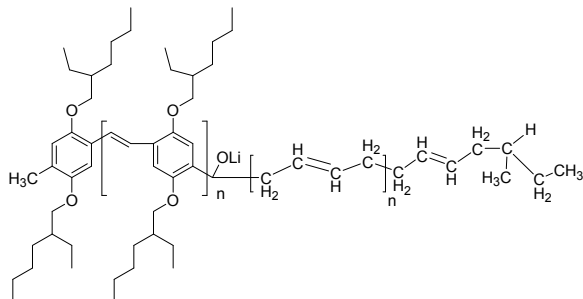


Poly(2,5-di(2'-ethylhexyloxy)-1,4-phenylenevinylene)-b-Bd (1,4 rich addition)

Structure:



Mn x 10 ³ DEHPPV-b-Bd	PDI
3.3-b-12.0	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 Seigrist 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 MgSO_4 and precipitated into cold methanol.

Reaction scheme showing the synthesis of a poly(1,3-butadiene) derivative. The starting materials are isobutylene (H₃C-C(CH₃)₂-CH₂-Li) and 1,3-butadiene (CH₂=CH-CH=CH₂). The reaction is carried out in cyclohexane. The product is a poly(1,3-butadiene) chain with a complex side group, represented as [CH₂-CH=CH-CH₂]_n-Li.

The molecular weight was obtained by ^1H 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, CHCl_3 hexane.

¹H NMR spectrum of 2,3-bis(2-ethylhexyloxy)toluene. The x-axis represents chemical shift in ppm (0.0 to 7.0), and the y-axis represents intensity (0 to 10000). The spectrum shows several peaks corresponding to the protons in the molecule. The peaks are labeled with their chemical shifts: 3.82, 2.24, 1.71, 1.37, and 0.94. Integration values are shown below the peaks: 3.00, 4.23, 3.09, 21.94, and 14.20.

CC(C)(C)CCBr + CC(C)(C)CCBr + Oc1cc(O)ccc1C(=O)O $\xrightarrow[80\text{ }^{\circ}\text{C}]{\text{KOH}}$ CC(C)(C)CCOC1=CC(OC(C)(C)CC)C(=O)O1

CC(C)(C)CCOC1=CC(OC(C)(C)CC)C(=O)O1 + Nc1ccccc1 $\xrightarrow[\text{POCl}_3]{\text{DMF}}$ CC(C)(C)CCOC1=CC(OC(C)(C)CC)C(=Nc2ccccc2)C1=O

CC(C)(C)CCOC1=CC(OC(C)(C)CC)C(=Nc2ccccc2)C1=O $\xrightarrow[\text{KtBu}]{\text{DMF}}$ $\left[\text{C}_6\text{H}_2(\text{OC(C)(C)CC})_2 \text{C(=O)} \right]_n$

2-benzylideneammine

¹H NMR spectrum (CDCl₃) of 2-benzylideneammine. The chemical structure is shown above the spectrum. The spectrum displays peaks at the following chemical shifts (ppm): 9.01, 7.51, 7.33, 7.09, 4.09, 2.01, 1.62, 1.47, and 1.39.

Size exclusion chromatography of poly(DEHPPV-Bd)

— Poly(2,5-di(2-ethylhexyloxy)-1,4-phenylenevinylene, $M_n=3300$, $M_w=4800$, $M_w/M_n=1.45$

— PBd $M_n=12,000$, $M_w/M_n=1.10$

— After linking reaction DEHPPV-Bd $M_n=\text{DEHPPV } (3300)\text{-}b\text{-(12,000)}$, $M_w/M_n=1.9$