Electronic Supplementary Information

Verification of Thermodynamic Theories of Strain-induced Polymer Crystallization

Chunbo Zhang[1,2], Chang, Liu[2,3], Lei Wang[1], Ying Zhao[2], Guoming Liu[2,3]*, and Dujin Wang[2,3]

1 Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China

2 CAS Key Laboratory of Engineering Plastics, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

3 University of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding author: gmliu@iccas.ac.cn

Section S1. Theory about Strain−Induced Crystallization (SIC)

According to the classical nucleation theory (CNT)[1], the relation between nucleation rate can be expressed as:

$$I = I_0 \exp\left(-\frac{\Delta E}{RT}\right)\exp\left(-\frac{\Delta G^*}{RT}\right)\#(S1)$$

in which I_0 is the pre-factor, ΔE is the activation energy of the movement of the crystal unit diffusing across the phase interface. It is generally considered that ΔE is not affected by the external field. ΔG^* is the free energy generated for the critical nuclei:

$$\Delta G^* = A\gamma - V\Delta G_m\#(S2)$$

where $A\gamma$ corresponds to the interface energy between the nucleus and the amorphous part. ΔG_m is the melting free energy per molar monomer, which can be expressed by changes in enthalpy and entropy:

$$\Delta G_m = \Delta H_m - T\Delta S_m\#(S3)$$

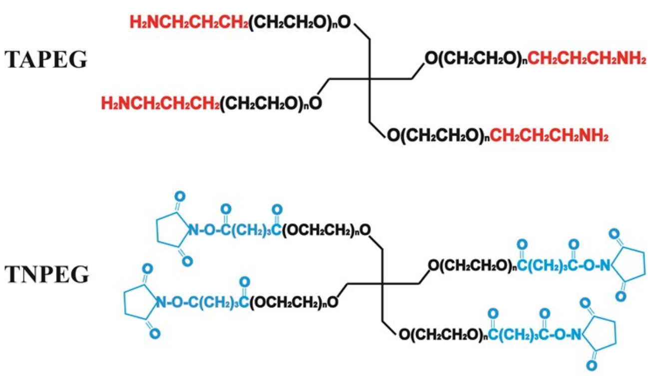
Combining the above eqn (S1)-(S3) and eqn (1)-(2) in the main text, ΔG^* of a deformed polymer chain with an extension ratio of λ can be expressed as:

$$\Delta G^* = A\gamma - V\left[\Delta H_m - T\Delta S_m - T\Delta S_{def}\right]\#(S4)$$

It is imperative to point out that ΔS_{def} strongly affects the nucleation rate of semicrystalline polymers.

Section S2. Preparation of Polyethylene Glycol (PEG) Network

PEG gel was prepared by reaction between tetra-amine-terminated PEG (TAPEG) and tetra-NHS-glutarate-terminated PEG (TNPEG), according to Shibayama et al.'s work[2, 3]. PEG derivatives were purchased from Xiamen SINOPEG Biotechnology Co., Ltd. The molecular structures of TAPEG and TNPEG are shown in Scheme S1.



Scheme S1 The molecular structures of TAPEG and TNPEG.

The weight average molecular weight (M_w) of TAPEG and TNPEG were determined by mass spectrometry. The polydispersity index of the PEG derivatives is less than 1.05. Considering the length of the four-arm PEG strand is nearly monodisperse, the M_c of the PEG network was the sum of the molecular weight of two strands. For example, the M_c of PEG network obtained by TAPEG and TNPEG with M_w of 20k g/mol is 10k g/mol (named as PEG-net-10k). Accordingly, PEG-net-20k was prepared by TAPEG and TNPEG with M_w = 40k g/mol.

First, the TAPEG and TNPEG were dissolved in a phosphate buffer solution of pH = 7.4 and pH = 5.8 with a salt concentration of 50 mM. The concentrations of PEG derivatives were 80 mg/mL and 60 mg/mL for PEG-net-10k and PEG-net-20k, respectively. The TAPEG and TNPEG solutions were mixed in equal amounts with vigorous stirring for ~10 min. The resultant solution was left for 24 h before dialyzing for 72 h to remove the ions in the gel. The ion-free gel was stored in tetrahydrofuran (THF) for 48 hours to replace the water with THF. The gel was then placed in a fume hood to evaporate the solvent for more than 5 days (until the weight was constant). Therefore, a dry film of the PEG network with a thickness of ~ 0.2 mm was obtained.

Section S3. FTIR Measurement and Results

FTIR measurements were performed on a Thermo Nicolet Avatar 6700 FTIR spectrometer by averaging 32 scans with a resolution of 4 cm^{-1}. The FTIR spectra of TNPEG, TAPEG, and PEG-net-10k were shown in Fig. 1b. For the spectrum of the network, the characteristic band of the imide group in TNPEG disappears and the characteristic band of the amide bond appears. This result indicates the formation of crosslinks.

The FTIR spectrum of the TNPEG shows the characteristic absorption peaks of imide at 1812 cm^{-1} and 1783 cm^{-1}, corresponding to the two carbonyl groups in the imide group, respectively. The band at 1739 cm^{-1} representing the stretching vibration of the carbonyl group in the ester group has two origins: one is the ester group formed by glutaric acid and ethylene glycol, and the other comes from the ester group formed with glutaric acid and succinimide. Only the latter can react with TAPEG to form an amide group. Therefore, in the FTIR spectrum of the PEG-net-10k, the absorption band at 1733 cm^{-1} of the ester group still exists, and the characteristic absorption peaks of the amide bond appear at 1672 and 1534 cm^{-1}, which are attributed to amide I and amide II[3]. Comparing the FTIR of the TNPEG, TAPEG, and the PEG-net-10k, we concluded that the reaction between amino and active ester group is completed.

Section S4. Small-Angle Neutron Scattering (SANS)

PEG gels as prepared in D_2O buffer and dry networks which are swollen in D_2O to equilibrium were characterized by SANS. SANS experiments were performed on a 2D SANS instrument at the China Spallation Neutron Source (CSNS). The distance between sample and detector was 2.5 m covering a q range of 0.005−0.45 Å^{-1}. The scattering intensity was corrected for detector sensitivity. The scattering contribution from empty quartz cells and the D_2O was subtracted.

The SANS data was fitted with the following eqn (S5)[4],

$$I(q) = \frac{A}{q^n} + \frac{C}{1 + (q\xi)^m} + B\#(S5)$$

In which the two multiplicative factors A and C, the incoherent background B, and the two exponents: n and m are the fitting parameters. The ξ is the correlation length for the mesh size of the network. The fitting results for ξ in Table S1 indicate that the PEG networks prepared in D_2O buffer and dry PEG networks which are swollen in D_2O to equilibrium exhibit similar mesh size.

Table S1 Correlation length for PEG networks

Sample	As-prepared in D_2O buffer ξ (Å)	Dry networks swollen in D_2O ξ (Å)
PEG-net-10k	14.00±0.02	13.98±0.14
PEG-net-20k	17.22±0.16	17.76±0.12

Section S5. Non-isothermal and Isothermal DSC Measurements

The crystallization and melting behavior of the PEG network samples were determined by DSC using Perkin Elmer 8500 DSC. The second heating curves of PEG-net-10k and PEG-net-20k are shown in Fig. S1, the T_ms of PEG networks are 53.5 and 56.1 °C, respectively. It can be seen that the T_m increases with M_c increasing.

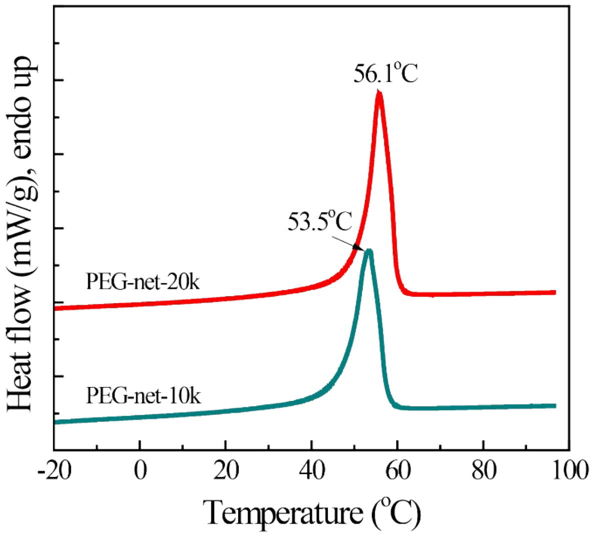


Fig. S1 DSC curves of PEG-net-10k and PEG-net-20k.

Section S6. *In-situ* WAXD and SAXS Measurements

As the amorphous PEG networks were stretched to a specified λ and fixed, the evolution of crystalline structure during cooling and heating with a rate of 10 °C/min was detected by WAXD with a temperature resolution of 0.5 °C. The effective λ was determined by measuring the displacement between ink marks on the surface of the tensile bar. The *in-situ* WAXD and SAXS measurements were performed at the beamline 1W2A in the Beijing Synchrotron Radiation Facility (BSRF). All diffraction patterns were captured *in-situ* by a Pilatus detector with a resolution of 981 * 1043 pixels (pixel size: 172 * 172 μm^2). The 2D WAXD patterns were converted to 1D intensity profiles by a home-written code using Python.

The overall crystallinity index (X_c) of the PEG network was calculated by the following eqn (S6):

$$X_c = \frac{\sum A_{crystalline}}{A_{Observed}} \times 100\% \#(S6)$$

where the $\Sigma A_{crystalline}$ is the sum of crystalline peak areas and the $A_{Observed}$ is the direct integration of the whole intensity profile. An example of calculation for $\Sigma A_{crystalline}$ is displayed in Fig. S2.

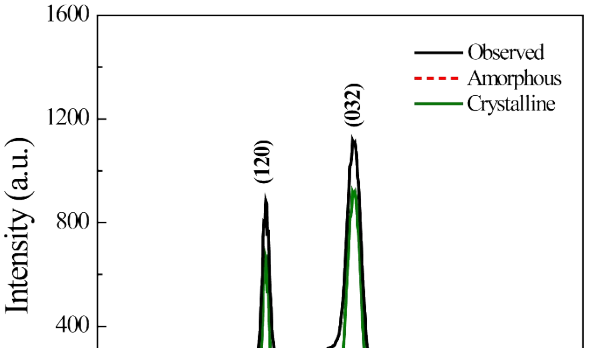


Fig. S2 Schematic illustrating the method of calculating the crystallinity index.

Fig. S3 displays the 2D-SAXS patterns of PEG-net-10k under different elongation ratios after cooling. The normal of the lamellae formed under stretching are parallel to the stretching direction. As shown in Fig. S4 and Table S2, the lamellar thickness of PEG-net-10k cooled from 100 to 20 °C, is obtained by long period from SAXS and crystallinity index from WAXD. The lamellar thickness increases from 6.9 to 8.2 nm when λ increases from 1 to 3.4.

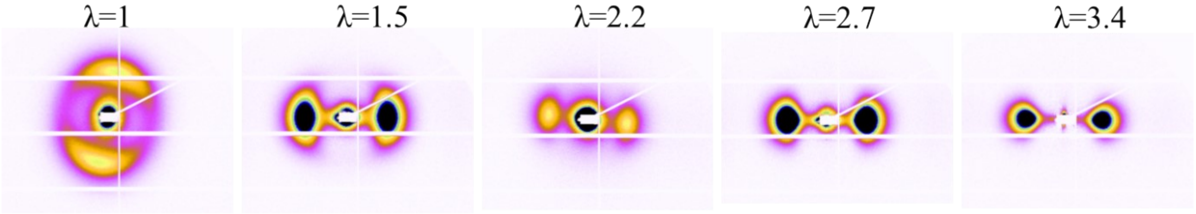


Fig. S3 2D-SAXS patterns of PEG-net-10k under different elongation ratios after cooling from 100 to 20 °C at a rate of 10 °C/min. The stretching direction is horizontal.

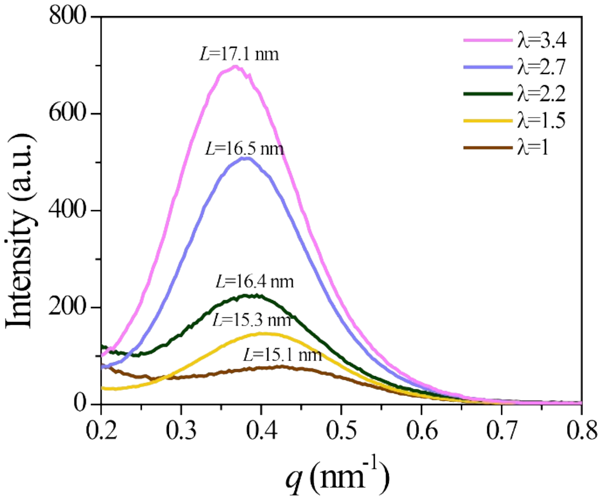


Fig. S4 SAXS profiles of PEG-net-10k after cooling from 100 to 20 °C at a rate of 10 °C/min. The long period (L) was calculated by $L = 2\pi/q_{\max}$, in which $q_{\max}$ is the q value at the intensity maximum.

Table S2. Lamellar thickness of PEG-net-10k cooled from 100 to 20 °C at a rate of 10 °C/min obtained by the long period and crystallinity index.

Stretching ratio	Crystallinity index (%)	Long period (nm)	Lamellar thickness (nm)
1	45.8	15.1	6.9
1.5	44.3	15.3	6.8
2.2	47.9	16.4	7.8
2.7	46.0	16.5	7.6
3.4	48.2	17.1	8.2

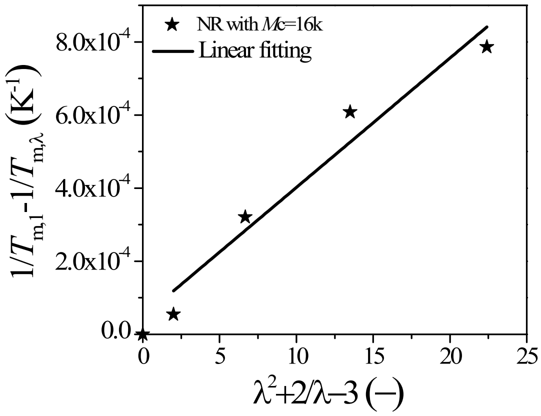


Fig. S5 Correlating the $^{1}/_{T_{m,1}} - {^{1}/_{T_{m,\lambda}}}$ with $\lambda^2 + {^{2}/_{\lambda}} - 3$ based on eqn (6) in NR from the work of Trabelsi et al[5].

References

1. B. Wunderlich, *In Macromolecular Physics, Academic Press*, 1976.
2. T. Sakai, T. Matsunaga, Y. Yamamoto, C. Ito, R. Yoshida, S. Suzuki, N. Sasaki, M. Shibayama and U. Chung, *Macromolecules*, 2008, **41**, 5379-5384.
3. Y. Akagi, T. Katashima, Y. Katsumoto, K. Fujii, T. Matsunaga, U. Chung, M. Shibayama and T. Sakai, *Macromolecules*, 2011, **44**, 5817-5821.
4. B. Hammouda, D. L. Ho and S. Kline, *Macromolecules*, 2004, **37**, 6932-6937.
5. S. Trabelsi, P. A. Albouy and J. Rault, Macromolecules, 2003, **36**, 7624-7639.