OC(C)CC)C(OC(C)CC)=CC1C=Nc1ccccc1N

CC1=CC(OC(C)CC)C(OC(C)CC)=CC1C=Nc1ccccc1N  $\xrightarrow[\text{KOtBu}]{\text{DMF}}$  CC1=CC(OC(C)CC)C(OC(C)CC)=CC1C=Nc1ccccc1N

**DEI**  
(PUGATRY)



### PREPARATION OF THE BLOCK COPOLYMER.



- Poly(2,5-di(2-ethylhexyloxy)-1,4-phenylenevinylene,  $M_n=2000$ ,  $M_w=3000$ ,  $M_w/M_n=1.45$
- PBd  $M_n=3,500$ ,  $M_w/M_n=1.10$
- After linking reaction DEHPPV-Bd  $M_n=DEHPPV(2000)-b-(3,500)$ ,  $M_w/M_n=1.9$