

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Competing Desulfonation and S<sub>N</sub>AR Reactions During Aromatic Poly(Ether-sulfone) Synthesis

R. S. Mani<sup>a</sup>; D. K. Mohanty<sup>b</sup>

<sup>a</sup> Michigan Molecular Institute, Midland, MI <sup>b</sup> Department of Chemistry and Center for Applications in Polymer Science, Central Michigan University, Mt. Pleasant, MI

**To cite this Article** Mani, R. S. and Mohanty, D. K.(1995) 'Competing Desulfonation and S<sub>N</sub>AR Reactions During Aromatic Poly(Ether-sulfone) Synthesis', *Journal of Macromolecular Science, Part A*, 32: 1, 1189 — 1197

**To link to this Article:** DOI: 10.1080/10601329508020340

**URL:** <http://dx.doi.org/10.1080/10601329508020340>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## COMPETING DESULFONYLATION AND S<sub>N</sub>AR REACTIONS DURING AROMATIC POLY(ETHER-SULFONE) SYNTHESIS

R. S. Mani <sup>a</sup> and D. K. Mohanty \*

Department of Chemistry and Center for Applications in Polymer Science  
Central Michigan University  
Mt. Pleasant, MI 48859

### ABSTRACT

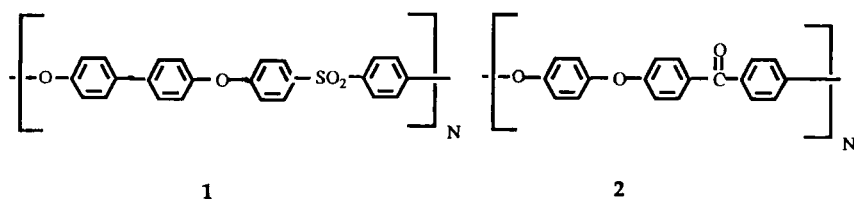
An activated bisfluoride, 4,4'-(4-fluorobenzoyl) diphenylsulfone, undergoes desulfonylation reactions during the preparation of polymers with a bisphenol in dimethylacetamide/toluene, in the presence of anhydrous potassium carbonate at 165 °C. Modified reaction conditions were developed to synthesize a moderately high molecular weight polymer via nucleophilic displacement of the fluorine atoms while circumventing desulfonylation reaction.

### INTRODUCTION

Aromatic polyethers are materials of significant academic and commercial interest.<sup>1</sup> Sulfone containing polyethers, e.g., **1**, shows exceptional oxidative stability and high glass transition temperature (T<sub>g</sub>).<sup>2</sup> On the other hand, keto functional polyethers, such as **2**, is semicrystalline and exhibits a high degree of crystallinity and the resulting solvent resistance.<sup>3</sup> We report herein our attempts at preparing a

---

a : Present Address : Michigan Molecular Institute, Midland, MI- 48640



family of macromolecules containing both sulfone and keto functionality in the repeat unit.

### EXPERIMENTAL

**Materials.** Bisphenol -A (4,4'-isopropylidene diphenol), a gift from Dow Chemicals, was recrystallized from toluene. Thionyl chloride (Aldrich) was distilled over triphenyl phosphite. Dimethyl acetamide (DMAc) (Aldrich) was distilled under reduced pressure over calcium hydride. 4-toluenesulfonyl chloride (Aldrich) was distilled under reduced pressure prior to use. All other chemicals were used as received.

**4,4'-Dimethyl diphenylsulfone.** A two liter, three-necked, round bottomed flask, fitted with a nitrogen inlet, an over-head stirrer and a condenser was charged with 4-toluenesulfonyl chloride, **4** (71.0 g, 0.37 mole) and toluene (500 mL). The flask was cooled externally by an ice bath. Aluminum chloride (74.48 g, 0.56 mole) was added to the reaction mixture over a period of twenty minutes. The ice bath was removed after thirty minutes and the reaction was allowed to continue with stirring over a period of 2h. The reaction mixture was then poured slowly into ice-cold concentrated aqueous hydrochloric acid solution. The crude product was extracted with dichloromethane, washed with a saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate, filtered and the filtrate was evaporated to isolate the crude product. The crude solid was recrystallized from ethyl acetate to yield **5** (79 % yield). mp 150-152 °C; IR (Solid film) 1598, 1317, 1298, 1154  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300  $\text{MHz}$ )  $\delta$  7.8 (m, 4H), 2.3 (m, 4H), 2.4 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75  $\text{MHz}$ )  $\delta$  19.7, 125.7, 128.0, 137.2, 142.1.

**4,4'- Diphenylsulfone dicarboxylicacid.** A three-necked (3L), round-bottomed flask fitted with an over-head stirrer and a condenser was charged with **5** (20.07 g, 0.08 mole), water (150 mL), pyridine (150 mL) and potassium permanganate (51.5 g, 0.32 mole). It was heated carefully until the initial reaction

exotherm was observed. The reaction vessel was cooled to room temperature and an additional amount of potassium permanganate (103.0 g, 0.64 mole) was added and the reaction was allowed to continue with vigorous stirring under reflux for five days. The reaction vessel was cooled, and the reaction mixture was filtered through celite. The filtrate was acidified with concentrated aqueous hydrochloric acid and the crude product was collected by filtration. The product, **6**, was dried in a vacuum oven at 80 °C for 24h (72 % yield). A small sample was purified further by recrystallization from ethyl acetate. mp 410 °C (DSC); IR (Solid film) 3086, 1698, 1329, 1284, 1159  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ , 300 MHz)  $\delta$  8.2 (br s, 8H), 13.2 (br s, 2H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 75 MHz)  $\delta$  127.9, 130.7, 135.6, 143.8, 166.0.

**4,4'-(4-Fluorobenzoyl) diphenylsulfone.** The diacid, **6** (50.4 g, 0.16 mole), was taken in a three-necked, round-bottomed flask fitted with a nitrogen inlet, a condenser and an over-head stirrer. Thionyl chloride (500 mL, excess), dimethylformamide (1 mL) were added and the reaction mixture was allowed to reflux for 14h. Excess thionyl chloride was removed by distillation from the homogeneous reaction mixture. The crude residue was dissolved in fluorobenzene (500 mL, excess) and aluminum chloride (66.2 g, 0.49 mole) was added in portions. The reaction mixture was heated under reflux with stirring for 14h. It was then cooled to room temperature and poured into ice/HCl mixture with constant stirring. The crude product was isolated by filtration, dissolved in dichloromethane, washed with a saturated solution of sodium bicarbonate, dried over anhydrous magnesium sulfate, filtered and the filtrate was evaporated to isolate the crude product, **3a**. It was purified by recrystallization from ethyl acetate (85 % yield). mp 183-184 °C (DSC); IR (Solid film) 1653, 1597, 1501, 1328, 1296, 1279, 1161, 748, 676  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.1-8.0 (m, 2H), 7.9-7.8 (m, 4H), 7.3-7.2 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  191.7, 165.8, 162.4, 142.1, 140.2, 131.0, 130.9, 128.6, 126.1, 114.2, 113.9.

**4,4'-(4-tert-Butylphenoxybenzoyl) diphenylsulfone.** A 100 mL round-bottomed, three-necked flask fitted with a nitrogen inlet, a thermometer, a magnetic stirring bar and a Dean-Stark trap fitted with a condenser was charged with **3a** (0.115 g, 0.25 mmole), 4-tert-butyl phenol (0.075 g, 0.5 mmole), anhydrous potassium carbonate (0.72 g, 0.52 mmole). This was followed by the addition of DMAc (20 mL) and toluene (15 mL). The reaction mixture was heated to a temperature of 125 °C and the reaction was allowed to continue with stirring for

16 h. Water, the by-product of the reaction mixture was azeotropically distilled with toluene and removed via the Dean-Stark trap. The reaction mixture was cooled to room temperature, diluted with dichloromethane, filtered and the filtrate was distilled under reduced pressure to remove all solvents. The crude product was percolated down a silica gel column with dichloromethane to yield **10** (80 %). mp 190-192°C; IR(Solid film) 1652, 1591, 1500, 1395, 1245, 1169, 956  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300MHz)  $\delta$  8.07(m, 4H), 7.85(m, 4H), 7.76(m, 4H), 7.41(m, 4H), 7.01(m, 8H);  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , 75 MHz)  $\delta$  193.0, 163.0, 152.6, 148.0, 143.7, 142.8, 132.6, 130.3, 127.8, 127.0, 119.9, 117.0, 34.4, 31.4.

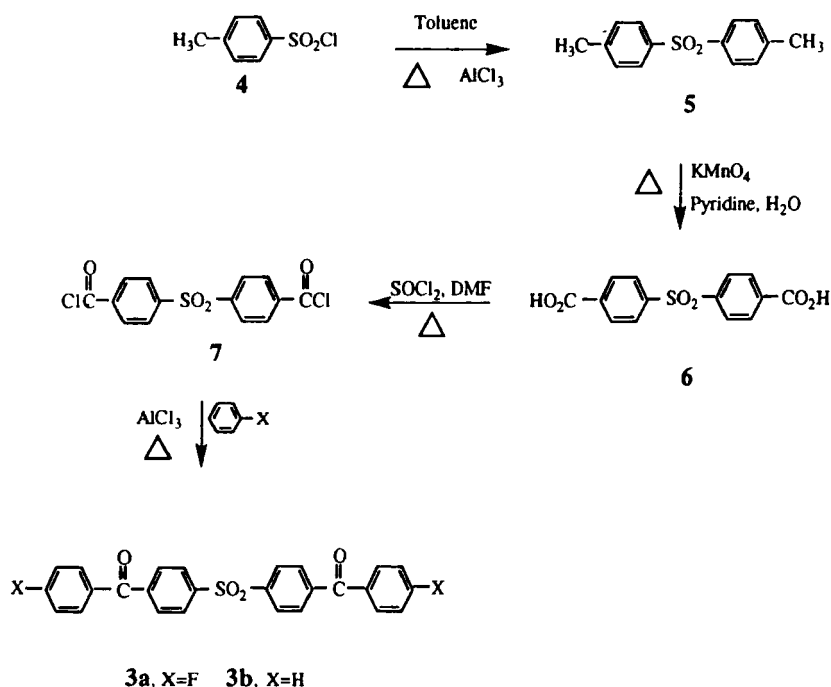
**Polymer Synthesis.** Polymerization reactions of bisphenol-A with **3a** was conducted in DMAc/toluene at 125 °C in presence of excess anhydrous potassium carbonate according to a previously reported procedure.<sup>4, 5</sup>

## RESULTS AND DISCUSSION

Sulfone containing polyether, **1**, is usually prepared by the reactions of 4,4'-dihydroxy biphenyl with 4,4'-dichlorodiphenyl sulfone in a dipolar aprotic solvent via nucleophilic aromatic substitution reactions ( $\text{S}_{\text{N}}\text{AR}$ ).<sup>4</sup> On the other hand aromatic polyether ketone, **2**, is synthesized by the reactions of hydroquinone with 4,4'-difluorobenzophenone. In order to achieve some of the important attributes of both sulfone and keto groups in the polyether repeat unit, monomer **3a** (Scheme 1) was prepared.

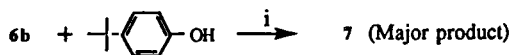
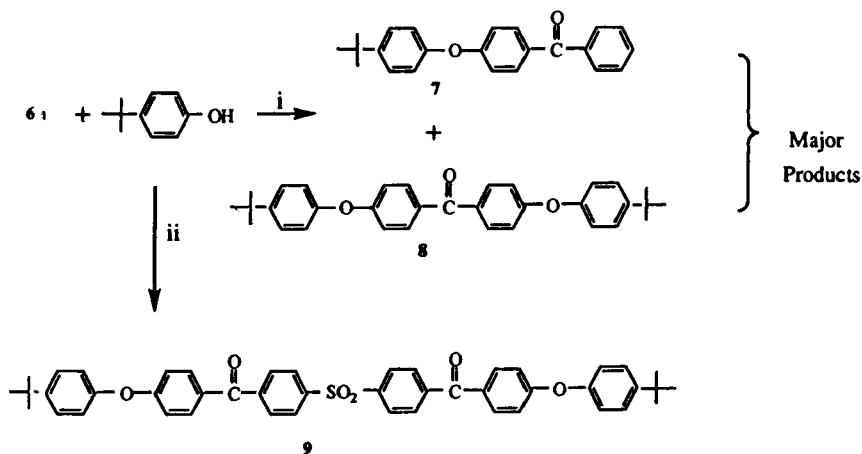
**Monomer Synthesis :** The difluoro sulfone monomer **3a** was synthesized starting from 4-toluenesulfonyl chloride, **4** (Scheme 1). Friedel Crafts acylation with toluene gave dimethyl sulfone, **5**, in excellent yield. Compound **5** was converted to the diacid, **6**, by oxidation with potassium permanganate in aqueous pyridine in 90% yield.<sup>6</sup> The diacid was converted to its acid chloride **7** and subsequently to the desired monomer **3a** in 80 % overall yield by Friedel- Crafts acylation with fluorobenzene.<sup>7</sup>

**Model Compound Studies :** Model compound studies were carried out to explore the feasibility of synthesizing high molecular weight polymers from monomer **3a** and two equivalents of 4-tert-butyl phenol (Scheme 2). The reactions were conducted in dimethyl acetamide, toluene, and potassium carbonate at a temperature of 140 °C for 2h to remove water, the byproduct, by azeotropic distillation with toluene. The temperature was then slowly raised to 165 °C and the



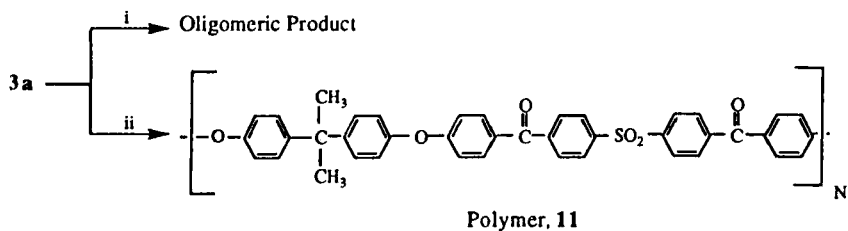
Scheme 1

reaction was allowed to continue at that temperature for an additional 8h. The two major components, **8** and **9**, isolated from the reaction mixture were devoid of the sulfonyl moieties (Scheme 2).<sup>7</sup> In order to further understand the desulfonation processes in the absence of  $\text{S}_{\text{N}}\text{AR}$  reactions of the fluoride atoms, model compound studies were conducted with the dehalogenated analog of compound **3a**. The desired compound, **3b**, prepared according to Scheme 1, was allowed to react with two equivalents of 4-*tert*-butyl phenol under the same reaction conditions (Scheme 2). Compound **8** was isolated as the major product.<sup>7</sup> These findings suggested that under these reaction conditions; a) compound **3a**, undergoes both desulfonation and nucleophilic  $\text{S}_{\text{N}}\text{AR}$  reactions with 4-*tert*-butyl phenoxide and b) because of desulfonation reactions, the 1:1 stoichiometry required to synthesize a high molecular weight polymer from bisphenol-A and **3a** would be disturbed and



Reagents: i, DMAc, toluene,  $\text{K}_2\text{CO}_3$ ,  $165^\circ\text{C}$ , 16h ; ii, DMAc, toluene,  $\text{K}_2\text{CO}_3$ ,  $125^\circ\text{C}$ , 16h

Scheme 2



Reagents: i, Bisphenol-A, DMAc, toluene,  $\text{K}_2\text{CO}_3$ ,  $165^\circ\text{C}$ , 16h ;  
ii, Bisphenol-A, DMAc, toluene,  $\text{K}_2\text{CO}_3$ ,  $125^\circ\text{C}$ , 16h

Scheme 3

only oligomeric products would be formed.<sup>8</sup> Nucleophilic desulfonation reactions of arylsulfones have been known for a long time.<sup>9,10</sup> They are facilitated by the presence of electron-withdrawing substituents at positions ortho and para to the sulfonyl moiety.<sup>11,12</sup> Desulfonation reactions have been used in organic synthesis to reach the target molecule, and a variety of these reactions involving aromatic sulfones are well documented.<sup>13, 14</sup>

Indeed, all polymerization reactions failed to yield even moderately high molecular weight polymers (Scheme 3). In order to suppress the undesirable desulfonation process, several different model reactions were conducted under modified reaction conditions. It was possible to synthesize the desired bisether, **10**, as the only product by lowering the reaction temperature to 125 °C (Scheme 2).

**Polymer Synthesis:** Polymerization reactions of monomer **3a** and bisphenol-A in dimethyl acetamide, toluene, and potassium carbonate at 125 °C for 16h (Scheme 3) afforded a moderately high molecular weight polymer. Polymer, **11**, was isolated by coagulation of the reaction mixture in a tenfold volume of methanol. The polymer which precipitated, was collected by filtration, dried at 60 °C under vacuum for 18h. The polymer was characterized<sup>15</sup> by a variety of techniques including viscometry, differential thermal analysis (DSC) and thermogravimetric analysis (TGA). These data are indicative of the low molecular weight nature of the polymers. Furthermore, the polymer undergoes desulfonation reactions and degrades to lower molecular weight fragments under alkaline conditions in DMAc at elevated temperatures.

## CONCLUSIONS

It is possible to prepare an alkali sensitive, moderately high molecular weight polymer from an activated sulfone/ ketone containing monomer and bisphenol-A under controlled reaction conditions while avoiding the undesirable desulfonation reactions.

## ACKNOWLEDGMENTS

The authors wish to acknowledge partial support of this project from PRF Grant 21146-AC7 administered by the American Chemical Society, Grant #62811 made available to DKM by the Department of Chemistry and the Michigan Polymer



Consortium, Grant #48450, from the FRCE committee, Central Michigan University, and Grant #62844 from the Research Excellence Fund, State of Michigan. A University Research Professorship award to DKM by Central Michigan University was extremely helpful. Partial support for the purchase of the GE QE-300 NMR Spectrometer used in this work was provided by NSF/ Grant #USE-8852049.

## REFERENCES AND NOTES

1. Johnson, R. N.; Harris, J. E. *Encyclopedia of Polymer Science*; 2nd Ed., Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G. Eds.; John Wiley and Sons, Inc.: New York, **1988**; Vol. 13, pp.196.
2. Atwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R. J.; Rose, J. B.; Staniland, P. A. *Polymer* **1981**, 22, 1096.
3. Johnson, R. N.; Farnham, A. G.; Callendining, R. A.; Hale, W. F.; and Merian, C. N. *J. J. Poly. Sci. Polym. Chem. Ed.* **1967**, 5, 2375.
4. Hedrick, J. L.; Mohanty, D. K.; Johnson, B. C.; Viswanathan, R.; Hinkley, J. A.; McGrath, J. E. *J. Polym. Sci. Polym. Chem. Ed.* **1986**, 24, 287.
5. a) Mani, R. S.; Zimmerman, B.; Bhatnagar, A.; Mohanty, D. K. *Polymer* **1993**, 34, 171. b) Bhatnagar, A.; King B.; Mohanty, D. K. *Polymer* **1994**, 35, 1111.
6. Morgan, P. W.; Herr, B. C. *J. Am. Chem. Soc.* **1952**, 74, 4526.
7. **3b** : mp 200-202°C; IR (Solidfilm) 1664, 1660, 1595, 1447, 1398, 1275, 1164, 924, 764 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.12-7.85 (m, 18H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 194.9, 143.9, 143.1, 136.3, 133.3, 130.5, 130.1, 128.6, 127.9.
- 8** : mp 74-76°C; IR (Solid film) 1658, 1592, 1497, 1277, 1245, 1169, 976, 748 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.83-6.69 (m, 13H), 1.34 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz) δ 195.5, 162.0, 153.0, 147.6, 138.1, 132.4, 132.1, 131.7, 129.8, 128.2, 126.9, 119.7, 116.9, 34.5, 31.5.
- 9** : mp 138- 140°C; IR (solid film) 2961, 1654, 1593, 1500, 1242, 1170, 928, 766 cm<sup>-1</sup>; <sup>1</sup>NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.79(m, 4H), 7.40(m, 4H), 7.02(m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 194.3, 161.7, 153.1, 147.5, 132.2, 130.9, 126.8, 119.6, 116.9, 34.4, 31.5.

8. Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*; Prentice Hall: 1990, pp. 25.
  9. Otto, R. *Chem.Ber.* **1886**, 19, 2425.
  10. Ingold, C. K.; Jessop, J. A. *J. Chem. Soc.* **1930**, 708.
  11. Loudon, J. D. *J. Chem. Soc.* **1935**,537.
  12. Levi, A. A.; Smiles, S. *J. Chem. Soc.* **1932**, 1488.
  13. Simpkins, N. S. in *Sulphones in Organic Synthesis*; Baldwin, J. E.; Magnus, P. D. Eds.; Tetrahedron Organic Chemistry Series, Pergamon, 1993, Vol. 10, Ch. 9.
  14. Cerfontain, H. in *Mechanistic Aspects in Aromatic Sulfonation and Desulfonation*, Interscience; 1968, Ch. 15.
  15. Polymer **11** was characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. According to the  $^{13}\text{C}$  NMR, it is very likely that polymer chains are hydroxyl terminated. The intrinsic viscosity value and the relatively low  $T_g$  are indicative of the moderate molecular weight nature of **11**.
- 11** : IR(solid film) 3059, 2969, 1659, 1591, 1499, 1277, 1244, 1169, 1014, 929, 731  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$  8.08(m, 4H), 7.86(m, 4H), 7.77(m, 4H), 7.28(m, 4H), 7.00(m, 8H), 1.72(s, 6H).  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , 75 MHz)  $\delta$  193.6, 163.0, 162.5, 153.0, 147.1, 143.7, 142.7, 132.5, 132.1, 130.5, 130.2, 129.6, 128.4, 128.3, 127.8, 127.7, 120.4, 119.8, 119.5, 117.1, 116.1, 113.7, 42.4, 30.9.  $T_g$  = 148  $^\circ\text{C}$  (DSC), third heating, heating rate, 10  $^\circ\text{C}/\text{min}$ . ( $\eta$ ) = 0.4,  $\text{CHCl}_3$ , 25  $^\circ\text{C}$ .  $T_{\text{onset}}$  = 435  $^\circ\text{C}$  (TGA), heating rate, 10  $^\circ\text{C}/\text{min}$ .