Electronic Supplementary Information

Theoretical consideration

A. Theory of scattering

When a light travels through a media, the molecules or atoms in the media produce induced polarization, and are forced into vibration at a certain frequency. These are named vibrated dipoles, which can emit electromagnetic wave in all directions. In a pure uniform media, due to the second-wave interference, light can only be spread in the direction of refraction. However, in other directions, they cancel each other out and no scattering light can be seen. But, when the media is not pure, or produces local density fluctuations or concentration fluctuation due to thermal movement of main chains (i.e. scatterers), the second-wave interference is damaged, scattering light spreads in other directions except the direction of refraction. The effect of local density fluctuation or concentration fluctuation on scattering is discussed as follows.[1]

Assuming that light travels through the media along x-axis, γ is the cross-angle between k_f and n_i (n_i is the electric field direction of incident light, along y-axis), α is the cross-angle between k_f and z-axis, and θ is the scattering angle, the scattering vector $q = k_i - k_f$, and its modulus $|q| = \sqrt{|k_i|^2 + |k_f|^2 - 2|k_i||k_i|\cos\theta}$, where k_f and k_i are the wave vectors of the scattering light and incident light, respectively, and their moduli $|k| = 2\pi n / \lambda$.

Since $|k_i| = |k_f|$, we have

$$|q| = \sqrt{2|k_i|^2 - 2|k_i|^2 \cos\theta} = \sqrt{2k_i^2 \sin^2 \frac{\theta}{2}} = 2k_i \sin\frac{\theta}{2} = \frac{4\pi n}{\lambda_i} \sin\frac{\theta}{2}.$$

When the tested system and light source are determined, the scattering vector is only related to the scattering angle θ.

The scattering intensity (I_u) is equal to the average of the total light intensity of two mutually perpendicular polarized incident light beam in the scattering direction, which can be expressed as:

$$I_u = \frac{1}{2}[I_{if} + I'_{if}] = \frac{1}{2}A(\sin^2\gamma + \sin^2\alpha)\left\langle\left|\delta\varepsilon_{if}(q)\right|^2\right\rangle = \frac{1}{2}A\frac{1+\cos^2\theta}{2}\left\langle\left|\delta\varepsilon_{if}(q)\right|^2\right\rangle \quad \text{(A-1)}$$

where $A = \dfrac{k_f^4 I_0}{16\pi^2 R^2 \varepsilon_0^2}$, and $\left|\delta\varepsilon_{if}(q)\right|$ is the fluctuation of permittivity tensor at a q

scattering vector, ε_0 is the mean permittivity. Then, the Rayleigh ratio $R(q)$ can be

obtained as following,

$$R_u(q) \equiv \frac{I}{I_0}R^2 = \frac{k_f^4}{16\pi^2\varepsilon_0^2}\frac{1+\cos^2\theta}{2}\left\langle\left|\delta\varepsilon_{if}(q)\right|^2\right\rangle \quad \text{(A-2)}$$

In the region of visible light, the relationship between permittivity (ε_0) and

refractive index (n) in an isotropic system can be expressed as:

$\varepsilon = n^2$, that is, $\delta\varepsilon^2 = 4n^2\delta^2 n$

So, the Rayleigh ratio is given by:

$$R_u = \frac{4\pi^2 n^2}{\lambda_i^4}\frac{1+\cos^2\theta}{2}V\cdot\left\langle\delta^2 n\right\rangle \quad \text{(A-3)}$$

To a single-component system, the mean square fluctuation of refractive index

$\left\langle\delta n^2\right\rangle_d$ is only related to the mean square fluctuation of density as shown below.

$$\left\langle\delta n^2\right\rangle_d = \left(\frac{\partial n}{\partial\rho}\right)^2\left\langle\delta\rho^2\right\rangle \quad \text{(A-4)}$$

Besides, in a single-component system, density is a function of temperature and

pressure. The density fluctuation can be expressed as:

$$\partial\rho = \left(\frac{\partial\rho}{\partial T}\right)_P\delta T + \left(\frac{\partial\rho}{\partial P}\right)_T\delta P$$

and the mean square fluctuation of density can be shown as:

$$\left\langle\delta\rho^2\right\rangle_d = \left(\frac{\partial\rho}{\partial T}\right)_P^2\left\langle\delta T^2\right\rangle + 2\left(\frac{\partial\rho}{\partial T}\right)_P\left(\frac{\partial\rho}{\partial P}\right)_T\left\langle\delta P\delta T\right\rangle + \left(\frac{\partial\rho}{\partial P}\right)_T^2\left\langle\delta P^2\right\rangle \quad \text{(A-5)}$$

where $\left\langle\delta T^2\right\rangle$ and $\left\langle\delta P^2\right\rangle$ are the mean square fluctuations of temperature and pressure,

respectively. $\left\langle\delta P\delta T\right\rangle$ is the cross-average fluctuation of temperature and pressure.

According to the statistical thermodynamic theory, the following relationships can

be obtained:

$$\langle \delta T^2 \rangle = rkT^2 / (rC_P - \alpha^2 TV)$$

$$\langle \delta P^2 \rangle = C_P kT / V (rC_P - \alpha^2 TV) \Bigg\} \qquad \text{(A-6)}$$

$$\langle \delta T \delta P \rangle = \alpha kT^2 / rC_P - \alpha^2 TV$$

where k is Boltzmann constant, C_P is molar heat capacity at constant pressure, V is

micro-volume element, $r \equiv -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$ is constant temperature compression

coefficient, and $\alpha \equiv -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$ is expansion coefficient at constant pressure.

$$\rho = \frac{NM}{V} \qquad \text{(A-7)}$$

Based on the derivative calculation on both sides of Eq. (A-7), a relationship can be

obtained: $\delta V / V = -\delta \rho / \rho$, so that $r = \dfrac{1}{\rho}\left(\dfrac{\partial \rho}{\partial P}\right)_T$ and $\alpha = -\dfrac{1}{\rho}\left(\dfrac{\partial \rho}{\partial T}\right)_P$.

Combining Eq. (A-5) and Eq. (A-6), we have:

$$\langle \delta \rho^2 \rangle_d = \rho^2 rkT / V \qquad \text{(A-8)}$$

and $\langle \delta n^2 \rangle_d = \left(\dfrac{\partial n}{\partial \rho}\right)^2 \rho^2 rkT / V \qquad \text{(A-9)}$

Then, the Rayleigh ratio induced by density fluctuation can be written as:

$$(R_u)_d = \frac{4\pi^2 n^2}{\lambda_i^4} \frac{1+\cos^2 \theta}{2} \left(\rho \frac{\partial n}{\partial \rho}\right)^2 rkT \qquad \text{(A-10)}$$

If a second component is added into the pure media, the contribution of the local

concentration fluctuation to the refractive index fluctuation in the blending system can

be expressed as:[2]

$$\langle \delta n \rangle_c = \left(\frac{\partial n}{\partial c}\right)\langle \delta c \rangle \quad \text{and} \quad \langle \delta n^2 \rangle_c = \left(\frac{\partial n}{\partial c}\right)^2 \langle \delta c^2 \rangle$$

The Rayleigh ratio induced by concentration fluctuation is written as:

$$(R_u)_c = \frac{4\pi^2 n^2}{\lambda_i^4} \frac{1+\cos^2\theta}{2} \left(\frac{\partial n}{\partial c}\right)^2 \frac{C}{\left(\dfrac{1}{M_2} + 2A_2 C + 3A_3 C^2 + \cdots\cdots\right)} \tag{A-11}$$

Considering the effect of both intensity fluctuation and concentration fluctuation on scattering intensity, the Rayleigh ratio can be given as follows:

$$R_u = (R_u)_d + (R_u)_c$$

When an electric charge particle undergoes accelerated motion, it radiates electromagnetic energy. Based on the electromagnetism theory, the corresponding Rayleigh scattering intensity can be expressed as:

$$I_s = \frac{c}{4\pi} E_s E_s^* = \frac{c}{4\pi} E_0^2 \frac{\alpha^2 \omega^4}{c^4 r^2} \sin^2\psi \tag{A-12}$$

Considering the effect of phase factor on scattering, the electric field strength of a multi-scatters system can be written as:

$$E_s = \sum_j (E_s)_j = -\frac{\omega^2 E_0}{c^2 r} \sin\psi \cdot e^{i(\omega t - kD)} \sum_j \alpha_j e^{-ik(rj\cdot s)} \tag{A-13}$$

where r is the distance between the scatter and the detector, which can be considered to be the same for each scatter, α is polarizability, and rj is the spatial position in the coordinate system. It can be seen from Eq. (A-13) that scattering is related to the polarizability and spatial distribution of the scatterers.

Taking the form factor into account, the scattering intensity can be expressed as:[1]

$$I_s = \frac{c}{4\pi} E_s E_s^* = \frac{c}{4\pi} K_R K_R^* F F^* \tag{A-14}$$

Scattering of two kinds of ideal structural scatterers are discussed as follows.

(1) Scattering of a spherulite

Being a spherical symmetry system, the polarizability of a spherulite is dependent on its radius (R_s) only, and the form factor as an integral of R_s can be given as,

$$
\begin{aligned}
f &= \frac{4\pi}{h}(\alpha_0 - \alpha_s)\int_0^{Rs} r\sin(hr)dr \\
&= \frac{4\pi}{h^3}(\alpha_0 - \alpha_s)[\sin(hR_s) - (hR_s)\cos(hR_s)] \\
&= V_{sph}(\alpha_0 - \alpha_s)\Phi_s(U)
\end{aligned}
\tag{A-15}
$$

in which V_{sph} is the volume of the spherulite, and $\Phi_s(U)$ is the scattering function.

$$\Phi_s(U) \equiv \frac{3}{U^3}(\sin U - U\cos U) , \tag{A-16}$$

where $U = hR_s = 4\pi\dfrac{R_s}{\lambda}\sin\dfrac{\theta}{2}$, θ is scattering angle, and λ is the incident wavelength.

Then, the Rayleigh ratio can be written as,

$$R(\theta) = KFF^* = KV_{\text{sph}}^2(\alpha_0 - \alpha_s)^2\Phi_s^2(U) \tag{A-17}$$

On the basis of the function of Rayleigh ratio $R(\theta) = \dfrac{I_s r^2}{I_0 V_{\text{sph}}}$, the scattering of a

spherulite can be acquired as the following,

$$I_s = \frac{KV_{\text{sph}}^3(\alpha_0 - \alpha_s)^2\Phi_s^2(U)I_0}{r^2} \tag{A-18}$$

in which $(\alpha_0 - \alpha_s)^2 = (n_0^2 - n_s^2)^2$, n_0 and n_s are refractive indexes of the media and

sphere, respectively. In this scattering measurement, the scattering angle is 90°,

consequently, it is easy to obtain:

$$U = hR_s = 4\pi\frac{R_s}{\lambda}\sin\frac{\theta}{2} = 2\sqrt{2}\pi\frac{R_s}{\lambda}$$

So the expression of I_s can be given as below:

$$I_s = \frac{K\lambda^6 R_s^3(\alpha_0 - \alpha_s)^2 I_0}{24\pi^3 r^2}(\sin U - U\cos U)^2 \tag{A-19}$$

Assuming that α_0 and α_s are constants, it can be concluded from Eq. (A-19) that the

scattering intensity of a spherulite is related to the volume of the spherulite.

(2) Scattering of the sheet

For an infinitely thin sheet of length L and width W, it has no spherical symmetry.

Supposedly, the polarizability of each scatter is the same. In the rectangular cartesian

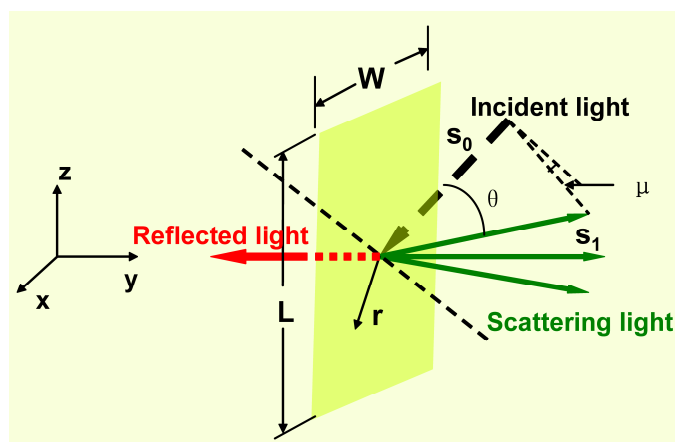coordinate (Scheme A-1), structure factor of the sheet can be expressed as:

$$F = \alpha_0 LW\left[\frac{\sin(aW/2)}{(aW/2)}\right]\left[\frac{\sin(bL/2)}{(bL/2)}\right] \tag{A-20}$$

$$a = k \sin \theta \sin \mu$$

$$b = k \sin \theta \cos \mu$$

In our experiment, the scattering angle θ is 90°, and the azimuth μ is zero. Hence the scattering intensity can be calculated from:

$$I_s(\mu = 0) = \frac{c}{4\pi} K^2 \left[\frac{\sin(bL/2)}{(bL/2)} \right]^2 \tag{A-21}$$

Evidently, the scattering intensity is only determined by the length of the sheet L, and has nothing to do with the width W.

Scheme A-1. The scattering of a sheet in rectangular cartesian coordinate.

B. Theory of resonance light scattering (RLS)

Resonance light scattering (RLS) spectrum is recorded with synchronous scanning at $\lambda_{ex} = \lambda_{em}$. On the basis of the ideas of Pasternack et al.,[3-6] Liu and Lu et al.,[7-10] we sum up the RLS theory as follows.[7]

(i) Generation of RLS. RLS is referred to an enhancement of scattering light in close proximity to an absorption band of scattering system. One of the necessary conditions of judging whether a light scattering is ascribed to RLS is based on whether an enhanced scattering peak is near or within some absorption band of a scattering system. Furthermore, self-aggregations or self-assemblies of chromophores formed in the target system are a vital light-scattering enhancement factor, which are distinguished from Rayleigh scattering (RS).

(ii) Theoretical calculation of RLS. The macroscopic fluctuation theory of resonance enhanced light scattering was modified by Mie.[11] The scattering cross section, C_{sca}, can be simply calculated from:

$$C_{sca} = \frac{24\pi^3 v^2 n_0^4}{\lambda_0^4}\left(\frac{m^2-1}{m^2+2}\right)^2 \tag{B-1}$$

where m is a complex refractive index. It is given as below,[9]

$$m = n - ik$$

where n and k evaluate the effects of refractive and absorption of a scattering system, respectively.

Self-aggregations or self-assemblies of chromophores greatly contribute to the enhancement of light scattering intensity, $I_{sca}(\lambda_0)$, which is estimated from:[7]

$$
\begin{aligned}
I_{sca}(\lambda_0) &= C_{sca}(\frac{N}{V})I_0(\lambda_0) \\
&= \frac{24\pi^3 v^2 n_0^4}{\lambda_0^4}\left(\frac{m^2-1}{m^2+2}\right)^2\left(\frac{N}{V}\right)I_0(\lambda_0) \\
&= Rv^2\left(\frac{\frac{m'}{\rho v}}{V}\right) = Rv\left(\frac{n'M}{\rho V}\right) = R\frac{M}{\rho}\cdot v \cdot c = K'\cdot v \cdot c
\end{aligned}
\tag{B-2}
$$

$$R = \frac{24\pi^3 n_0^4 I_0(\lambda_0)}{\lambda_0^4}\left(\frac{m^2-1}{m^2+2}\right)^2, \quad K' = \frac{24\pi^3 n_0^4 M I_0(\lambda_0)}{\rho\lambda_0^4}\left(\frac{m^2-1}{m^2+2}\right)^2$$

where λ_0 is the wavelength of incident light, $I_0(\lambda_0)$ is the incident light intensity at λ_0, n_0 is the refractive index of media, m', ρ, N and v are mass, density, number and volume of the scatters, respectively. n', M and c represent amount of substance, molar mass and molar concentration of the scattering material, respectively. When the determination conditions and the medium are fixed, K' is constant.

As displayed by Eq. (B-2), under certain condition, $I_{sca}(\lambda_0)$ is directly proportional to $c \cdot v$. That is to say, the scattering light intensity depends on number of the scatterer per unit volume and volume of each scatterer. Lu et al. pointed out that $I_{abs}(\lambda_0)$ is independent of v,[7] while Pasternack et al. did not give a clear explanation to the enhancement of RLS.[7,12]

(iii) Enhancement mechanism of RLS. Liu et al.[8-10] gave a good complement to

Pasternack's RLS theory based on discussing m as a function of real (n) and imaginary (k) parts of m in RLS of a scattering system, respectively (i.e., $m=n-ki$). The relationship between n and molar absorption coefficient ($\varepsilon(\lambda)$) at any wavelength within the absorption band can be described with Kronig-Kramers equation:[7,13]

$$n = n_0 + \frac{2.303\lambda_0^{\,2}}{2\pi^2}\int_0^\infty \frac{\varepsilon(\lambda)}{\lambda_0^{\,2}-\lambda^2}d\lambda \qquad (B\text{-}3)$$

Therefore, the increment of n with the fluctuation of c can be specified by:

$$\frac{\partial n}{\partial c} = \frac{2.303\lambda_0^{\,2}}{2\pi^2}\int_0^\infty \frac{\varepsilon(\lambda)}{\lambda_0^{\,2}-\lambda^2}d\lambda \qquad (B\text{-}4)$$

As for k, it can be expressed as:

$$k = \frac{2.303\varepsilon(\lambda_0)c\lambda_0}{4\pi} \qquad (B\text{-}5)$$

in which $\varepsilon(\lambda_0)$ is the molar absorption coefficient at λ_0. So, the increment of k with the fluctuation of c can be given as:

$$\frac{\partial k}{\partial c} = \frac{2.303\varepsilon(\lambda_0)\lambda_0}{4\pi} \qquad (B\text{-}6)$$

Eq. (B-4) and Eq. (B-6) show that, with the withdrawal of λ_0 from absorption bands, both $\partial n/\partial c$ and $\partial k/\partial c$ become weaker. On the other hand, when λ_0 moves towards absorption bands, they both get increased. Especially, when λ_0 is slightly higher than λ_{max} (the maximum absorption wavelength), m reaches the maximum, explaining why RLS is strictly termed pre-resonance light scattering.[7,14]

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