

## **Poly(*N*-phenylenebenzimidazoles) as an alternative to classical polybenzimidazoles**

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### *Experimental*

3,3',4,4'-Tetraaminodiphenyloxide (Rubezhnoye Chemical Factory) was used without recrystallization, that is necessary for traditional PBI synthesis method.

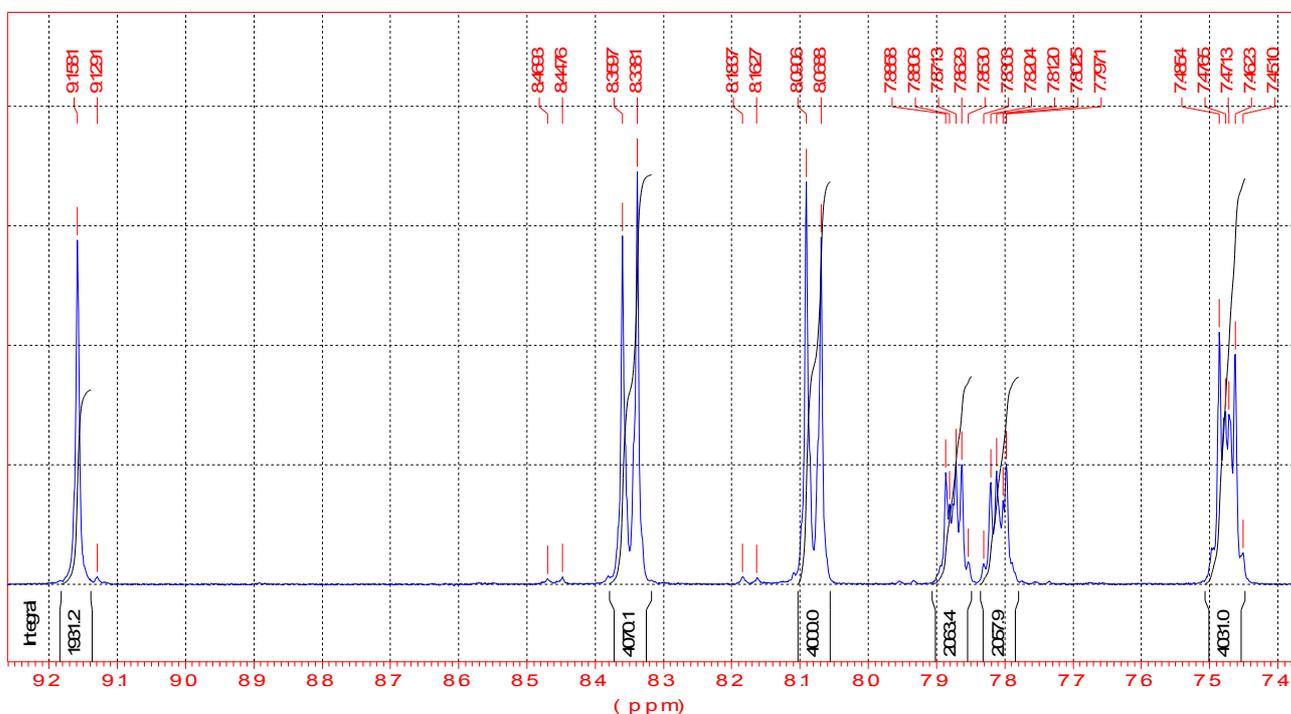
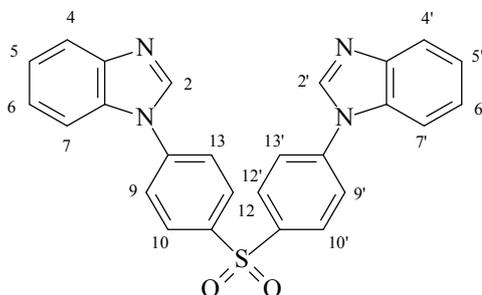
4,4'-Dichlorodiphenylsulphone and 4,4'-difluorodiphenylsulphone (Sigma-Aldrich) were dried in vacuum oven at 110 °C. Benzimidazole, formic (99%), phosphoric (85%), sulfuric (98%) and hydrochloric (35%) acids, *N,N*-dimethylacetamide (DMAc) and toluene were purchased from Acros Organics and used without additional purification. K<sub>2</sub>CO<sub>3</sub> was dried for 4 h at 160 °C in oven with air circulation.

<sup>1</sup>H NMR spectra of the studied compounds were recorded on a Bruker Avance 400 spectrometer in DMSO-D<sub>6</sub> solutions. Chemical shifts in δ scale were calculated using residual proton signals of the deuterated solvent as an internal reference (<sup>1</sup>H). Dynamic TGA was carried out with a MOM Q 1000 derivatograph (Hungary) in air at 5 K·min<sup>-1</sup> heating rate. TMA measurements were made on UIP-70M instrument (USSR) with 0.1 MPa constant pressure at 2.5 K·min<sup>-1</sup> heating rate. Melting points were measured on a Boetius heating bench and not corrected. DSC experiments were carried out with a Perkin-Elmer Diamond DSC in argon flow with heating rate 20 K·min<sup>-1</sup>. Reaction course and purity of isolated products were monitored by TLC using Silufol UV 254 plates, visualization under UV light or by exposing to iodine vapors. Reduced viscosity was measured at 25 °C with a capillary Ubbelohde viscometer at polymer concentration of 0.5 g·dL<sup>-1</sup>.

### *Bis[4,4'-(*N*-benzimidazolyl)phenylene]sulfone (Model reaction)*

Benzimidazole (1.04 g, 8.8 mmol), 4,4'-difluorodiphenylsulfone (1.02 g, 4 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.22 g, 8.8 mmol) were mixed with DMAc (3 ml) and toluene (1 ml) in a flask equipped with a stirrer. The mixture was heated under a flow of dry argon at 90 °C for 8 h and then at 150 °C for 4 h until the spot of 4,4'-difluorodiphenylsulfone became invisible on TLC. The mixture was poured into water (50 ml) and the white precipitate (1.75 g, 97%) was filtered off, washed with

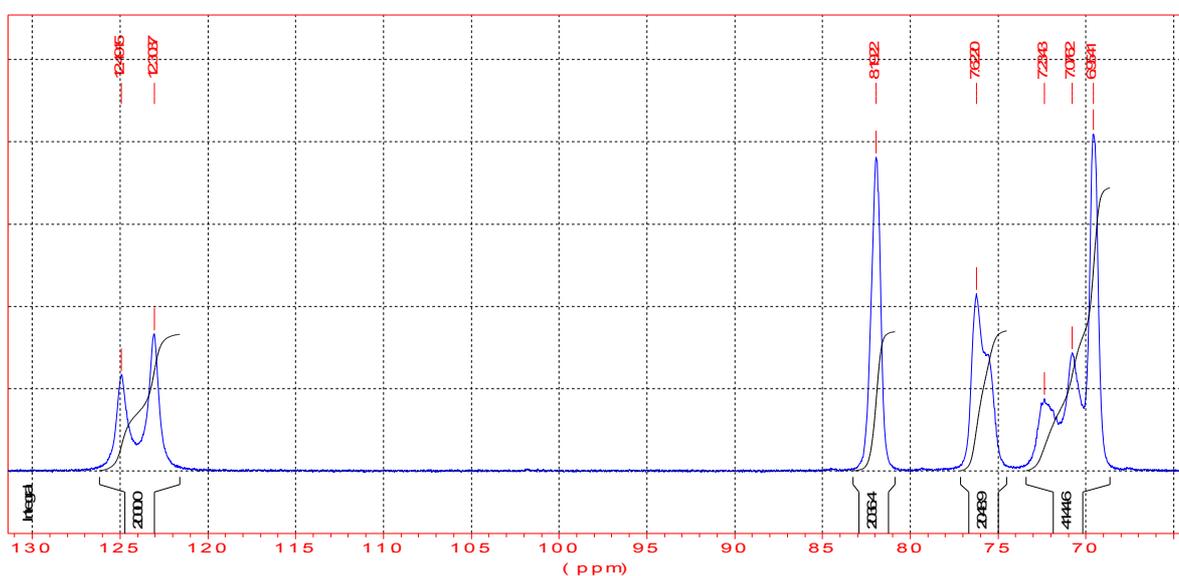
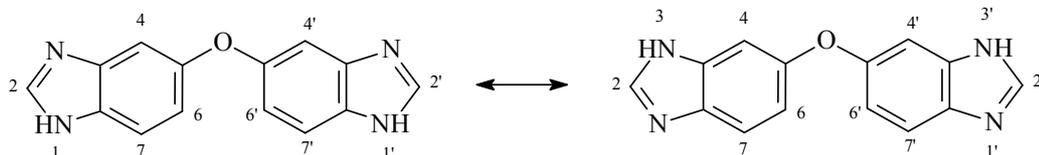
water and dried.  $^1\text{H NMR}$  (DMSO- $\text{D}_6$ ):  $\delta = 9.16$  (s, 2H,  $\text{H}^2$  and  $\text{H}^{2'}$  of benzimidazole moieties), 8.35 (part A of AB system  $J = 8.6$  Hz, 4H,  $\text{H}^{10}$ ,  $\text{H}^{12}$ ,  $\text{H}^{10'}$  and  $\text{H}^{12'}$  of phenylene moieties), 8.08 (part B of AB system  $J = 8.6$  Hz, 4H,  $\text{H}^9$ ,  $\text{H}^{13}$ ,  $\text{H}^{9'}$  and  $\text{H}^{13'}$  phenylene moieties), 7.89-7.86 (m, 2H,  $\text{H}^4$  and  $\text{H}^{4'}$  of benzimidazole moieties), 7.82-7.79 (m, 2H,  $\text{H}^7$  and  $\text{H}^{7'}$  of benzimidazole moieties), 7.49-7.46 (m, 4H,  $\text{H}^5$ ,  $\text{H}^6$ ,  $\text{H}^{5'}$  and  $\text{H}^{6'}$  of benzimidazole moieties).



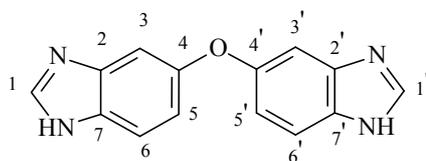
#### Synthesis of 5(6), 5'(6')-bis(benzimidazole)oxide monomer.

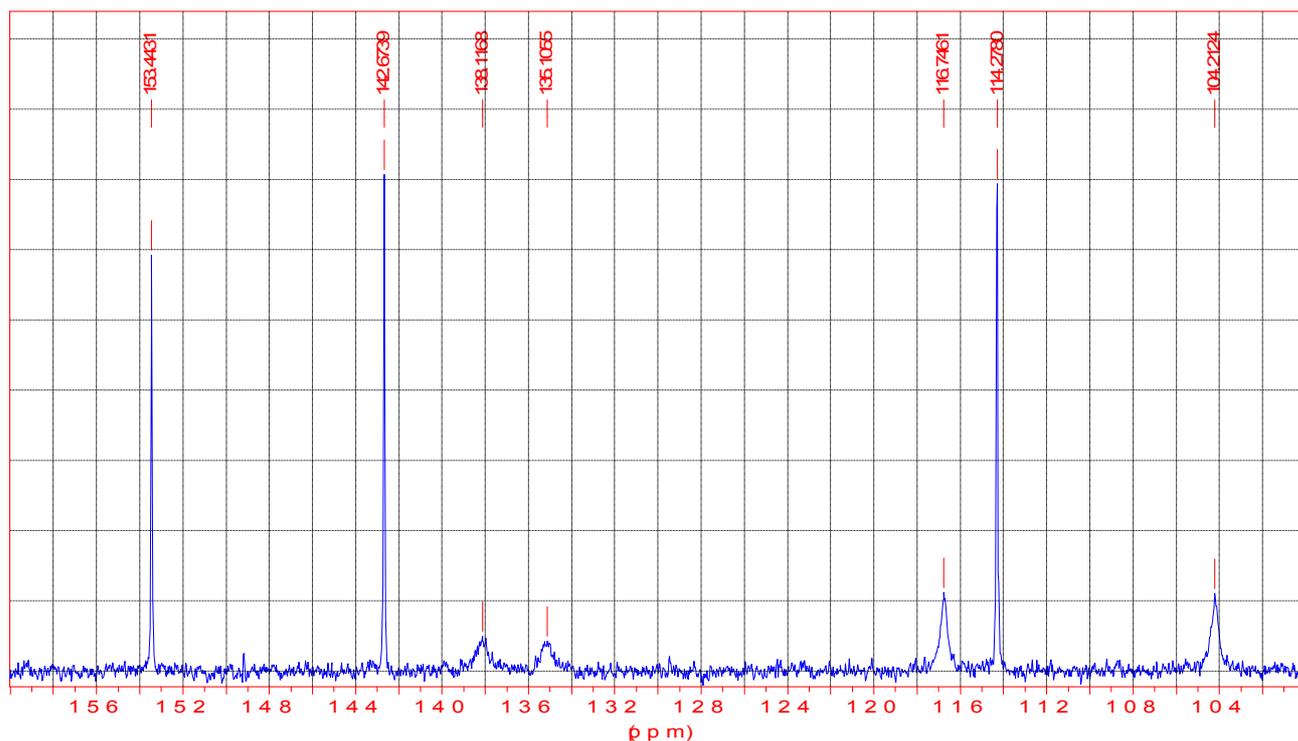
3,3',4,4'-Tetraaminodiphenyloxide (32 g, 0.14 mol) was diluted in the mixture of  $\text{H}_2\text{O}$  (42 ml),  $\text{H}_2\text{SO}_4$  (3 ml) and  $\text{HCOOH}$  (28 ml) and heated at reflux temperature for 4 h. Then the mixture was poured into  $\text{H}_2\text{O}$  (300 ml), and  $\text{Na}_2\text{CO}_3$  (5 g) was added in small portions (to avoid excessive gas emission and foaming). Some amount of  $\text{NH}_3_{[\text{aq}]}$  was added to adjust pH 10. The precipitate was filtered off and dissolved in a hot mixture of  $\text{H}_2\text{O}$  (500 ml) and i-PrOH (250 ml) with the addition of activated charcoal. The hot solution was passed through a filter and left for the crystallization of a hydrate product; then, the crystals were filtered off. DSC data of dried

crystals contain significant endothermic peaks at 119 °C (hydrate form), 227 and 241 °C (free product in isomeric forms). The pure and dry product (28.4 g, 81 % yield) was obtained by the azeotropic drying of a suspension of the hydrate form in toluene (300ml) with further filtering and drying under vacuum at 160 °C. DSC: peak at 241°C. <sup>1</sup>H NMR (DMSO-D<sub>6</sub>): δ = 12.49, 12.30 (2s, 2H, H<sup>1</sup>, H<sup>1'</sup>, H<sup>3</sup>, H<sup>3'</sup>, -NH- isomeric forms), 8.19 (s, 2H, H<sup>2</sup> and H<sup>2'</sup>), 7.70-7.45 (m, 2H, H<sup>7</sup> and H<sup>7'</sup>), 7.40-6.85 (m, 4H, H<sup>4</sup>, H<sup>5</sup>, H<sup>4'</sup> and H<sup>5'</sup>)

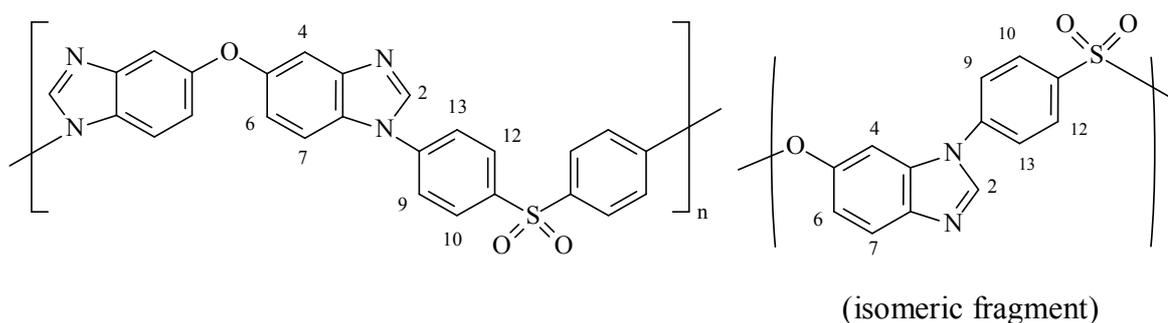


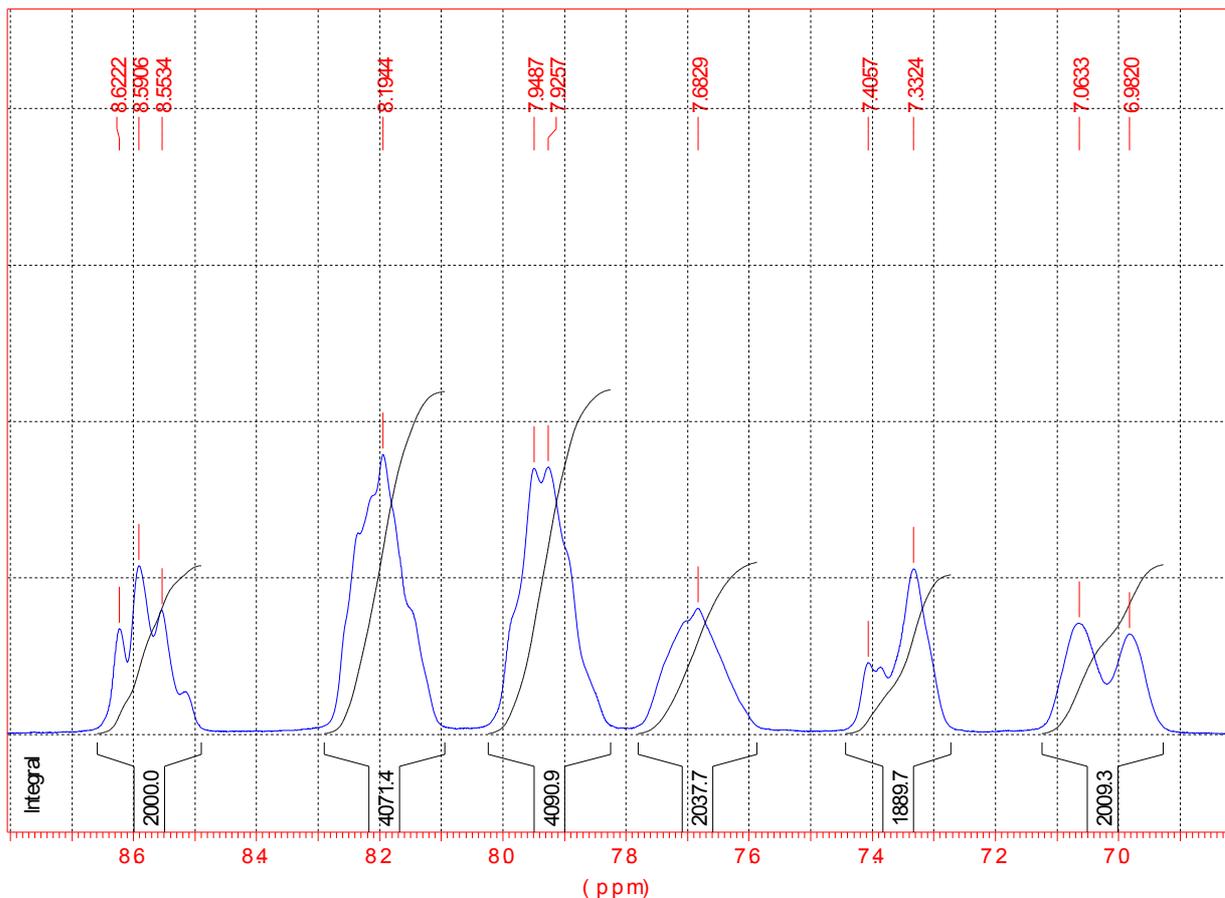
<sup>13</sup>C NMR (DMSO-D<sub>6</sub>): δ = 153.44 (C<sup>4</sup>, C<sup>4'</sup>), 142.67 (C<sup>1</sup>, C<sup>1'</sup>), 138.12 (C<sup>2</sup>, C<sup>2'</sup>), 135.11 (C<sup>7</sup>, C<sup>7'</sup>), 116.7 (C<sup>6</sup>, C<sup>6'</sup>), 114.3 (C<sup>5</sup>, C<sup>5'</sup>), 104.2 (C<sup>3</sup>, C<sup>3'</sup>).



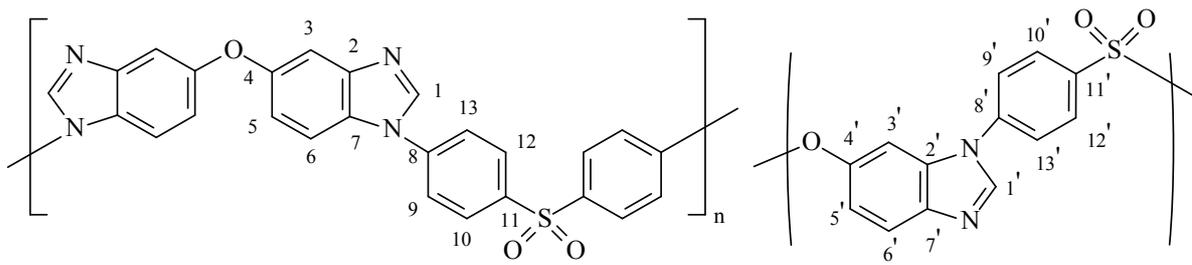


The Polymer.  $^1\text{H}$  NMR (DMSO- $\text{D}_6$ ):  $\delta = 8.66\text{-}8.49$  (m, 2H,  $\text{H}^2$  of benzimidazole moieties within different isomeric segments), 8.29-8.09 (m, 4H,  $\text{H}^{10}$  and  $\text{H}^{12}$  of phenylene moieties), 8.02-7.83 (m, 4H,  $\text{H}^9$  and  $\text{H}^{13}$  of phenylene moieties), 7.78-7.58 (m, 2H,  $\text{H}^7$  of benzimidazole moieties), 7.44-7.25 (m, 2H,  $\text{H}^4$  of benzimidazole moieties), 7.13-6.90 (d, 2H,  $\text{H}^6$  of benzimidazole moieties).

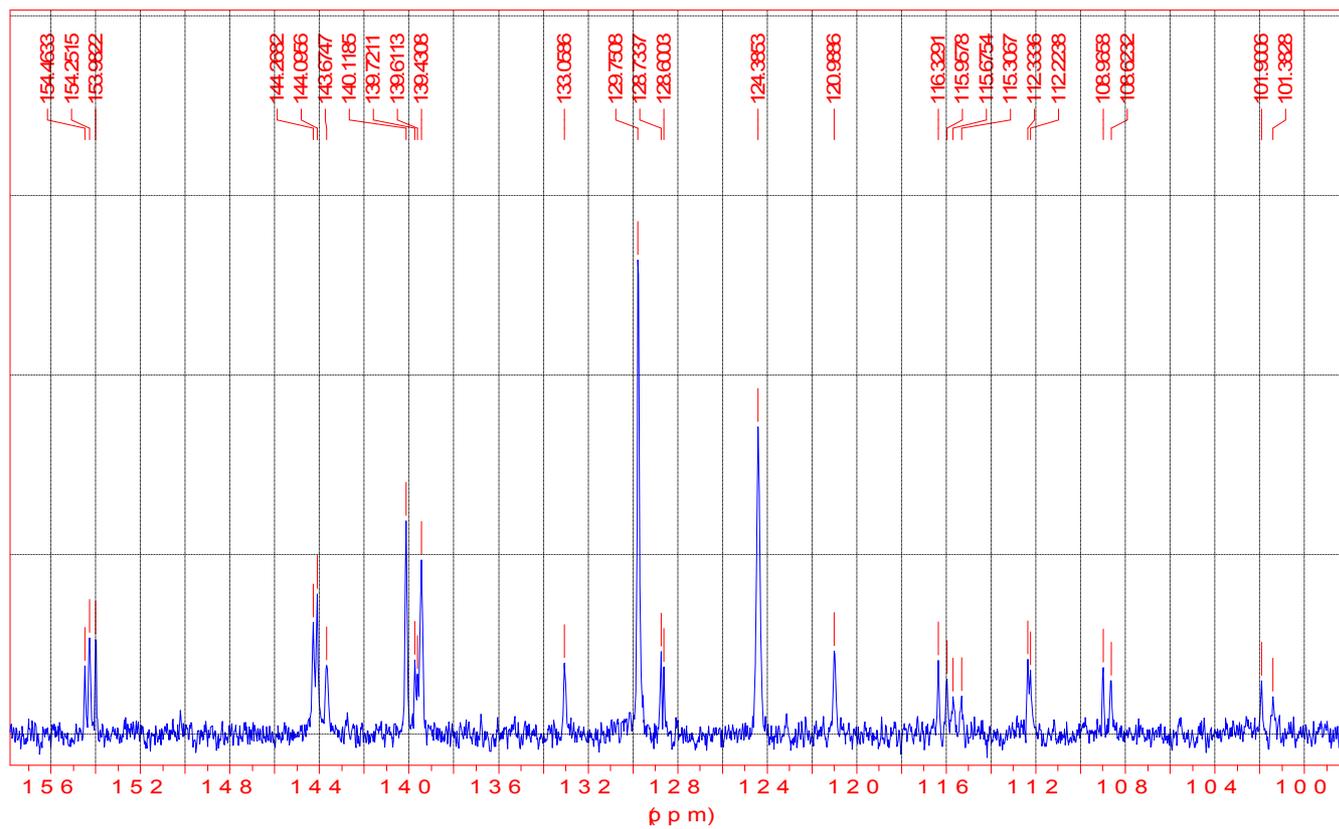




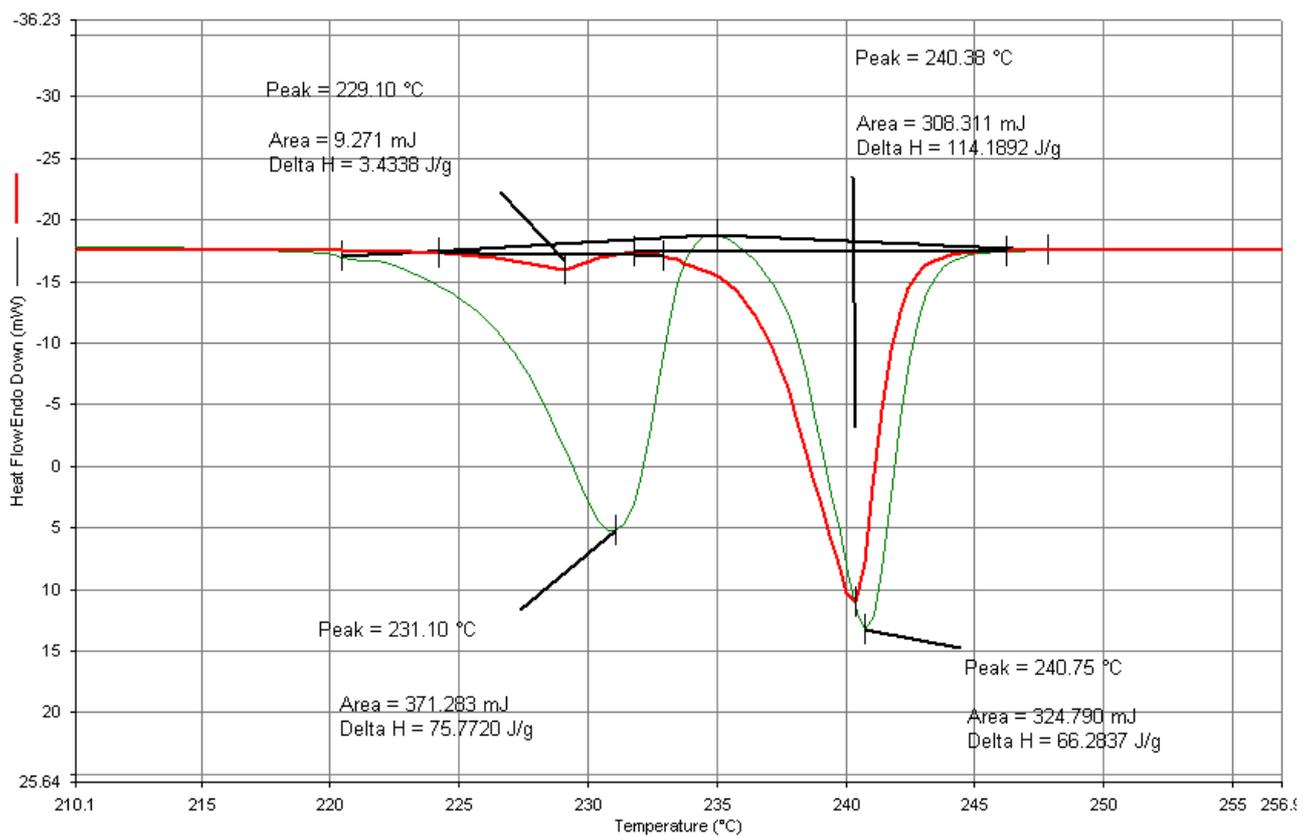
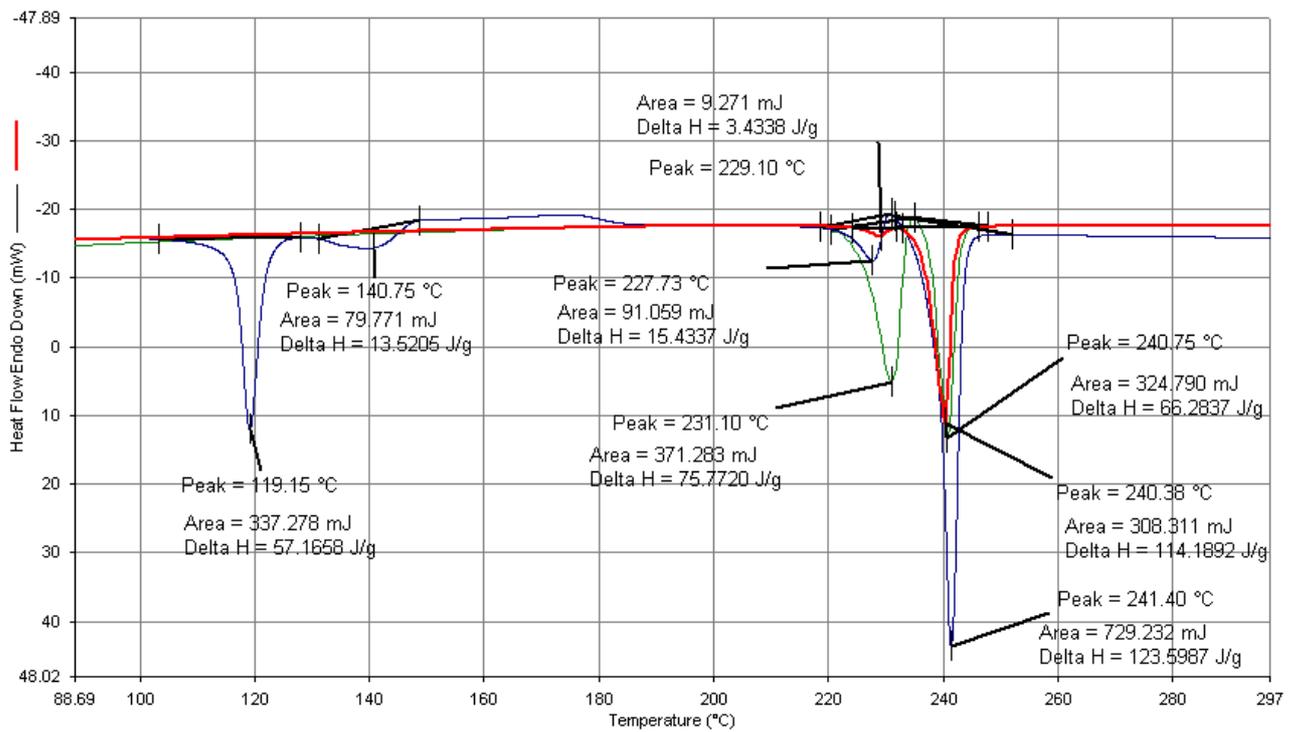
$^{13}\text{C}$  NMR (DMSO- $\text{D}_6$ ):  $\delta = 154.46\text{-}153.98$  ( $\text{C}^4$ ,  $\text{C}^{4'}$ ),  $144.27$  ( $\text{C}^{8'}$ ),  $144.10$  ( $\text{C}^2$ ),  $143.67$  ( $\text{C}^8$ ),  $140.11$  ( $\text{C}^1$ ,  $\text{C}^{1'}$ ),  $139.67$  ( $\text{C}^{2'}$ ),  $139.43$  ( $\text{C}^7$ ,  $\text{C}^{7'}$ ),  $133.06$  ( $\text{C}^{11}$ ,  $\text{C}^{11'}$ ),  $129.75$  ( $\text{C}^{10}$ ,  $\text{C}^{10'}$ ,  $\text{C}^{11}$ ,  $\text{C}^{11'}$ ),  $128.66$  ( $\text{C}^{6'}$ ),  $124.38$  ( $\text{C}^9$ ,  $\text{C}^{13}$ ),  $120.99$  ( $\text{C}^{9'}$ ,  $\text{C}^{13'}$ ),  $116.33\text{-}115.31$  ( $\text{C}^5$ ,  $\text{C}^{5'}$ ),  $112.27$  ( $\text{C}^6$ ),  $108.96\text{-}108.62$  ( $\text{C}^3$ ),  $101.90\text{-}101.38$  ( $\text{C}^{3'}$ ).



(isomeric fragment)



**DSC of 5(6),5'(6')-Bis(benzimidazole)oxide**

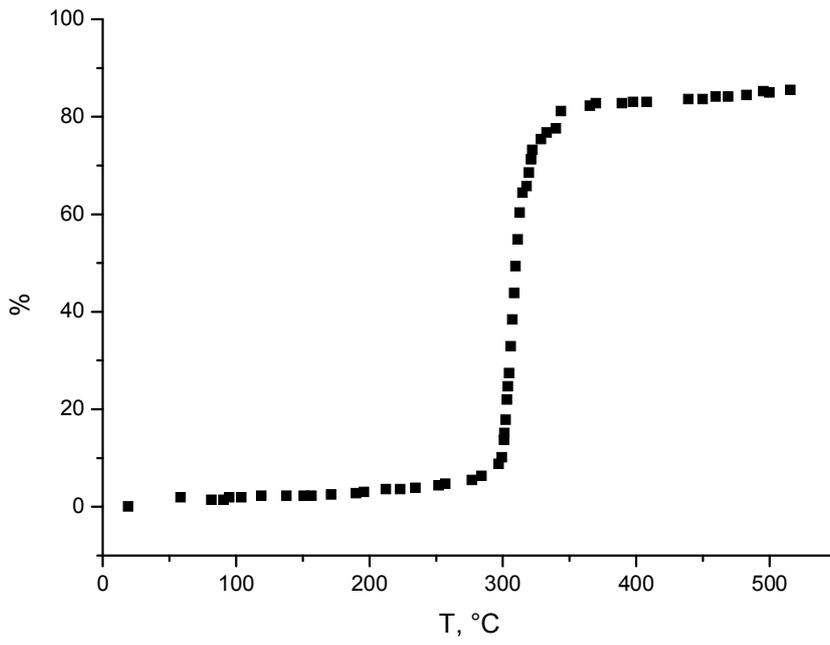


**Blue** – product after reaction and drying at 120 °C

**Red** – azeotropic drying in toluene and 160 °C in vac oven

**Green** – product after azeotropic drying with different isomer ratio

### TMA of the Polymer



### TGA of the Polymer:

