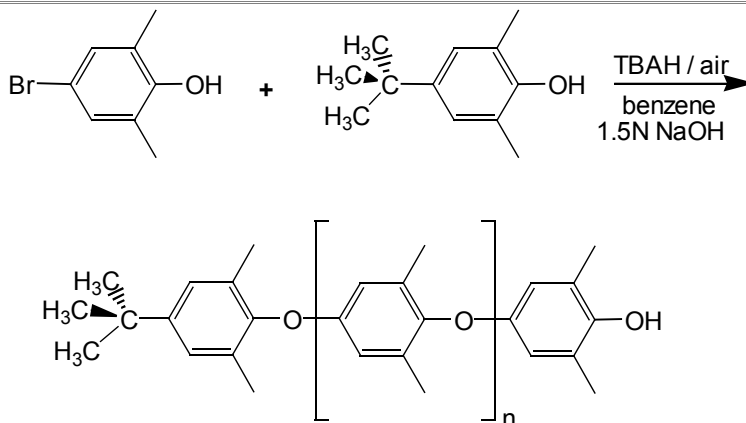


"-(4-*TERT*-BUTYL-2,6-DIMETHYLPHENOXY)-T-(3,5-DIMETHYL-4-HYDROXYPHENYL)-POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

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1. Procedure

The title polymer is synthesized by a phase transfer catalyzed (PTC) copolymerization of 4-bromo-2,6-dimethylphenol with 4-*tert*-butyl-2,6-dimethylphenol. The polymerization is performed in an open single-neck 250 ml round-bottom flask (Note 1), equipped with an octagonal magnetic stirring bar (1 1/2" x 5/16" coated with Teflon, Fisher) on a stirring plate. 4-*tert*-butyl-2,6-dimethylphenol³ (0.44 g, Note 2) is dissolved in 50 ml 1.5N aqueous NaOH under stirring at room temperature. 4-Bromo-2,6-dimethyl phenol (5.00 g, Note 3) is subsequently dissolved in the reaction flask. Benzene (30 ml) and 0.476 g tetrabutylammonium hydrogen sulfate (TBAH, Note 4) are then added. The reaction mixture is stirred vigorously at room temperature in the presence of air for 13 h (Note 5). Excess 1.5N aqueous hydrochloric acid (55 ml) is added to the flask under vigorous stirring. The benzene layer of the cooled mixture is separated and poured into 500 ml methanol. The precipitate is filtered, washed with 200 ml methanol, and dried *in vacuo* to give "-(4-*tert*-butyl-2,6-dimethylphenoxy)-T-(3,5-dimethyl-4-hydroxyphenyl)-poly(2,6-dimethyl-1,4-phenylene oxide) (yd 35 ± 5%).

2. Characterization

The dried polymer is obtained as a white powder. The molecular weight and molecular weight distribution of the polymer are determined by size-exclusion chromatography (SEC, Note 6): $M_n = 2400 \pm 200$ g/mol, $M_w/M_n = 1.2 \pm 0.1$. (M_n of 2500 g/mol was obtained by the checkers with 42% yd.) The 200 MHz ¹H NMR spectrum (Note 7) exhibits resonances at 1.33 [s, -C(CH₃)₃ of the 4-*tert*-butyl-2,6-dimethylphenoxy chain end], 2.09 (s, CH₃ of the 2,6-dimethyl-1,4-phenylene unit), 3.99 (s, OH of the 3,5-dimethyl-4-hydroxyphenyl chain end), 6.24 (s, Ph-H of the 3,5-dimethyl-4-hydroxyphenyl chain end), 6.39 (s, Ph-H of the 2,6-dimethyl-1,4-phenylene repeating unit), 7.00 (s, Ph-H of the 4-*tert*-butyl-2,6-dimethylphenoxy chain end) (Notes 8 and 9). The glass transition temperature (T_g) of the polymer is 150 ± 5°C as determined by DSC (Note 10).

3. Significance

The phase transfer catalyzed (PTC) homopolymerization of 4-bromo-2,6-dimethylphenol produces poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with one 3,5-dimethyl-4-hydroxyphenyl chain end/PPO molecule (PPO-OH).⁴ However, the polydispersities of the resulting PPO-OH are high and tedious fractionation is usually required for macromonomer applications.⁵ The molecular weight of the resulting PPO-OH can only be controlled by stopping the polymerization at very low conversions (typically <10%).⁴ This PTC copolymerization procedure leads to PPO-OH of narrow polydispersities (<1.40) at relatively high polymer yield (up to 74%).⁶ The molecular weight of the resulting PPO-OH can be conveniently controlled by the molar ratio of the 4-bromo-2,6-dimethylphenol to 4-*tert*-butyl-2,6-dimethylphenol in the initial monomer mixture.⁶ PPO can also be synthesized

by alternative polymerization of 2,6-dimethylphenol catalyzed by copper-amine complex⁷ or by a two-phase polymerization of 4-bromo-2,6-dimethylphenol in the presence of an oxidant.⁸ PPO with narrow molecular weight distribution was previously prepared by complexation of PPO oligomers with CH₂Cl₂ or CH₂Br₂.⁹

4. Notes

1. The polymerization can also be carried out in a 250 ml Erlenmeyer flask or beaker capable of allowing excellent stirring.
2. 4-*tert*-Butyl-2,6-dimethylphenol is synthesized by a modification of a literature procedure.³ H₂SO₄ (72%, 236 g) is added dropwise to a mixture of 2,6-dimethylphenol (71 g, 0.58 mol) and *t*-butanol (72 g, 0.72 mol), and the reaction is stirred at 60°C for 4 h. Three portions of diethyl ether are used to extract the reaction mixture. The ether extracts are then washed with saturated NaHCO₃ and water, and dried with anhydrous CaCl₂. Ether is removed on a rotary evaporator. The residue is recrystallized from petroleum ether to yield white crystals (70 g, 68%); mp 78-80°C (lit. mp 81-82°C); purity >99% by HPLC (Note 11).⁶ ¹H NMR (CDCl₃, TMS, 25°C): 1.28 [s, 9H, -C(CH₃)₃], 2.25 (s, 6H, Ph-CH₃), 4.46 (s, 1H, Ph-OH), 7.00 (s, 2H, Ph-H). Less 4-*tert*-butyl-2,6-dimethylphenol than 0.44 g will lead to PPO-OH of higher molecular weight.⁶ The reaction yields a crude product of 91% as analyzed by the checkers using gas chromatography.
3. 4-Bromo-2,6-dimethylphenol (97%, Aldrich) is recrystallized from petroleum ether; mp 78-79°C.
4. Tetrabutylammonium hydrogen sulfate (TBAH, 97%, Aldrich) phase transfer catalyst is used as received.
5. Longer reaction time results in higher polymer yield. A detailed study of the influence of polymerization time on both the yield and the molecular weight of the polymer has been described in detail.⁶
6. SEC measurements are performed on a Perkin-Elmer series 10LC instrument equipped with an LC-100 column oven, an LC-600 autosampler, and a Nelson Analytical 900 series data station. The measurements are made using a UV detector set at 254 nm, chloroform as solvent (1 ml/min), a set of PL-gel columns (500 and 10⁴Å), and a calibration plot constructed with polystyrene standards (Supelco).
7. 200 MHz ¹H NMR spectra are recorded on a Varian XL-200 spectrometer. The spectra are recorded in CCl₄ with TMS as the internal standard using a delay between transients of 2 s and an acquisition time of 2 s.
8. The checkers confirmed incorporation of the "4-*tert*-butyl-2,6-dimethyl phenoxy group by ¹³C NMR (Figure 1) which shows the *tert*-butyl methyl groups at 31.5 ppm and the quaternary carbon at 34.2 ppm.
9. The PPO-OH synthesized at high molar ratio of 4-bromo-2,6-dimethylphenol to 4-*tert*-butyl-2,6-dimethylphenol also exhibits a resonance due to 4-bromo-2,6-dimethylphenoxy chain end.⁶
10. DSC analyses are performed with a Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station, at a heating rate of 20°C/min. The instrument is calibrated with an indium standard. The glass transition temperature (T_g) is read at the middle of the change in the heat capacity during the second heating scan. The T_g value varies strongly with the molecular weight of the polymer.
11. HPLC analyses are made on the same instrument (Note 6) on a 100Å PL-gel column using chloroform as eluent (1.0 ml/min).

5. References

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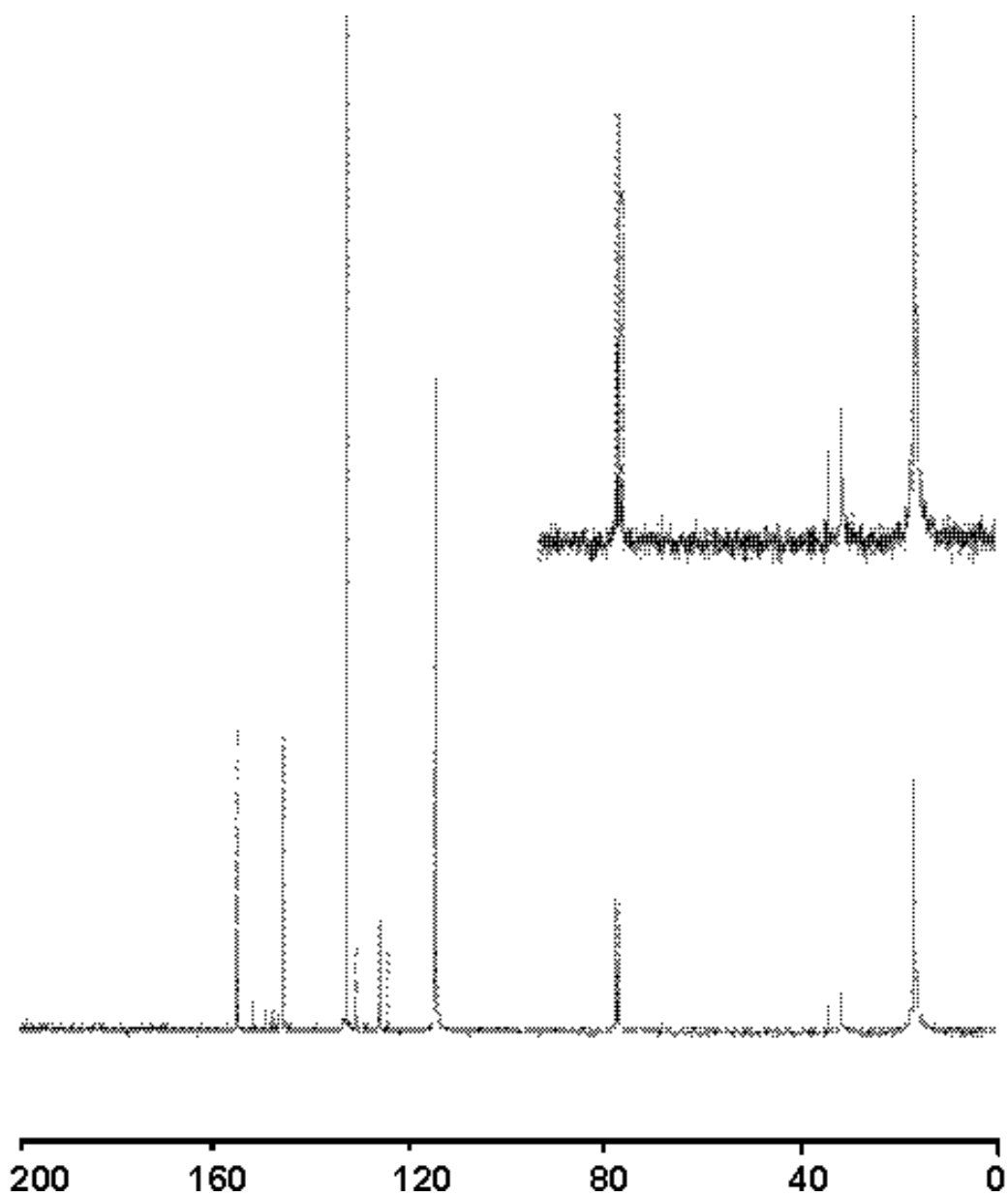


Figure 1. ^{13}C NMR spectrum in CDCl_3 of α -4-*tert*-butyl-2,6-dimethyl-phenoxy- ω -(3,5-dimethyl-4-hydroxyphenyl)-poly(2,6-dimethyl-1,4-phenylene oxide).