On the Origin of Mesoscopic Inhomogeneity of Conducting Polymers

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Supporting Information

The effect of the molar volume on the polymer nucleation according to the Kelvin model

The Kelvin equation gives the value of the critical radius r^* in the simplest case of the so-called capillarity approximation for clusters comprising sufficiently large number of molecules:[1,2]

$$r^* = \frac{2 \cdot \sigma \cdot V_M}{R_{gas} T \cdot \ln(\frac{c}{c_s})} \qquad (S1)$$

where r^* is the critical radius of a cluster;

c is the concentration of a nucleating species;

c_s is its saturated concentration;

σ is the surface tension at the polymer/solution interface;

V_M is the molar volume of the polymer;

R_{gas} is the gas constant;

T is the absolute temperature;

$r*$ is the critical radius of a nucleus;

$\dfrac{c}{c_s} = \zeta$ is the supersaturation ratio.

In addition to solubility, the molecular weight (Mw) of a polymer fraction may affect also other parameters found in Eq. (S1), specifically, the polymer molar volume. At a first glance, the molar volume should increase with the molecular weight thus increasing the resulting critical radius and favoring a larger critical grain size. However, this apparent contradiction is easily resolved if we remember that, in the case of nucleation of molecules with different Mw, the nuclei of the same size are comprised by a different number of molecules, and the survival of a nucleus will be determined not by its radius *per se*, but rather by the number of molecules required to form a nucleus of this size. Evidently, a critical nucleus that comprises a smaller number of molecules is more likely to be formed than a nucleus containing a larger number of molecules.

In order to better demonstrate this reasoning, the Kelvin equation (Eq. S1) can be re-written as (see Appendix for details):

$$n* = \frac{\pi}{6} \cdot \frac{(4\sigma)^3 \cdot V_M^2}{\left[R_{gas} T \cdot \ln(\zeta) \right]^3} \tag{S2}$$

where n^* is the number of molecules of given Mw in a critical nucleus;

V_M is the molar volume of the polymer;

$$V_M = N_A \cdot V_0 ; V_0 = \frac{V_{nucl}}{n}$$ (S3)

where V_{nucl} is the volume of a single nucleus made of n polymer molecules;

N_A is Avogadro's number.

Equation (S2) allows one to see more clearly the predominant effect of supersaturation on the polymer nucleation from solutions containing a mixture of polymer molecules with different molecular weights. It is worth noting that it is assumed here that the volume of a polymer nucleus consisting of n polymer molecules is obtained by simple addition of the volumes occupied by individual molecules (a so-called liquid droplet model). However, longer chains can be expected to fold more efficiently upon forming a solid phase, thus resulting in a more densely packed and more crystalline structure.[3,4] Therefore, one could expect that in fact the volume of the polymer nuclei formed by polymer molecules with higher Mw will be less than the value calculated using Eq. (S3). This should make the effect of supersaturation even more pronounced than predicted by Eq. (S2).

APPENDIX

Following the paper of F.Q. Yu,[5] let us use the liquid droplet model to find the Gibbs free energy for the addition of one polymer molecule to a cluster of *n-1* polymer molecules of the same molecular weight:

$$\Delta G_{n-1,n} = -kT \cdot \ln(\zeta) + \sigma \cdot (A_n - A_{n-1}) \tag{A1}$$

Here $\zeta = \dfrac{c}{c_s}$ is the supersaturation ratio;

σ is the surface tension at the polymer/solution interface;

A_n is the surface area of the polymer cluster containing n polymer molecules;

A_{n-1} is the surface area of the polymer cluster containing n-1 polymer molecules;

k is the Boltzmann constant;

T is the absolute temperature.

Since the volume V_n of the cluster containing *n* polymer molecules in terms of the liquid droplet model is equal to

$$V_n = n \cdot V_0 \tag{A2}$$

where V_0 is the volume taken by one polymer molecule in the cluster,

we find the cluster radius r_n,

$$r_n = \left(\frac{3nV_0}{4\pi} \right)^{\frac{1}{3}} \tag{A3}$$

Therefore,

$$A_n - A_{n-1} = 4\pi \cdot (r_n^2 - r_{n-1}^2) =$$

$$= 4\pi \cdot (\frac{3V_0}{4\pi})^{\frac{2}{3}} \cdot \left[n^{2/3} - (n-1)^{2/3} \right] = \tag{A4}$$

$$= (4\pi)^{1/3} \cdot (3V_0)^{2/3} \cdot n^{2/3} \cdot \left[1 - (1 - \frac{1}{n})^{2/3} \right]$$

from where we find   when $n \gg 1$,

$$A_n - A_{n-1} = (4\pi)^{1/3} (3V_0)^{2/3} \cdot \frac{2}{3} n^{-1/3} \tag{A5}$$

For a critical nucleus,

$$\Delta G_{n-1,n} = 0$$

and

$$kT \cdot \ln(\zeta) = \sigma \cdot (A_n - A_{n-1}) =$$

$$= \sigma \cdot (4\pi)^{1/3} (3V_0)^{2/3} \cdot \frac{2}{3} n *^{-1/3} =$$

$$= 4 \cdot \sigma \cdot V_0^{2/3} \cdot (\frac{\pi}{6})^{1/3} \cdot n *^{-1/3} \tag{A6}$$

From Eq. (A6) it is easy to find the number of polymer molecules in a critical nucleus n^*,

$$n *^{1/3} = \frac{4 \cdot \sigma \cdot V_0^{2/3} \cdot (\frac{\pi}{6})^{1/3}}{kT \cdot \ln(\zeta)} \tag{A7}$$

Equation (A7) can be readily transformed to the form of (Eq. S2) by cubing and replacing the volume V_0 with the molar volume V_M and the Boltzmann constant k with the gas constant R_{gas}.

REFERENCES AND NOTES

(1)   Ruckenstein, E.; Djikaev, Y. S. *Adv. Colloid Interfac.* **2005**, 118, 51.

(2)   Kashchiev, D. Nucleation: Basic Theory with Applications;   Butterworth-Heinemann: Oxford, **2000**, p. 74.

(3)   Zen, A.; Saphiannikova, M.; Neher, D.; Grenzer, J.; Grigorian, S.; Pietsch, U.; Asawapirom, U.; Janietz, S.; Scherf, U.; Lieberwirth, I.; Wegner, G. *Macromolecules* **2006**, 39, 2162.

(4)   Osawa, S.; Ito, M.; Iwase, S.; Yajima, H.; Endo, R.; Tanaka, K. *Polymer* **1992**, 33, 914.

(5)   Yu, F. Q. *J. Chem. Phys.* **2005**, 122.