Reactive and Functional Polymers 125 (2018) 70–76

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react

Synthesis of linear polymer of intrinsic microporosity from 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane and decafluorobiphenyl

Hiromasa Sato, Shiduko Nakajo, Yoshiyuki Oishi, Yuji Shibasaki*

Department of Chemistry & Biological Sciences, Faculty of Science and Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan

ARTICLE INFO

Keywords:
Polymer of intrinsic microporosity
Spirobisindane
Poly(aryl ether)
Decafluorobiphenyl
Low-k material

ABSTRACT

A linear ladder polymer having a high molecular weight ($M_n > 13{,}000$) and reasonable molecular weight distribution ($M_w/M_n = 4.4$) is successfully prepared by the solution polycondensation of 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (TTSBI) with decafluorobiphenyl (DFBP) under reaction conditions that are determined using the model reaction of catechol (CC) with DFBP. Further, we observe an undesired intermolecular reaction of the condensed intermediate (CC*-DFBP) with another molecule of DFBP in the model reaction. Thus, polymerization is conducted in two steps under dilute conditions (0.17 mol/L) to suppress the formation of undesired byproducts. Finally, we successfully obtain an approximately linearly connected desired polymer in a good yield (ca. 80%). This controlled linear polymer has better thermal stability (glass transition (T_g) = 125 °C, 5 wt% loss temperature (T_{d5}) = 490 °C, N_2) than the related uncontrolled branched gel polymer.

1. Introduction

The recent development of a novel soluble low-density polymer called the *polymer of intrinsic microporosity* (PIM), which exhibits a rigid ladder-like backbone chain having a kinked structure, has paved the way to develop a new class of processable organic polymers having applications such as highly effective gas storage and separation membranes [1–24]. Budd et al. initially investigated the formation of PIM polymers using 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (TTSBI) and various other activated fluoroarenes. Thus, they developed PIM-1, which is a novel high porous polymer that has become the most extensively studied PIM, by the polymerization of TTSBI with 1,4-dicyanotetrafluorobenzene (DCTB) in (*N*,*N*-dimethylformamide) DMF in the presence of K_2CO_3 at a temperature ranging from 60 °C to 120 °C for a period of 72 h [25]. Among the polymers that were studied, PIM-1 achieved the highest number-average molecular weight (M_n) of 96,400 and a considerably high surface area of 850 m^2/g. However, Kricherdorf et al. obtained a polymer having a M_n of 18,000 only and a considerably large M_w/M_n value of 15 in their unsuccessful attempt at repeating the successful synthesis of PIM-1, which was hindered by the formation of cyclic oligomers [26–29]. Further, Guiver et al. investigated polymerization in detail and finally observed a very effective method (high-temperature polycondensation within a few minutes) to prepare a linear PIM-1 having a high M_n of 100,000 with reasonable M_w/M_n value of 2.5 that was devoid of cyclic oligomers [30]. The polymerization of TTSBI with decafluorobiphenyl (DFBP) was also studied by Budd and his coworkers [25]. They prepared the corresponding polymer having an M_n of 8400 with a relatively large M_w/M_n of 4.3. The compounds also showed a comparatively lower surface area of 600 m^2/g. Because of our interest in the development of a novel polymeric material having a low value of k [31–33] and motivated by the reported syntheses of low-density PIM polymers with fluorinated arenes such as DFBP, we focused our attention on the preparation of a film-forming high-molecular weight polymer from TTSBI and DFBP. Here, we describe the detailed study of the polymerization of TTSBI with DFBP on the basis of the model reaction using catechol (CC) and DFBP, in which selective intramolecular cyclization leads to the formation of dibenzoxane rings in the main chain.

2. Experimental

2.1. Materials

N,*N*-dimethylformamide (DMF) was purified by distillation over calcium hydride under a reduced pressure. All the other chemicals, including TTSBI and DFBP monomers purchased from Tokyo Chemical Industry (TCI) Co., Ltd., were used as received without any further purification.

2.2. Measurements

Fourier transform infrared (FTIR) spectra were measured on a Jasco

---

* Corresponding author.
E-mail address: yshibasa@iwate-u.ac.jp (Y. Shibasaki).

https://doi.org/10.1016/j.reactfunctpolym.2018.02.006
Received 18 December 2017; Received in revised form 9 February 2018; Accepted 13 February 2018

FT/IR-4200 spectrometer (Jasco Co. Ltd) by transmittance absorption spectroscopy (KBr tablet method). The number-average molecular weights (M_n), weight-average molecular weights (M_w), and dispersities (M_w/M_n) were determined using a Tosoh HLC-8120 gel permeation chromatograph (GPC), which was equipped with a refractive index and UV detectors along with consecutive polystyrene gel columns (TSK-GEL α-M × 2) that was maintained at 40 °C, which was eluted with chloroform that was maintained at a flow rate of 1.0 mL/min. Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker AC-400P spectrometer at 400 MHz for ^{1}H and at 100 MHz for ^{13}C measurements. Deuterated chloroform ($CDCl_3$) and dimethyl sulfoxide (DMSO-d_6) were used as solvents with tetramethylsilane as an internal reference. Thermal analyses were performed on a HITACHI TG/DTA7220 system at a heating rate of 10 °C/min under exposure to air or N_2. Differential scanning calorimetry (DSC) was performed on a HITACHI X-DSC7000 system at a heating rate of 20 °C/min under exposure to nitrogen.

High-resolution fast atom bombardment mass spectroscopy (HR-FABMS) was performed using a JEOL JMS-700 mass spectrometer. FAB was generated using xenon as the primary beam with 6-keV energy, and the ion accelerating voltage was 10 kV. 3-Nitrobenzyl alcohol was used for the FAB ionization matrix.

2.3. Reaction of catechol with DFBP (model reaction)

2.3.1. Typical procedure

In the presence of nitrogen, we added CC (0.110 g, 1.00 mmol), K_2CO_3 (0.276 g, 2.00 mmol), and 8 mL DMF into a 50-mL two-necked flask equipped with a three-way stopcock, reflux condenser, and magnetic stirring bar. DFBP (0.334 g, 1.00 mmol) was added into the solution, and the reaction was maintained at 100 °C for 24 h. The resulting reaction mixture was poured into a 5-wt% K_2CO_3 aq. solution, and the organic phase was extracted using diethyl ether thrice and by drying over $MgSO_4$. The solvent was further removed, and the products were separated using gradient silica gel-column chromatography ($CHCl_3$:hexane, 1:15 to 1:5). The yields for the separated products are summarized in Table 1. The overall yield of the compounds was observed to be 0.396 g (98.0%), among which the targeted compound, 1,2,4-trifluoro-3-(perfluorophenyl)dibenzodioxane (compound **1**, CC-DFBP), was obtained in a yield of 0.1086 g (26.9%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.97–7.03 (m, 4H, Ar—H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 99.2 (t), 102.6 (dd), 117.0 (d), 125.2, 125.6, 129.1 (dd), 134.8, 134.9, 135.3, 135.5, 136.6, 137.8, 137.9, 138.0, 139.0, 139.1, 139.9, 140.4, 140.9, 142.0, 142.1, 142.7, 142.8, 143.4, 143.6, 144.5, 144.6, 145.2, 145.3, 144.4, 146.0. Positive-ion HR-FABMS (NBA) *m/z* Calculated for $C_{18}H_4F_8O_2$ [M] +: 404.01, Found 404.0080.

Table 1
Results of the model reaction using CC and DFBP.[a]

Run	Conc (mol/L)	Temp (°C)	Yield (%)[b]						Selectivity[c]
			1	**2**	**3**	**4**	**5**	**6**	
1	0.50	50	38	6	5	15	5	31	0.73
2	0.50	100	44	14	7	1 <	1 <	36	0.74
3	0.25	100	60	12	10	1 <	1 <	14	0.79

[a] Conditions: with K_2CO_3 in DMF for 24 h.
[b] Each compound was separated by column chromatography, and the structure was determined by HR-FAB-MS. Compound **6** is a mixture of the condensed products that are described in the supplemental information.
[c] These results are estimated using compounds **1** to **5**.

Table 2
Results of the polymerization of TTSBI and DFBP[a].

Sample	$[M]_0$ (mol/L)	Temp (°C)	Yield (%)[b]	M_n[c]	M_w/M_n[c]	Appearance
1[d]	0.17	50	71	-[f]	-[f]	Brown
2[d]	0.17	100	71	-[f]	-[f]	Brown-yellow
3[e]	0.15	25 → 100	78	-[f]	-[f]	Pale yellow
4[e]	0.33	100	80	11,890	6.5	Pale yellow
5[e]	0.17	100	78	13,510	4.4	Pale yellow

[a] Conditions: with K_2CO_3 in DMF.
[b] MeOH-insoluble part.
[c] These results are estimated using compounds **1** to **5**.
[d] TTSBI and DFBP were mixed together and polymerized for 24 h.
[e] DFBP was added dropwise into the TTSBI solution in DMF at 25 °C or 100 °C for 24 h, followed by polymerization at 100 °C for 24 h.
[f] We observed that only a gel was formed.

2.4. Polymerization

2.4.1. Typical procedure for the preparation of a linear high-molecular weight polymer (sample 5, Table 2)

In the presence of nitrogen, we added TTSBI (0.681 g, 2.00 mmol), K_2CO_3 (0.276 g, 2.00 mmol), and 4 mL DMF into a 50-mL two-necked flask that was equipped with a three-way stopcock, reflux condenser, and magnetic stirring-bar. The mixture was heated to 100 °C for 30 min, and DFBP (0.668 g, 2.00 mmol) solution in DMF (20 mL) was added dropwise for 30 min. We observed that the polymerization solution turned black. Further, it was stirred for another 24 h, resulting in a transparent yellowish solution. The mixture was poured into a 5-wt% HCl aq. solution to precipitate the polymer, which was then collected and dried at 170 °C for 12 h under reduced pressure to produce the target polymer as a pale yellow powder giving 77.7% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.36–1.58 (6H, CH_3), 2.17–2.40 (2H, CH_2), 6.46 (s, 1H, Ar—H), 6.80 (s, 1H, Ar—H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 30.1, 31.6, 43.6, 57.3, 59.1, 100.4, 110.5, 112.4, 128.9, 129.0, 134.3, 135.4, 137.8, 137.9, 139.7, 140.1, 142.3, 142.9, 143.5, 144.7, 145.3, 146.5, 146.8, 149.1, 149.4. Elemental analysis ($C_{33}H_{20}F_6O_4$) Calculated C: 66.67, H: 3.39 (%); Found C: 65.91, H: 3.74 (%).

3. Results and discussion

3.1. Reaction of catechol with DFBP (model reaction)

Previously, the synthesis of PIM-1 polymer was demonstrated to produce the corresponding linear high-molecular weight polymer [2–4], whereas the preparation of other PIM polymers, such as those obtained from TTSBI and DFBP resulted in low-molecular weight mixtures only, as described in the introduction. To elucidate the mechanism of the reaction, we performed the model reaction using CC and DFBP (Scheme 1 and Table 1), and the resulting mixture was further separated by silica gel column chromatography and analyzed by HR-FABMS. When the reaction was performed at 50 °C for 24 h, a mixture containing the compounds **1** to **6** was obtained. Compound **1**, which was obtained in 26.9% yield, was confirmed to be the desired 1,2,4-trifluoro-3-(perfluorophenyl)dibenzodioxane (CC-DFBP) by IR, ^{1}H, ^{13}C NMR, and HR-FABMS spectroscopic methods. Fig. 1 depicts the ^{13}C NMR spectrum of compound **1** in $CDCl_3$. In addition to the aromatic carbon signals at 117.0, 112.53, 112.56, 139.9, and 140.4 ppm assignable to catechol moiety, small and complex signals corresponding to the DFBP unit were observed at 99 to 148 ppm. The coupling constant between adjacent ^{13}C and ^{19}F atoms in the spectrum was found to be a reasonable value of about 250 Hz.

Fig. 2 displays the structures of compounds **1**–**5**, which were further characterized. Compound **6** was observed to be a mixture (**6a**–**6f**) of the condensed products, as described in the supporting information.

The initial step of the reaction is most likely to be the nucleophilic