Supplementary Information for

Blocky bromination of poly(ether ketone ketone) as a means to preserve crystallizability and rapid crystallization kinetics

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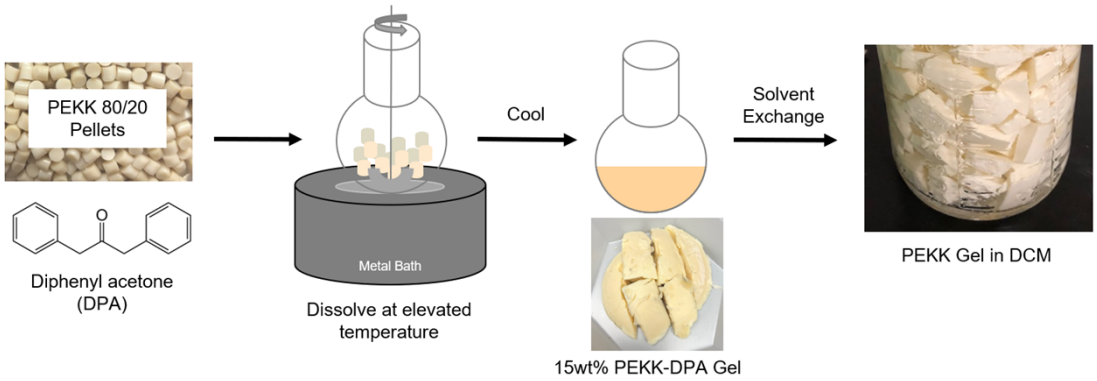

Figure S1. Schematic representing the gelation and solvent exchange process of PEKK in DPA. First, PEKK is dissolved in DPA using a metal bath under constant argon purge. After dissolving, the solution is cooled to room temperature. The gel is manually broken and solvent exchanged by Soxhlet.

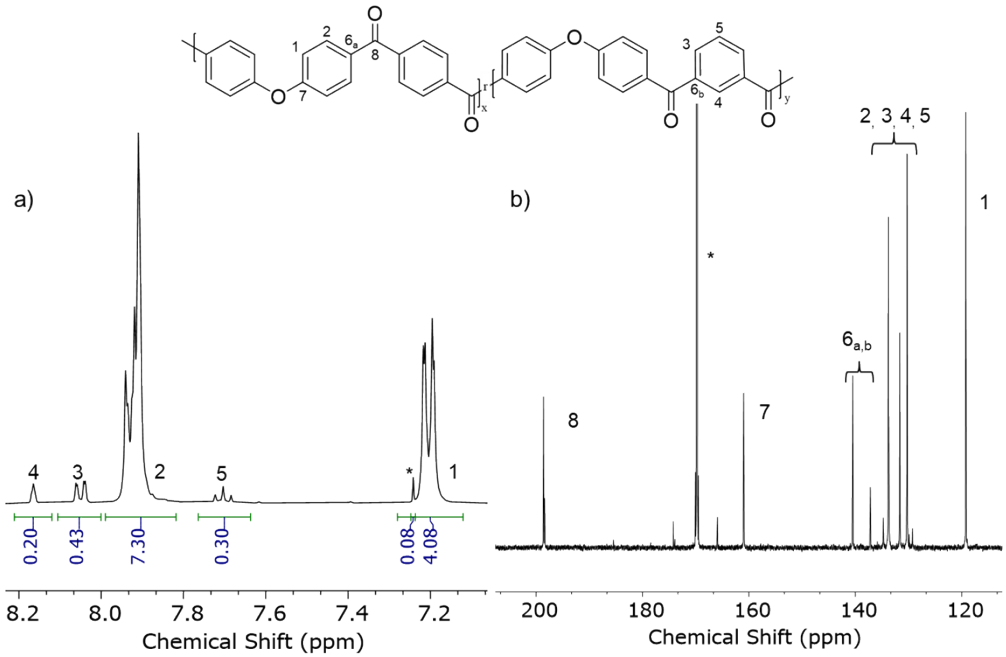

Figure S2. Previously reported[1] ^{1}H and ^{13}C NMR of PEKK with resonance peak assignments. Figure redesigned for clarity.

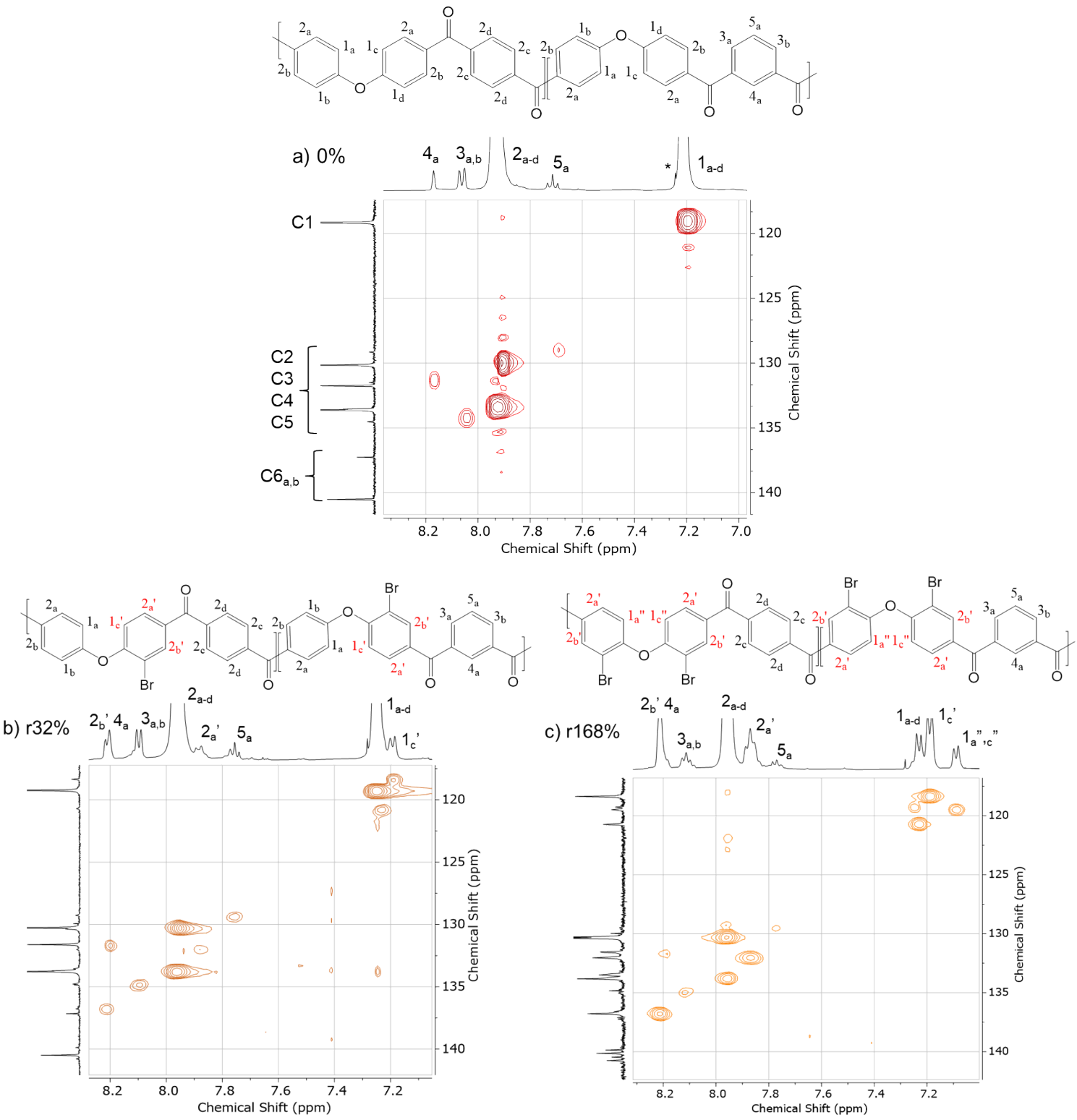

Figure S3. 2D NMR of (a) PEKK, (b) rBrPEKK30, and (c) rBrPEKK168. Refer to **Figure S2** for ^{13}C naming conventions.

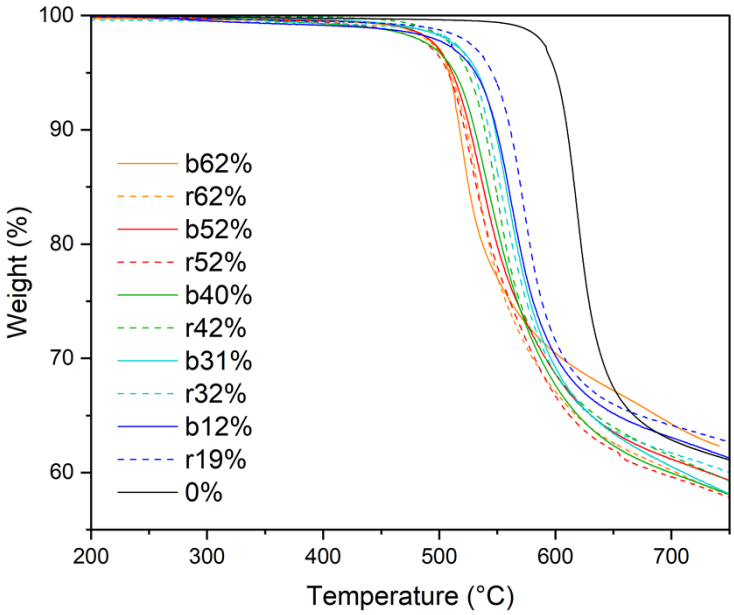

Figure S4. Thermogravimetric analysis of PEKK and BrPEKK materials. All materials are stable up to 500 °C. Experiments were performed with a 20 °C/min ramp rate in nitrogen.

Table S1. $T_{D5\%}$ of PEKK and BrPEKK materials.

Sample	$T_{D5\%}$ (°C)
PEKK	600
rBrPEKK19	546
bBrPEKK12	534
rBrPEKK31	531
bBrPEKK32	532
rBrPEKK42	520
bBrPEKK40	510
rBrPEKK52	508
bBrPEKK52	507
rBrPEKK62	508
bBrPEKK62	506

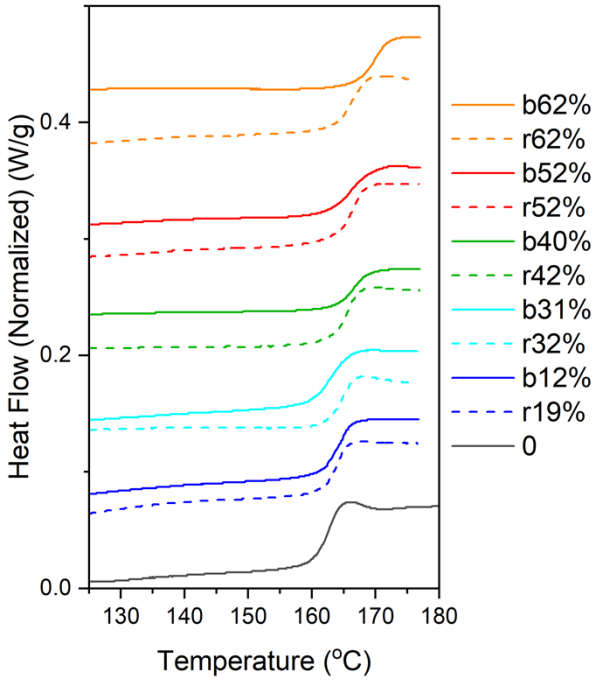

Figure S5. The DSC heating scans of melt quenched BrPEKK to determine T_g. Experiments were performed with a 10 °C/min ramp rate in nitrogen.

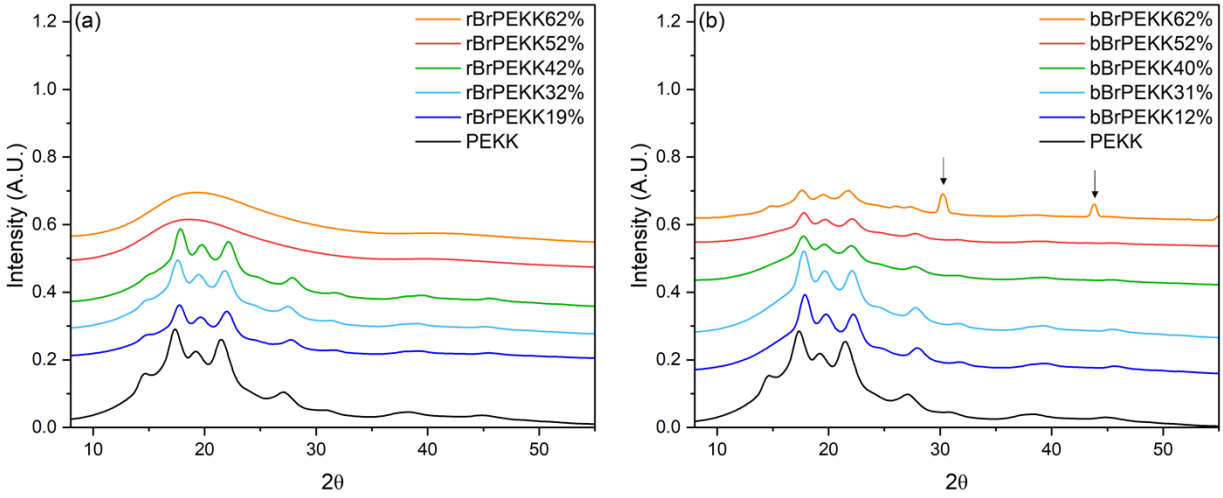

Figure S6. The WAXS plotted versus 2Θ and offset for clarity. The arrows indicate the significant presence of form II polymorph of PEKK.

Calculations estimating the electron density contrast between amorphous and crystalline components of the PEKK copolymers

To explain the decrease in intensity of the scattering feature at q=0.38 nm^{-1} for bBrPEKK40, estimations of scattering length density (SLD) were calculated for PEKK, rBrPEKK42, bBrPEKK40, and bBrPEKK62. The SLD was estimated utilizing the NIST Center for Neutron Research Neutron activation and scattering calculator[2]. In the SLD calculations, the densities were corrected to remove contributions of crystalline density. Densities (ρ) of monosubstituted BrPEKK and disubstituted BrPEKK were calculated based on density changes of a brominated small molecule benzophenone analog. The calculated SLDs are shown in **Table S2** with the parameters shown.

Table S2. Degree of crystallinity of sample, amorphous density (no crystalline component included in this calculation unless specified otherwise), scattering length density calculated from NIST's neutron activation and scattering calculator, and the difference of the 100% crystalline SLD from the calculated SLDs.

Sample	$\%X_c$	$\%X_c$ from WAXS	ρ (g/mL)	Calculated Amorphous Density (ρ_a)	Scattering Length Density (SLD) ($10^{-6}/A^2$)	SLD Difference from Crystalline PEKK
PEKK (Crystalline)	100	-	1.390[3]	-	12.296	-
PEKK (Amorphous)	0	-	1.250[3]	-	11.057	1.239
rBrPEKK42	-	2	-	1.377	11.951	0.345
bBrPEKK40	-	22	-	1.394	12.109	0.187

Estimations of amorphous density/electron density for rBrPEKK42 and bBrPEKK40

The amorphous phase densities of rBrPEKK40 and bBrPEKK40, shown above, are estimated by assuming that the densities of small molecule analogs increase upon bromination comparable to the polymer counterparts. For example, the increase in density from benzophenone to 3-bromobenzophenone is used to represent the increase in density upon monosubstitution of PEKK. The analogs are shown below.

Table S3. Table of small molecule analog densities and increase in density upon bromination.

Small molecule analog	Density (g/mL)	Increase in density with additional Br Unit
benzophenone	1.11	-
3-bromobenzophenone	1.42	0.311
3,3'-dibromobenzophenone	1.70	0.279

The theoretical densities of a fully monosubstituted PEKK (MonoBrPEKK) and a fully disubstituted PEKK (DiBrPEKK) were calculated by adding the increase in density of the additional Br unit to the density of amorphous PEKK.

Table S4. Table of PEKK, MonoBrPEKK, DiBrPEKK amorphous densities. PEKK amorphous density is known. BrPEKK densities are calculated using the increase in density of the small molecule analog.

Sample	Amorphous Density (g/mL)	Calculated Amorphous Density (g/mL)
PEKK	1.25	-
MonoBrPEKK	-	1.561
DiBrPEKK	-	1.840

SLD calculations for rBrPEKK42 and bBrPEKK40

rBrPEKK42 contains both pure PEKK monomers and monosubstituted PEKK monomers (as seen by NMR, **Figure 7**). After correcting for the amount of crystalline component (2%, **Table S2**), the amorphous density (ρ_a) of rBrPEKK42 was calculated by the following equation:

$$\rho_{a,rBrPEKK42} = (\rho_{a,PEKK})(Fraction\ of\ amorphous\ PEKK) + (\rho_{a,MonoBrPEKK})(Fraction\ of\ amor$$

$$= \left(1.25\frac{g}{mL}\right)(0.592) + \left(1.561\frac{g}{mL}\right)(0.408) = 1.377\frac{g}{mL}$$

Using the molecular formula of $C_{20}H_{11.58}O_3Br_{0.42}$ (where $Br_{0.42}$ and $H_{11.58}$ account for the average chemical formula for rBrPEKK42) and density of 1.377 g/mL for rBrPEKK42, the SLD was calculated to be 11.951 $10^{-6}/A^2$.

bBrPEKK40 contains pure PEKK monomers and both monosubstituted and disubstituted PEKK monomers (as seen by NMR, **Figure 7**). The fraction of monomers that are monosubstituted and disubstituted were calculated using **Figure 6**. After correcting for the amount of crystalline component (22%, **Table S2**) the amorphous density (ρ_a) of bBrPEKK40 was calculated by the following equation:

$$\rho_{a,bBrPEKK40} = (\rho_{a,PEKK})(Fraction\ of\ amorphous\ PEKK) + \left[(\rho_{a,MonoBrPEKK})(Fraction\ of\ amorphous\ MonoB\right.$$
$$\left.(Fraction\ of\ amorpous\ BrPEKK)\right.$$

$$= \left(1.25\frac{g}{mL}\right)(0.632) + \left[\left(1.561\frac{g}{mL}\right)(0.7144) + \left(1.84\frac{g}{mL}\right)(0.2856)\right](0.368) = 1.394\frac{g}{mL}$$

Using the molecular formula of $C_{20}H_{11.6}O_3Br_{0.40}$ and density of 1.394 g/mL for bBrPEKK40, the SLD was calculated to be 12.109 $10^{-6}/A^2$.

The differences in SLD of crystalline PEKK to amorphous rBrPEKK42 and bBrPEKK40 are 0.345 $10^{-6}/A^2$ and 0.187 $10^{-6}/A^2$, respectively (**Table S2**). The difference is smallest for bBrPEKK40, which supports the observed trend of the reduction in the intensity of the long period peak at q=0.38nm^{-1} for blocky analogs compared to the random analogs. The blocking up of the bromine functionality in addition to the crystallinity concentrating the electron-rich bromine atoms into the amorphous domains increases the electron density of the amorphous phase. As shown by SLD calculations, the electron density of the amorphous component more closely matched that of

the crystalline PEKK component thus, decreasing the intensity of the crystalline feature at q=0.38 nm^{-1}. The SLD for bBrPEKK62 was also calculated and the difference from the SLD of crystalline PEKK was -0.083. Thus, further supporting the decrease in intensity observed in **Figure 11**.

References

1. Pomatto, M. E.; Moore, R. B., Crystallization kinetics and equilibrium melting temperature of poly (ether ketone ketone) with high terephthalate content utilizing fast scanning calorimetry. *Polymer* **2023**, 125810.
2. NIST Center for Neutron Research Neutron Activation and Scattering Calculator. https://www.ncnr.nist.gov/resources/activation/ (accessed 12/1/2023).
3. Josh Kemppainen, V. V., Evan Pineda, Gregory Odegard *Thermomechanical Property Prediction of Amorphous and Crystal PEKK via Molecular Dynamics*; E-20122; NASA: NTRS, June 9, 2023, 2022.