Supplementary material for

Synthesis and characterization of poly(phthalazinone ether ketone ketone) copolymers with 4,4'-dihydroxybiphenyls

Dalin Dong [1], Yuezhen Bin [1] and Xigao Jian[1]

[1]Institution of Chemical Engineering, Dalian University of Technology, Dalian , People's Republic of China.

Corresponding author:
Yuezhen Bin, Institution of Chemical Engineering, Dalian University of Technology, Dalian 116024, People's Republic of China.
Email: binyz@dlut.edu.cn

Structures of meta-PPBEKKs

Structures of meta-PPBEKKs are shown in Figure S1 to S4.

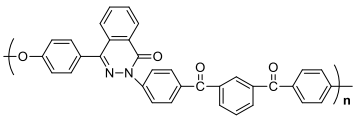

Figure S1. Structure of meta-PPBEKK-1

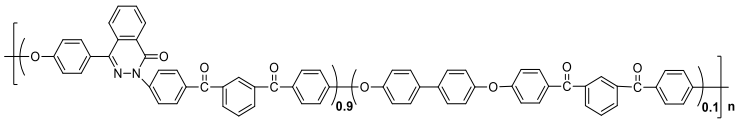

Figure S2. Structure of meta-PPBEKK-2

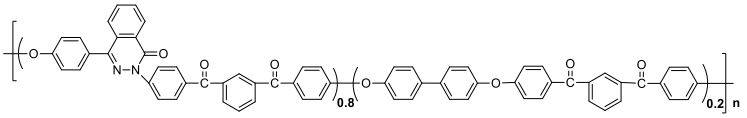

Figure S3. Structure of meta-PPBEKK-3

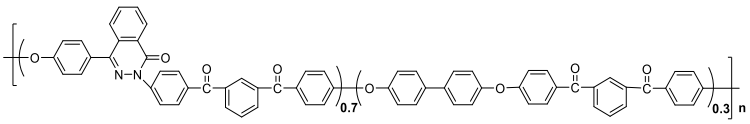

Figure S4. Structure of meta-PPBEKK-4

Purification of meta-PPBEKKs

Copolymers were dissolved in chloroform. Reverse-phase sedimentation was done in ethanol. After filtration, copolymers were dried in vacuum oven at 60°C for 24 hours.

Proton nuclear magnetic resonance (^{1}H NMR) of meta-PPBEKKs

^{1}H NMR spectra were determined on a ADVANCE III 500M NMR spectrometer (Brucker, Germany) at room temperature with tetramethylsilane as the internal reference and $CDCl_3$ as the solvent, respectively. ^{1}H NMR spectra of meta-PPBEKK-1 to 4 are shown in Figure S5.

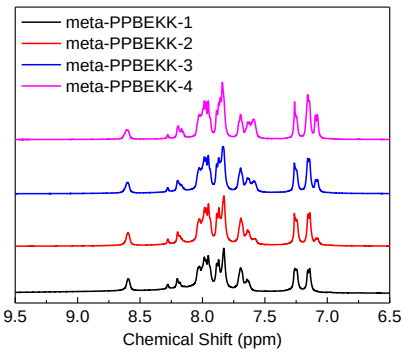

Figure S5. ^{1}H NMR spectra of meta-PPBEKKs

Solution casting of meta-PPBEKKs

Meta-PPBEKKs were made into films by solution casting in solvent H. 0.4 gram of specific meta-PPBEKK was dissolved in 6 ml solvent H. With the solution, meta-PPBEKK films were casted at 60°C. After 60°C at 1 atm for 48 hours, 80°C at 1 atm for 24 hours and 100°C in vacuum for 24 hours, meta-PPBEKK films were obtained.

Mark-Houwink equation

Polymer synthesis

Ratios of monomers in meta-PPBEKKs are shown in Table S1. Meta-PPBEKKs were synthesized and purified as mentioned above.

Table S1. Ratios of monomers in meta-PPBEKKs

Sample	DHPZ (mmol)	BP (mmol)	meta-DFKK (mmol)
meta-PPBEKK-1-A	3.0	0.0	3.015
meta-PPBEKK-1-B	3.0	0.0	3.030
meta-PPBEKK-1-C	3.0	0.0	3.045
meta-PPBEKK-1-D	3.0	0.0	3.060
meta-PPBEKK-1-E	3.0	0.0	3.075
meta-PPBEKK-2-A	2.7	0.3	3.015
meta-PPBEKK-2-B	2.7	0.3	3.030
meta-PPBEKK-2-C	2.7	0.3	3.045
meta-PPBEKK-2-D	2.7	0.3	3.060
meta-PPBEKK-2-E	2.7	0.3	3.075
meta-PPBEKK-3-A	2.4	0.6	3.015
meta-PPBEKK-3-B	2.4	0.6	3.030
meta-PPBEKK-3-C	2.4	0.6	3.045
meta-PPBEKK-3-D	2.4	0.6	3.060
meta-PPBEKK-3-E	2.4	0.6	3.075
meta-PPBEKK-4-A	2.1	0.9	3.015
meta-PPBEKK-4-B	2.1	0.9	3.030
meta-PPBEKK-4-C	2.1	0.9	3.045
meta-PPBEKK-4-D	2.1	0.9	3.060
meta-PPBEKK-4-E	2.1	0.9	3.075

Number-average molecular masses

Fluorine nuclear magnetic resonance (^{19}F NMR) was adopted in calibration of number-average molecular masses.[1] ^{19}F NMR spectra were determined on a ADVANCE III 500M NMR spectrometer (Bruker, Germany) at room temperature with trifluoroacetic acid as internal reference and concentrated sulfuric acid as solvent, respectively. Details of reagents are shown in Table S2. ^{19}F NMR spectrum of meta-PPBEKK-1-A is shown in Figure S6. Peak “a” stands for chemical shift of fluorine in trifluoroacetic acid, while peak “b” and peak “c” stand for chemical shift of fluorine in meta-PPBEKKs.

Table S2. Reagents adopted in ^{19}F NMR

Sample	Concentrated sulfuric acid (mL)	Trifluoroacetic acid (g)	Sample weight (g)
meta-PPBEKK-1	0.5	0.0002	0.01
meta-PPBEKK-2	0.5	0.0002	0.01
meta-PPBEKK-3	0.5	0.0002	0.01
meta-PPBEKK-4	0.5	0.0002	0.01
meta-PPBEKK-1-A	0.5	0.0002	0.01
meta-PPBEKK-1-B	0.5	0.0002	0.01
meta-PPBEKK-1-C	0.5	0.0002	0.01
meta-PPBEKK-1-D	0.5	0.0002	0.01
meta-PPBEKK-1-E	0.5	0.0002	0.01

meta-PPBEKK-2-A	0.5	0.0002	0.01
meta-PPBEKK-2-B	0.5	0.0002	0.01
meta-PPBEKK-2-C	0.5	0.0002	0.01
meta-PPBEKK-2-D	0.5	0.0002	0.01
meta-PPBEKK-2-E	0.5	0.0002	0.01
meta-PPBEKK-3-A	0.5	0.0002	0.01
meta-PPBEKK-3-B	0.5	0.0002	0.01
meta-PPBEKK-3-C	0.5	0.0002	0.01
meta-PPBEKK-3-D	0.5	0.0002	0.01
meta-PPBEKK-3-E	0.5	0.0002	0.01
meta-PPBEKK-4-A	0.5	0.0002	0.01
meta-PPBEKK-4-B	0.5	0.0002	0.01
meta-PPBEKK-4-C	0.5	0.0002	0.01
meta-PPBEKK-4-D	0.5	0.0002	0.01
meta-PPBEKK-4-E	0.5	0.0002	0.01

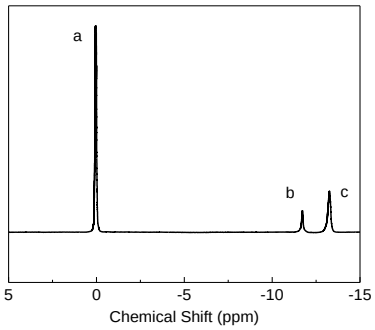

Figure S6. ^{19}F NMR spectrum of meta-PPBEKK-1-A

Number-average molecular masses are calibrated by Eq (S1). Results are shown in Table S3.

$$M_n = \frac{2S_t M_t m_p}{S_p m_t} \quad \text{(S1)}$$

Here, "M_n" stands for number-average molecular masses of meta-PPBEKKs. "S_t" stands for relative area of peak "a" to total area of peak "b" and peak "c" in Figure S6. "M_t", molecule weight of trifluoroacetic acid, is 114.02 g mol^{-1}. "m_p" stands for weight of meta-PPBEKKs. "S_p" stands for total area of peak "b" and peak "c" in Figure S6. Here, "S_p" was set as "1". "m_t" stands for weight of trifluoroacetic acid.

Table S3. Number-average molecular masses of meta-PPBEKKs

Sample	S_t	S_p	M_n (g mol^{-1})
meta-PPBEKK-1	3.75	1.00	42800
meta-PPBEKK-2	3.88	1.00	44200
meta-PPBEKK-3	3.97	1.00	45300
meta-PPBEKK-4	3.60	1.00	41000
meta-PPBEKK-1-A	3.63	1.00	41400
meta-PPBEKK-1-B	3.46	1.00	39500
meta-PPBEKK-1-C	3.24	1.00	36900
meta-PPBEKK-1-D	3.05	1.00	34800
meta-PPBEKK-1-E	2.85	1.00	32500
meta-PPBEKK-2-A	3.71	1.00	42300
meta-PPBEKK-2-B	3.55	1.00	40500
meta-PPBEKK-2-C	3.31	1.00	37700
meta-PPBEKK-2-D	3.11	1.00	35500
meta-PPBEKK-2-E	2.87	1.00	32700
meta-PPBEKK-3-A	3.89	1.00	44400
meta-PPBEKK-3-B	3.72	1.00	42400
meta-PPBEKK-3-C	3.50	1.00	39900

meta-PPBEKK-3-D	3.29	1.00	37500
meta-PPBEKK-3-E	3.04	1.00	34700
meta-PPBEKK-4-A	3.44	1.00	39200
meta-PPBEKK-4-B	3.23	1.00	36800
meta-PPBEKK-4-C	3.02	1.00	34400
meta-PPBEKK-4-D	2.79	1.00	31800
meta-PPBEKK-4-E	2.48	1.00	28300

Intrinsic viscosity

Inherent viscosities (η_{inh}) were determined on an Ubbelohde viscometer (JC522-1835, China) at 25 ± 0.1°C with chloroform as solvent at concentration of 0.08 g dL^{-1}. Results are shown in Table S4.

Weight-average molecular masses

Light scattering measurements were performed on a PS-21 light scattering photometer (Shimadzu, Japan) at 546 nm wavelength. Refractive index increments (dn/dc) (25°C, 546 nm, $CHCl_3$) were determined on a DR-1 refractometer (Waters, America). Weight-average molecular masses are calculated by Eq (S2-S4) and shown in Table S5. Zim plot of meta-PPBEKK-1-A is shown in Figure S7.

$$K = \frac{4\pi^2 n^2 (\frac{dn}{dc})^2}{N_A \lambda_0^4} \quad \text{(S2)}$$

$$\lim_{\theta \to 0} \frac{Kc}{R(\theta)} = \frac{1}{M_W} + 2A_2 c \quad \text{(S3)}$$

$$\lim_{c \to 0} \frac{Kc}{R(\theta)} = \frac{1}{M_W} + \frac{16\pi^2 n^2}{3M_w \lambda_0^2} < R_g^2 >_z \sin^2(\frac{\theta}{2}) \quad \text{(S4)}$$

Here, "N_A" stands for Avogadro constant. "n" stands for refractive index of chloroform. "λ_0" stands for wavelength of incident light in vacuum. "A_2" stands for the second virial coefficient. "c" (g L^{-1}) stands for polymer concentration. "$R(\theta)$" stands for Rayleigh ratio. "$<R_g^2>$" stands for mean square radius of gyration.

Table S4. Intrinsic viscosity of meta-PPBEKKs

Sample	η_{inh} (dL g^{-1})
meta-PPBEKK-1-A	0.3295
meta-PPBEKK-1-B	0.3227
meta-PPBEKK-1-C	0.3124
meta-PPBEKK-1-D	0.3044
meta-PPBEKK-1-E	0.2946
meta-PPBEKK-2-A	0.3637
meta-PPBEKK-2-B	0.3568
meta-PPBEKK-2-C	0.3468
meta-PPBEKK-2-D	0.3372
meta-PPBEKK-2-E	0.3245
meta-PPBEKK-3-A	0.3975
meta-PPBEKK-3-B	0.3903
meta-PPBEKK-3-C	0.3805
meta-PPBEKK-3-D	0.3708
meta-PPBEKK-3-E	0.3551
meta-PPBEKK-4-A	0.3710
meta-PPBEKK-4-B	0.3593
meta-PPBEKK-4-C	0.3491
meta-PPBEKK-4-D	0.3369
meta-PPBEKK-4-E	0.3185

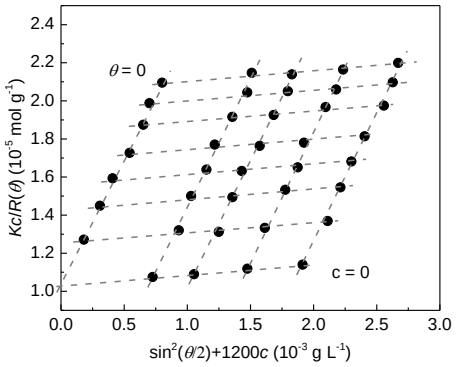

Figure S7. Zim plot of meta-PPBEKK-1-A

Table S5. Weight-average molecular masses of meta-PPBEKKs

Sample	dn/dc (mL g^{-1})	M_w (g mol^{-1})
meta-PPBEKK-1-A	0.2319	97000
meta-PPBEKK-1-B	0.2319	93800
meta-PPBEKK-1-C	0.2319	89300
meta-PPBEKK-1-D	0.2319	85100
meta-PPBEKK-1-E	0.2319	80300
meta-PPBEKK-2-A	0.2324	99500
meta-PPBEKK-2-B	0.2324	96400
meta-PPBEKK-2-C	0.2324	91800
meta-PPBEKK-2-D	0.2324	87500
meta-PPBEKK-2-E	0.2324	82300
meta-PPBEKK-3-A	0.2330	103000
meta-PPBEKK-3-B	0.2330	100300
meta-PPBEKK-3-C	0.2330	95800
meta-PPBEKK-3-D	0.2330	92200
meta-PPBEKK-3-E	0.2330	85600
meta-PPBEKK-4-A	0.2326	92000
meta-PPBEKK-4-B	0.2326	87500
meta-PPBEKK-4-C	0.2326	83500
meta-PPBEKK-4-D	0.2326	78500
meta-PPBEKK-4-E	0.2326	71600

Calibration of Mark-Houwink equation parameters

$$\eta = KM_w{}^{\alpha} \tag{S5}$$

$$\ln\eta = \ln K + \alpha \ln M_W \tag{S6}$$

"K" and "α" were calibrated by Eq (S6) and used in GPC measurements. Parameters of meta-PPBEKKs are shown in Table S6.

Table S6. Parameters (25°C, $CHCl_3$) of Mark-Houwink equation

Sample	K (10^{-4} dL g^{-1})	α	Regression coefficient
meta-PPBEKK-1	3.77	0.59	0.9982
meta-PPBEKK-2	3.69	0.60	0.9997
meta-PPBEKK-3	3.62	0.61	0.9993
meta-PPBEKK-4	3.58	0.61	0.9998

References

1. Devaux J, Daoust D, Legras R, et al. ^{19}F n.m.r. end-group analysis of a poly(aryl ether ether ketone) (PEEK). *Polymer* 1989; **30**(1): 161-164.