

## Supporting Information

### Boron “Stitching” Reaction: A Powerful Tool for the Synthesis of Polyethylene-Based Star Architectures

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#### Materials

Benzene (Sigma Aldrich, 99%) was purified over CaH<sub>2</sub> and distilled under high vacuum in a round bottom flask containing polystyryllithium oligomers [PS<sup>(-)</sup>Li<sup>(+)</sup>], with the characteristic yellow-orange color. Tetrahydrofuran (THF) (Sigma Aldrich, 99.9%) was refluxed over sodium, stirred in the presence of CaH<sub>2</sub> overnight and distilled over Na/K alloy. Styrene (Sigma Aldrich, 99%) was purified by distillation over CaH<sub>2</sub> and subsequently over di-*n*-butylmagnesium (Sigma-Aldrich, 1 M solution in heptane) and stored at -20 °C in pre-calibrated ampoules. Isoprene (Sigma Aldrich, 99%) was purified over CaH<sub>2</sub>, distilled twice over *n*-BuLi, remained under stirring for 30 min at 0 °C and finally stored at -20 °C in pre-calibrated ampoules.

Trimethylsulfoxonium iodide (Aldrich, ≥98%), benzyltributylammonium chloride (Aldrich, 98%), boron trifluoride diethyl etherate (Aldrich, ≥46.5%), 3-ethyl-3-pentanol (98%, Aldrich), *n*-butyllithium in hexane (1.6M, Aldrich) and trimethylamine-*N*-oxide dihydrate (TAO·2H<sub>2</sub>O) (≥99%) were used as received without further purification. Toluene (VWR) refluxed over sodium/benzophenone. Dichloromethyl methyl ether (98%, Aldrich) was distilled over CaH<sub>2</sub> in pre-calibrated ampoules and diluted in THF. All the rest reagent's purification, polymerizations and subsequent organoboron reactions were conducted under high-vacuum standards.

## Measurements

Gel permeation chromatography (GPC) analysis of the molecular weight and polydispersity index ( $\bar{M}_w/\bar{M}_n$ ) was performed via Viscotek GPCmax VE-2001 with THF as eluent solvent (1.0 ml/min, 35 °C). The instrument was equipped with triple detection array including a differential refractive index (DRI) detector, a two-angle light scattering (LS) detector (15°, 90°) and a four-bridge capillary viscometer. The laser wavelength was 658 nm. In the case of PE-based copolymers, high temperature gel permeation chromatography (HT-GPC) with 1,2,4-trichlorobenzene (TCB) as eluent solvent (1 ml/min, 150 °C) was conducted by Viscotek HT-GPC Module 350 with DRI detector. Calibration for DRI was based on PS standards. Proton nuclear magnetic resonance spectroscopy ( $^1\text{H-NMR}$ ) (Bruker ADVANCE III-600 MHz spectrometer) spectra were recorded in 1,1,2,2-tetrachloroethane- $d_2$  for PS-*b*-PE and toluene- $d_8$  for PI-*b*-PE at 80 °C. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1/TC 100 instrument by heating samples up to 120 °C and cooling to a) 25 °C for PS-*b*-PE and b) -80 °C for PI-*b*-PE at a rate of 10 °C/min. DSC thermograms were obtained until subsequent cycles produced overlapping thermograms to determine glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ).

Morphological observation of linear and 3-arm star copolymers was performed by bright field transmission electron microscopy (TEM) using a FEI-Technai Twin operated at 120 kV. Prior to sectioning and staining, a thermal history matching DSC thermograms with cooling and heating rate of 10 °C/min, was imposed onto the samples. Thickness of 50 nm sections were obtained under cryogenic conditions using a diamond knife (Diatome-45 °C) and collected on top of copper grids. The contrast for morphological observation was achieved by vapor staining from 0.5% stabilized  $\text{RuO}_4$  aqueous solution (2h) for PS-*b*-PE and  $\text{OsO}_4$  (3h) for PI-*b*-PE samples.

## Experimental section

All manipulations (monomers purification, polymerizations and chemical modifications) were carried out under high-vacuum (HV) techniques, using custom-made glass reactors (Fig. S1), equipped with break-seals for the addition of reagents and constrictions for removal of aliquots.<sup>1</sup>For the synthesis of dimethylsulfoxonium methylide and lithium triethylcarboxide ( $\text{Et}_3\text{COLi}$ ) Schlenk's line technique under argon was applied.

$\text{Et}_3\text{COLi}$  was synthesized by the following process. In a dried three necked round flask equipped with reflux condenser and a magnetic bar, 20 ml of distilled THF and 3-ethyl-3-pentanol (15 mmol, 2.13 ml) were added and the mixture cooled to 0 °C under argon. After 10 min, 9.4 mL (15 mmol) of *n*-butyllithium (1.6 M in hexane) was added dropwise by a syringe. The solution was kept under stirring for 90 min and then transferred into a degassed glass apparatus through septum. After distillation of proper amount of THF, the apparatus was sealed-off from the HV-line.

The preparation of dimethylsulfoxonium methylide was based on Corey's method followed by the switch of the solvent from THF to toluene.<sup>2</sup>

### **Synthesis of PS<sub>3</sub>B and PI<sub>3</sub>B 3-arm stars**

3-arm stars were derived by linking reaction of anionically synthesized living polystyrene or polyisoprene with BF<sub>3</sub>OEt<sub>2</sub>. In a typical experiment, living PILi was synthesized in 180 mL benzene by adding isoprene (8.0 g, 117 mmol) and *sec*-BuLi (1,21 mmol). The polymerization was left to completion for 24h at 25 °C. Then, a small aliquot from the solution was extracted for GPC analysis. Then, 0.330 mmol of BF<sub>3</sub>OEt<sub>2</sub> solution in benzene, was slowly added to the main reactor. The solution was stirred for three days protected from intense light to obtain the PI<sub>3</sub>B. Upon following the same method, 3-arm boron-linked star PS<sub>3</sub>B was synthesized.

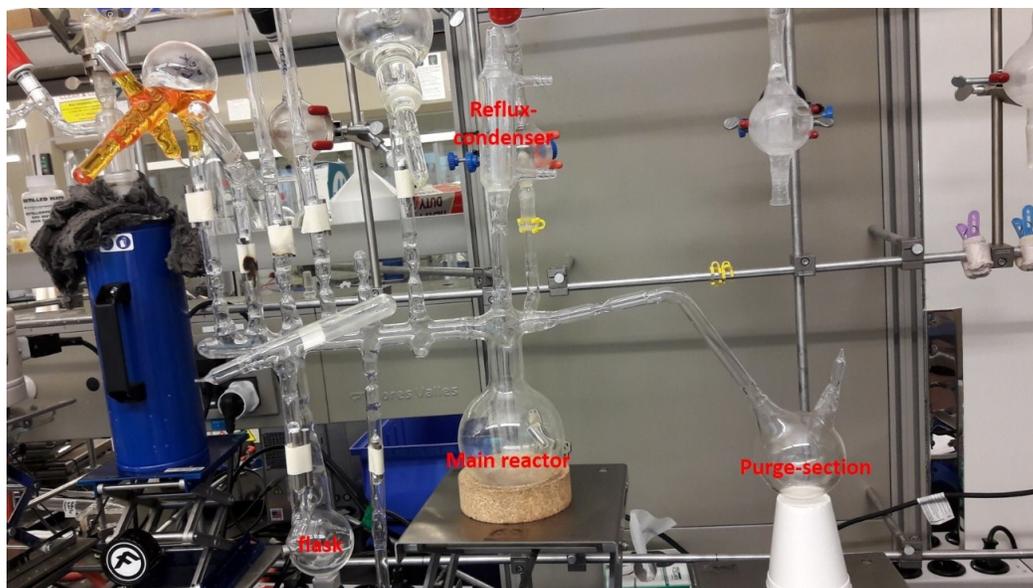
### **Synthesis of PS<sub>3</sub>C-OH and PI<sub>3</sub>C-OH via “stitching”-oxidation-hydrolysis reaction**

The conversion of PI<sub>3</sub>B into 3-arm star PI<sub>3</sub>C-OH was obtained via the following procedure. The solvent (benzene) was removed from the above mentioned solution in HV line and exchanged with equal amount of freshly distilled THF. Afterwards, the PI<sub>3</sub>B solution was cooled down to 0 °C and 5.5 eq. DCME (1.82 mmol diluted in THF), with regard to macroboron species, was added. After 10 min. 5.0 eq. Et<sub>3</sub>COLi (1.65 mmol in THF/hexane) was slowly added. The solution kept under stirring for 30 min at 0 °C and 24h at room temperature. Oxidation/hydrolysis was accomplished by adding TAO·2H<sub>2</sub>O (0.36 g, 3.30 mmol) and the solution stirred at 70 °C (reflux) for 12h. To monitor the progress of the reaction, aliquots for GPC analysis, were extracted before and after oxidation/hydrolysis step. Afterwards, the reaction solution was poured into cold methanol (350 ml) to precipitate the polymer. The resultant polymer was collected by centrifugation and dried under vacuum. Following the same procedure, 3-arm star (PS)<sub>3</sub>C-OH was synthesized.

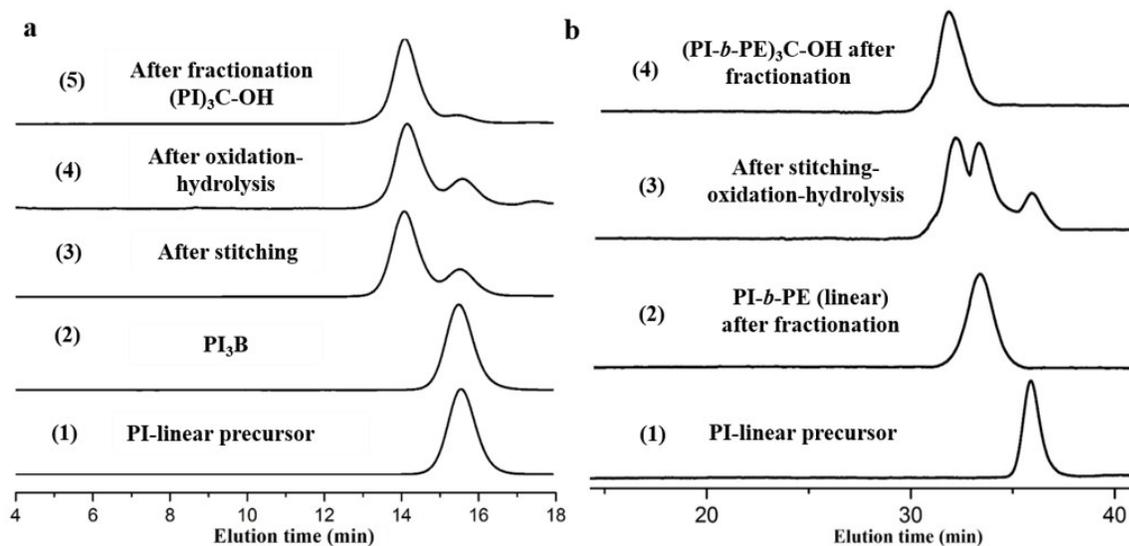
### **Polyhomologation of dimethylsulfoxonium methylide by macro-boron initiator and “stitching”-hydrolysis oxidation reaction.**

In a typical procedure, 180 mL of PS<sub>3</sub>B in benzene (0.10 mmol) introduced to a 500 ml flask. Then, dimethylsulfoxonium methylide solution (120 mL, 0.71 M) was added and the mixture was heated to 80 °C for 1.5 h to afford (PS-*b*-PE)<sub>3</sub>B. Afterwards, the solution was separated in two different flasks. In the first flask (30% of the total volume), TAO·2H<sub>2</sub>O (72.0 mg, 0.65 mmol) was added and the oxidation/hydrolysis was left to proceed at 70 °C for 12 h. Then the solution was poured into cold methanol and the precipitated polymer was dried under vacuum to obtain PS-*b*-PE block copolymer. In the second flask (70% of the total volume), 5.5 eq. DCME and 5.0 eq. Et<sub>3</sub>COLi with regard to the (PS-*b*-

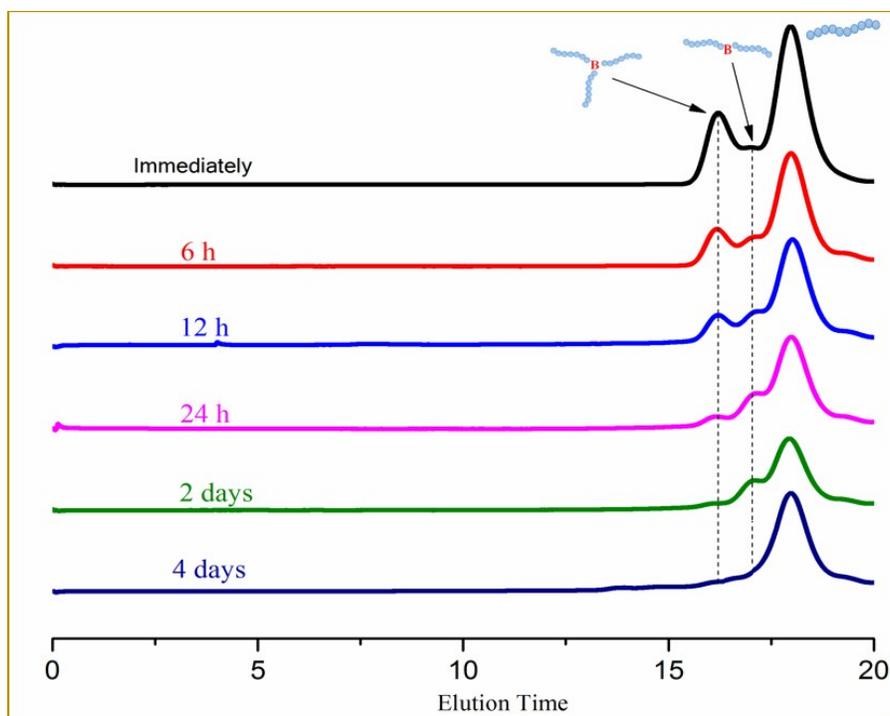
PE)<sub>3</sub>B were added and the solution was subjected to “stitching” reaction at 55 °C for 24 h. Then oxidation/hydrolysis with TAO·2H<sub>2</sub>O (140 mg, 1.30 mmol) took place as described above. The final solution was poured into methanol and the precipitated polymer was dried under vacuum to give (PS-*b*-PE)<sub>3</sub>C-OH. The same procedure was adopted for the synthesis and purification of (PI-*b*-PE)<sub>3</sub>C-OH and its linear counterpart (PI-*b*-PE).



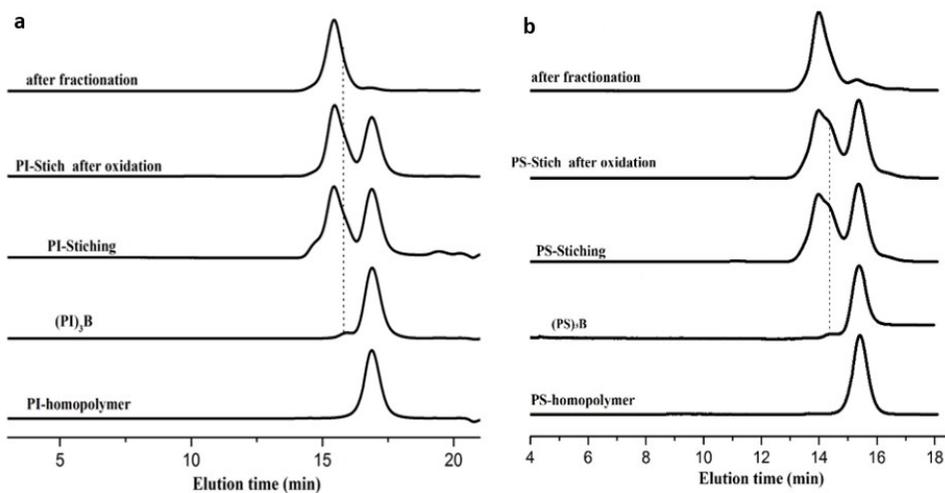
**Figure S1.** Glass apparatus attached on HV-line for the consecutive steps of linking, stitching and oxidation/hydrolysis reaction.



**Figure S2.** Monitoring the synthesis/fractionation of a) (PI)<sub>3</sub>C-OH (entry 1) and b) (PI-*b*-PE)<sub>3</sub>C-OH (entry 6) by GPC in THF, 35 °C and TCB, 150 °C respectively.



**Figure S3.** GPC traces obtained from withdrawn aliquots at different time intervals during the decomposition of 3-arm boron-linked polyisoprene star.



**Figure S4.** GPC (THF at 35 °C) traces for 3-arm star PI (Table 1, entry 2) (a) and PS (Table 1, entry 4) (b) after subsequent steps (from down to up): homopolymer precursor, after linking reaction with  $\text{BF}_3\text{OEt}_2$ , after stitching, after hydrolysis-oxidation and after fractionation.

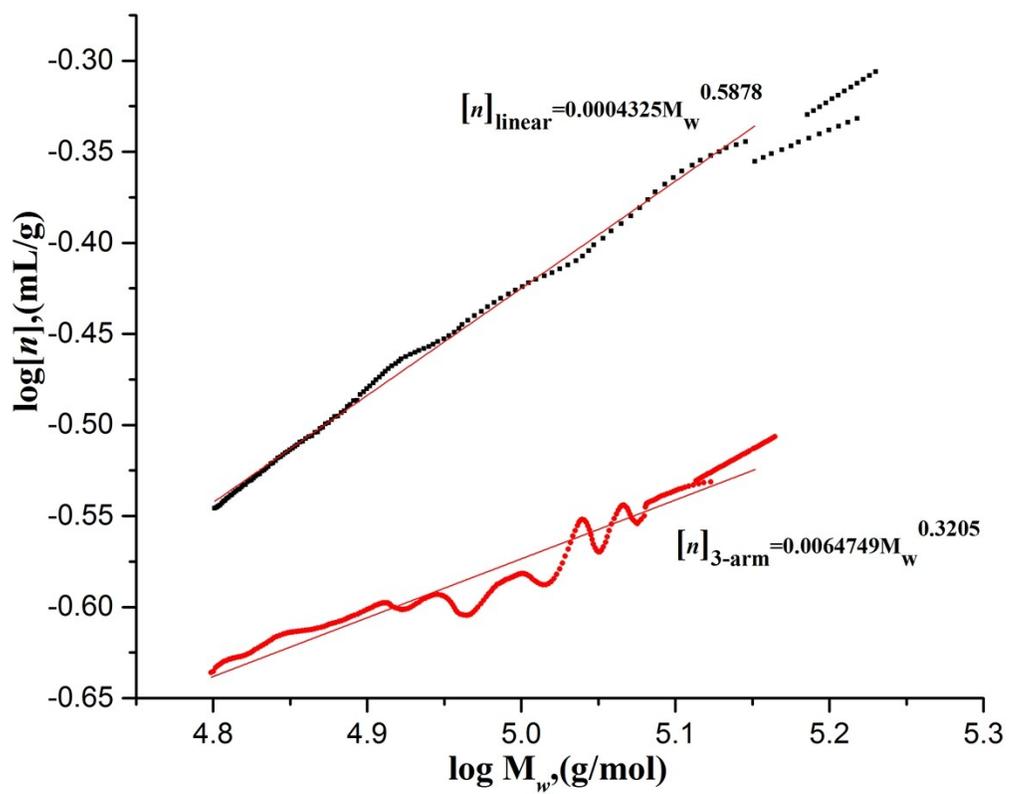
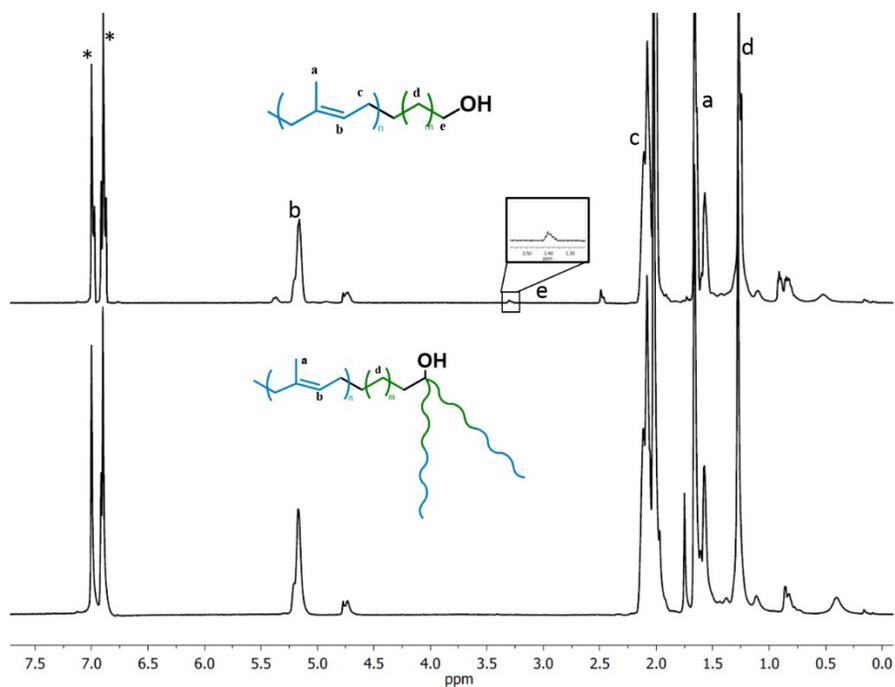
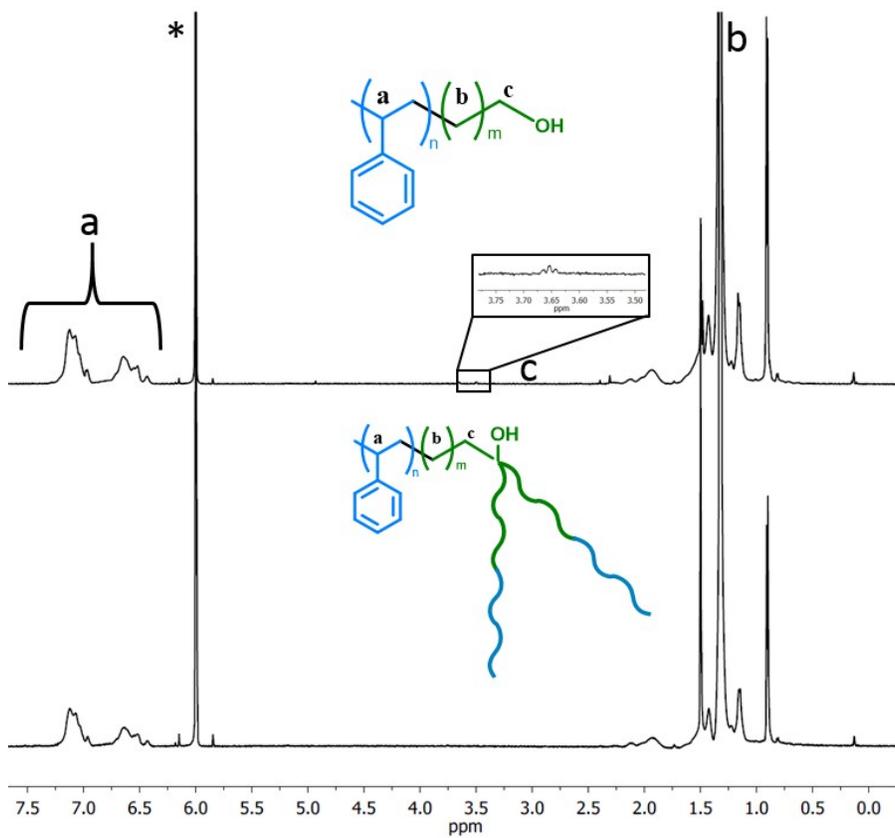


Figure S5. Mark-Houwink-Sakurada plot of linear PS and star PS<sub>3</sub>C-OH with identical molecular weights.



**Figure S6.** <sup>1</sup>H-NMR spectra of linear PI-*b*-PE-OH (top) and (PI-*b*-PE)<sub>3</sub> star block (down) in toluene-*d*<sub>8</sub> at 80 °C.



**Figure S7.** <sup>1</sup>H-NMR spectra of linear PS-*b*-PE-OH (top) and (PS-*b*-PE)<sub>3</sub>C-OH star-block copolymers (down) in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at 90 °C.

## References

1. N. Hadjichristidis, H. Iatrou, S. Pispas and M. Pitsikalis, *J. Polym. Sci. Part A: Polym. Chem.* 2000, **38**, 3211-3234.
2. E.J Corey and M. Chaykovsky, *J. Am. Chem. Soc.* 1965, **87**, 1353-1364.