Electronic Supplementary Information

Micro-kinetics of pitch polymerization with regards to molecular weight distribution

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1. Detailed describe and explanation of the falling ball method

A falling ball viscosity apparatus is shown in **Fig. S1**. The instrument includes an aluminum ball, a tungsten wire, two ceramic pulleys, a regulating weight and a ruler. The diameter of the aluminum ball is 1.9×10^{-2} meters. The diameter of the tungsten wire is 3×10^{-5} meters. The inner diameter of the ceramic pulley is 3×10^{-3} meters. Before measurement, the aluminum ball was immersed in the pitch melt and the regulating weight was held. After release the movement of the regulating weight was recorded by video. The displacement with time was read out by analyzing the video and the moving speeds were calculated.

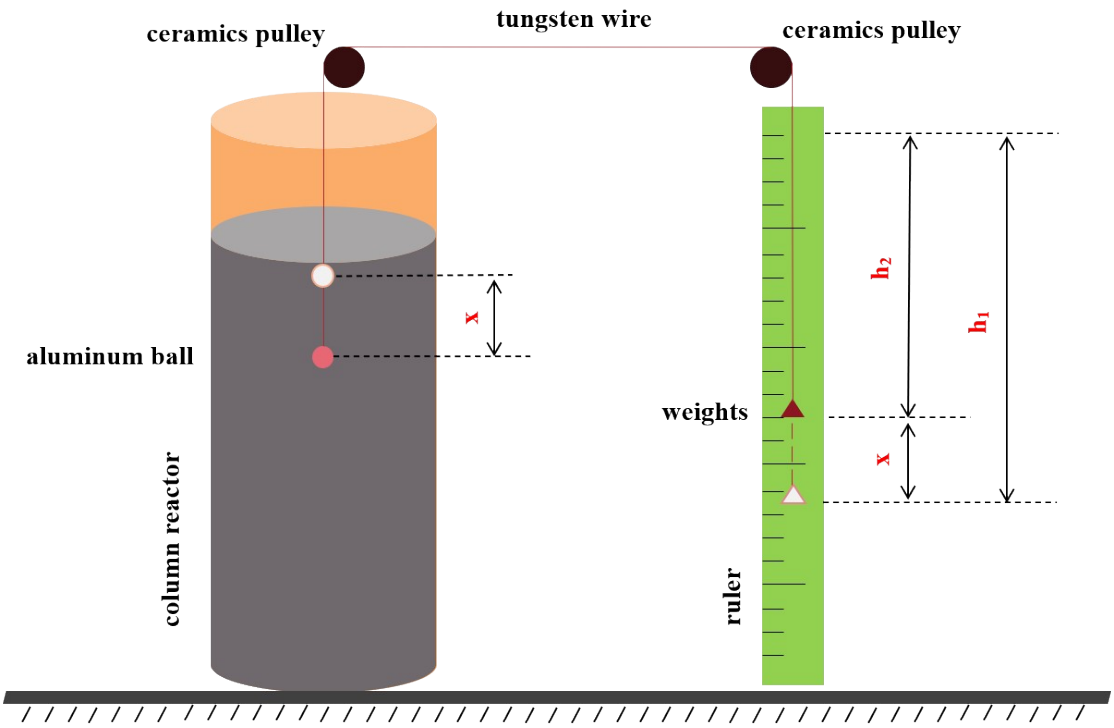

Fig. S1. The falling ball viscosity apparatus.

The viscosity of the pitch can be regressed by simulating the movement of the ball in consideration of the force analysis. Take the displacement to be x in time t, and set u is the dropping speed of the ball, then according to the force analysis of the ball,

$$\frac{d^2x}{dt^2} = \frac{(m_1 - m_2)g - F_L - F_1 - F_2 - F_i}{m_1 + m_2} \qquad (1)$$

$$u = \frac{dx}{dt} \qquad (2)$$

where, m_1 and m_2 are the masses of the ball and the regulating weight, g is the gravitational acceleration, F_L and F_1 are the buoyancy force and the viscous resistance that are given to the ball by the pitch melt. F_2 is the frictional drag that is given to the tungsten wire by the pitch melt. F_i is the friction force of the pulley bock. The mass of the tungsten wire and its buoyancy given by the pitch melt are neglected.

Set the radius of the ball as r_1 and the density of the pitch melt is ρ, so the buoyancy on the ball is

$$F_L = \frac{4}{3}\pi r_1^3 \rho \tag{3}$$

Set the friction coefficient of the ball with the pitch melt and projected area of the ball along the movement direction as ζ and A, and u_1 as the ball's speed relative to the pitch melt, so according to the equation about ball dropping in a liquid, the viscous resistance is

$$F_1 = \zeta A \frac{\rho {u_1}^2}{2}$$

where calculation of the friction coefficient depends on the Reynolds numbers Re, according to $\zeta = \frac{18.5}{Re^{0.6}}$ or $\zeta = \frac{24}{Re}$ when $1<Re<1000$ and $Re<1$ respectively.

Setting the viscosity of the pitch melt as μ, the Reynolds numbers is

$$Re = \frac{2r_1 u_1 \rho}{\mu}$$

Setting u to be the speed of the ball, when the ball dropping, the isometric pitch melt is pushed upside, therefore the ball's speed relative to the pitch melt should be corrected by the following equation.

$$u_1 = u\frac{R^2}{R^2 - {r_1}^2}$$

where R is the inner diameter of the reaction.

So, when $1<Re<1000$,

$$F_1 = \frac{18.5}{(\frac{2r_1 u\rho}{\mu})^{0.6}(\frac{R^2}{R^2 - {r_1}^2})^{1.2}} \cdot \pi r_1^2 \cdot \frac{\rho u^2}{2}(\frac{R^2}{R^2 - {r_1}^2})^2 \tag{4}$$

when $Re<1$,

$$F_1 = \frac{24}{\frac{2r_1 u\rho}{\mu} \cdot \frac{R^2}{R^2 - {r_1}^2}} \cdot \pi r_1^2 \cdot \frac{\rho u^2}{2} (\frac{R^2}{R^2 - {r_1}^2})^2 \qquad (5)$$

The viscous resistance given to the tungsten wire by the pitch melt increases with its immersed length, and can be calculated as follows according to the basic formula

$$F_2 = 2\pi r_2 x \cdot \mu \cdot \frac{du}{dr}$$

where, r_2 is the radius of the tungsten wire. The velocity gradient can be simplified to the following equation because the diameter of the tungsten wire is much smaller than that of the reactor inner referred to the literature[S1].

$$\frac{du}{dr} = \frac{u}{r_2 ln\left(\frac{R}{r_2}\right)}$$

So, the viscous resistance given to the tungsten wire by the pitch melt can be calculated by the following equation.

$$F_2 = 2\pi x \cdot \mu \cdot \frac{u}{ln\left(\frac{R}{r_2}\right)} \qquad (6)$$

The friction force F_i is proportional to the press force exerted on the pulleys by the tungsten wire. However, the friction coefficient was found varying with the press force, so a formula must be set up. **Fig. S2** is the relationship between the friction coefficient and the press force exerted by the tungsten obtained through hanging different weights. The curve is identically regressed to the empirical formula.

$$K_{fi} = 0.3288 * e^{-\frac{F_p}{0.0342}} + 0.0598$$

where, K_{fi} is the friction coefficient, F_p is the total press force on the pulleys .

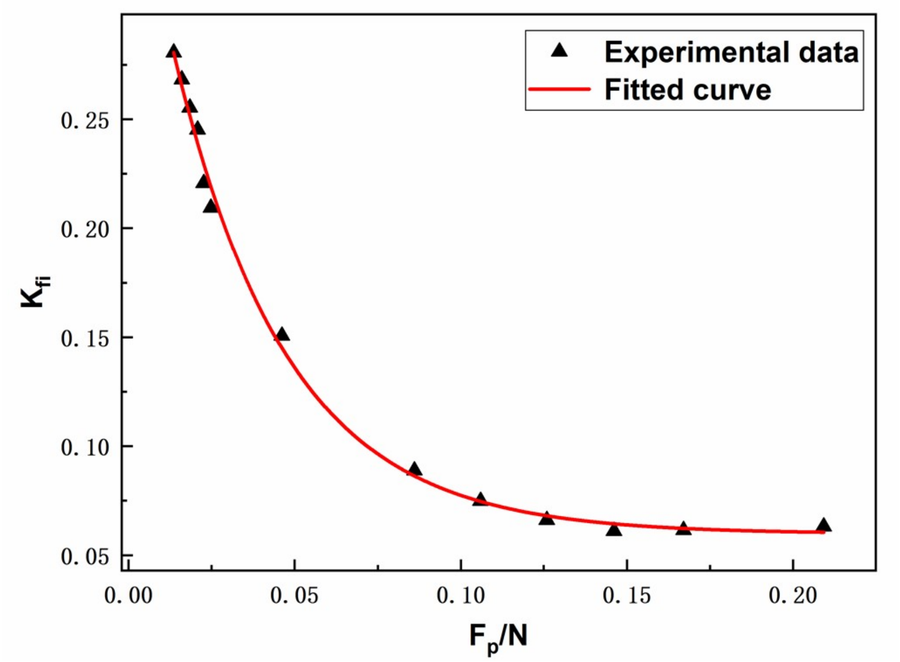

Fig. S2. Regressed curve of the friction coefficient of the pulley block with the total press force.

Because the total force $F_p=(m_1+m_2)g-F_L-F_1-F_2$, therefore, the friction force F_i can be calculated by the following equation.

$$Fi = \left(0.3288 * e^{-\frac{(m_1+m_2)g-F_L-F_1-F_2}{0.0342}} + 0.0598\right) * ((m_1+m_2)g - F_L - F_1$$

$$)$$

(7)

A series of data about the distance and time of the falling ball can be obtained by experiment. Then from equation (1) to (7), the viscosity of the pitch melts can be solved by Ordinary Differential Equation (ODE) fitting with MATLAB, as shown in **Fig. S3**.

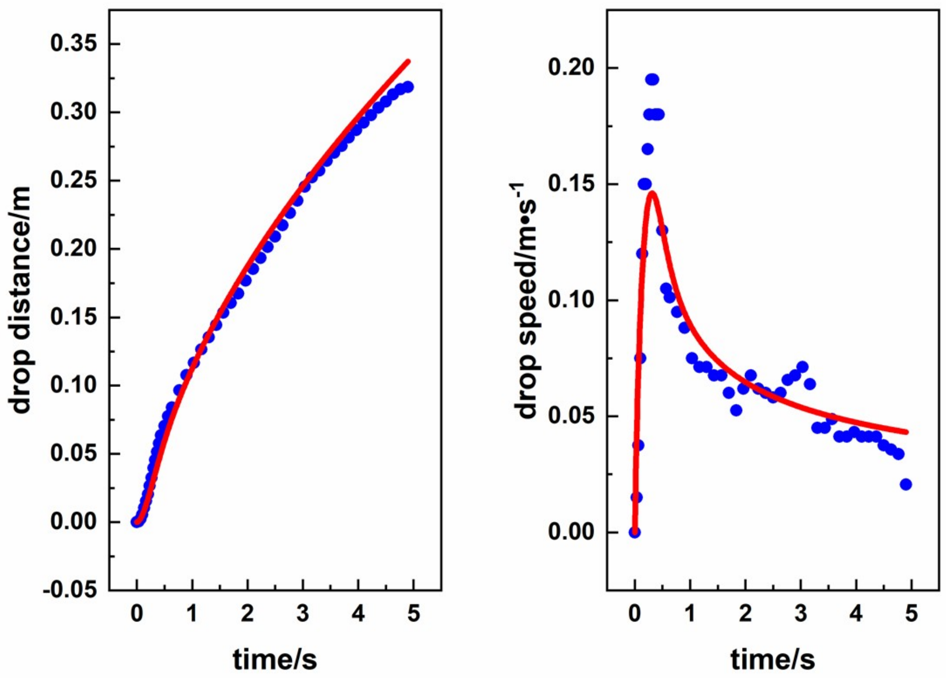

Fig. S3. The drop distance and speed of the ball with drop time and the regressed curves. The rounds symbolize the experimented data and the lines symbolize the fitted curves

[S1] Inagaki M, Kang F. Chapter 3 - Engineering and Applications of Carbon Materials[M]. Materials Science and Engineering of Carbon: Fundamentals (Second Edition), Inagaki M, Kang F, Oxford:Butterworth-Heinemann, 2014, 219-525.

2. The as-recorded MALDI-TOF-MS spectra of the pitch during polymerization

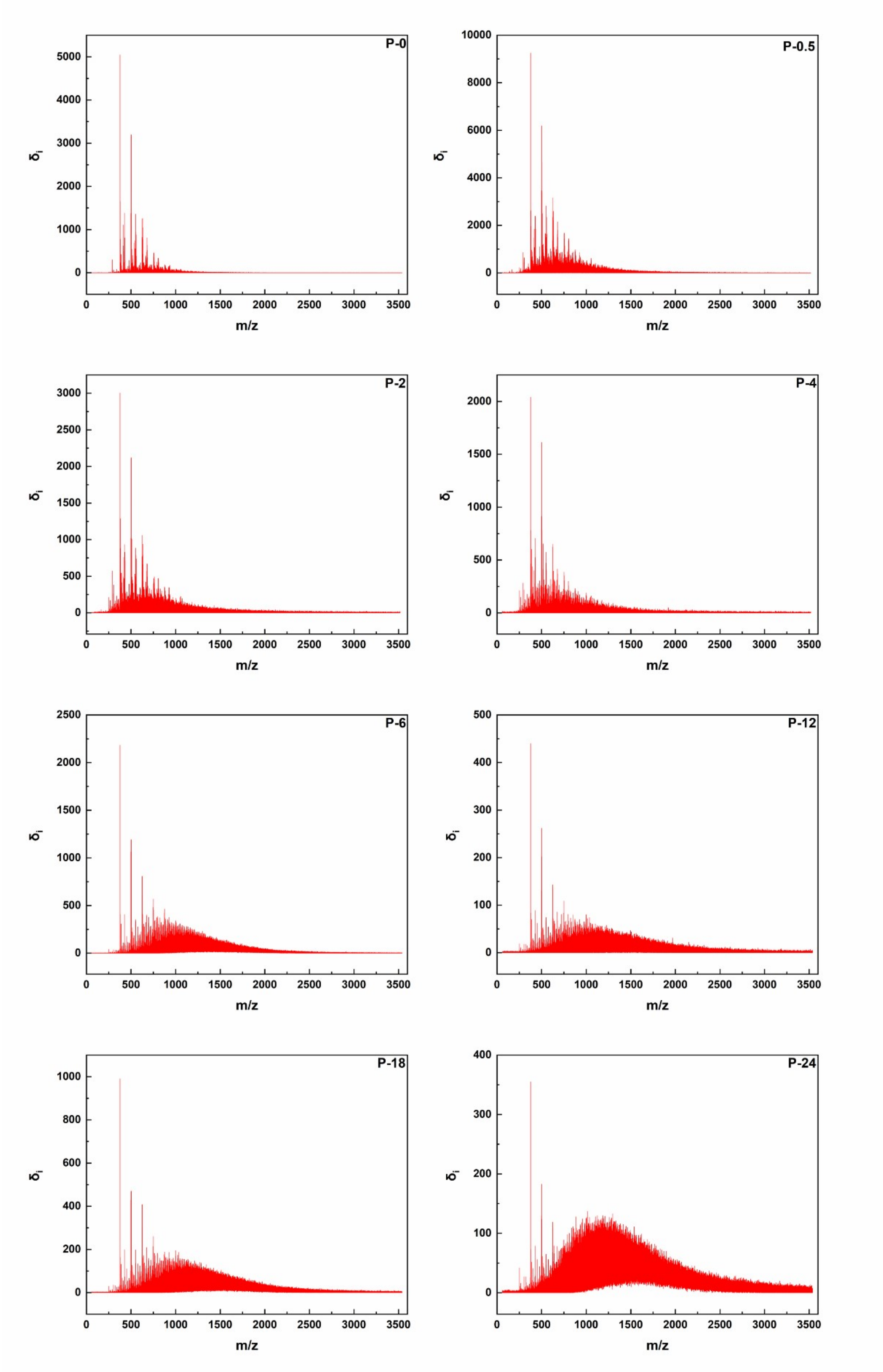

Fig. S4. The as-recorded MALDI-TOF-MS spectra of the pitch during polymerization. P-0: the raw pitch; P-0.5 to P-24: polymerized for 0.5-24h

3. The MATLAB program of the micro-kinetics model

```
function dzdt = polykinetics_3_1_1(~,x,k)
global n n1 ke
dzdt=rand(3*n+n1,1);
ke=rand(1,n);
for i=1:n
    ke(i)=k(2).*exp((i-1).*k(3));
end
dzdt(1,1)=k(4).*x(n+1).*x(2*n+1)-ke(1).*x(1);
for i=2:n
    dzdt(2*n+n1+i,1)=-k(5).*x(2*n+n1+i,1);
end
    for i=2:n
        for m=1:floor(i/2)
            dzdt(2*n+n1+i,1)=dzdt(2*n+n1+i,1)+k(4).*x(n+m).*x(n+i-m);
        end
    end
    for i=2:n
        dzdt(i,1)=k(4).*x(n+i).*x(2*n+1)-ke(i).*x(i)+k(5).*x(2*n+n1+i,1);
    end
    for i=1:n1
        dzdt(n+i,1)=k(1).*x(2*n+1+i)+ke(i).*x(i)-k(4).*x(n+i).*x(2*n+1)-
k(4)*x(n+i).^2;
        for m=1:n-i
            dzdt(n+i,1)=dzdt(n+i,1)-k(4).*x(n+i).*x(n+m);
        end
    end
    for i=n1+1:n
        if i<n/2
            dzdt(n+i,1)=ke(i).*x(i)-k(4).*x(n+i)*x(2*n+1)-k(4)*x(n+i).^2;
```

```
        else
            dzdt(n+i,1)=ke(i).*x(i)-k(4).*x(n+i)*x(2*n+1);
        end
        for m=1:n-i
            dzdt(n+i,1)=dzdt(n+i,1)-k(4).*x(n+i).*x(n+m);
        end
    end
    dzdt(2*n+1,1)=-2*k(4).*x(2*n+1).^2;
    for i=1:n1
        dzdt(2*n+1,1)=dzdt(2*n+1,1)+k(1).*x(2*n+1+i);
    end
    for i=1:n
        dzdt(2*n+1,1)=dzdt(2*n+1,1)+ke(i).*x(i)-k(4).*x(n+i).*x(2*n+1);
    end
    for i=1:n1
        dzdt(2*n+1+i,1)=-k(1).*x(2*n+1+i);
    end
end
```