Electronic Supplementary Material (ESI) for Soft Matter.

Sonocrystallization of Conjugated Polymers with Ultrasound Fields

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Supporting Information

Table S1. Summary of molecular weight and dispersities of polymers.

Polymers	Lot #	M_n	$Đ$
Regiorandom P3HT	BS20-92	26k	2.4
P3DDT	BS21-87	22k	1.8
PQT-12	DL158	24k	1.7

P3HT solution in chloroform changes to dark color after exposing to acoustic wave in sonication bath for 10 min, indicating fiber formation. In contrast, the reference sample without sonication stays in orange color.

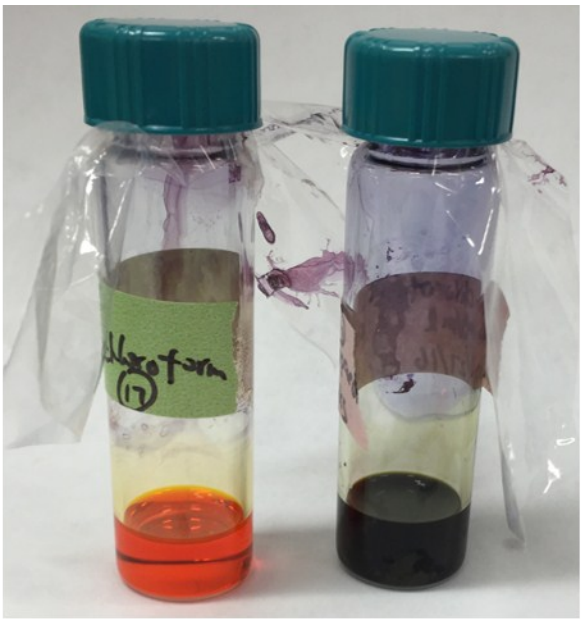

Figure S1. Photograph of 4 mg/ml P3HT solutions in chloroform with 10 min and without application of acoustic wave in sonication bath.

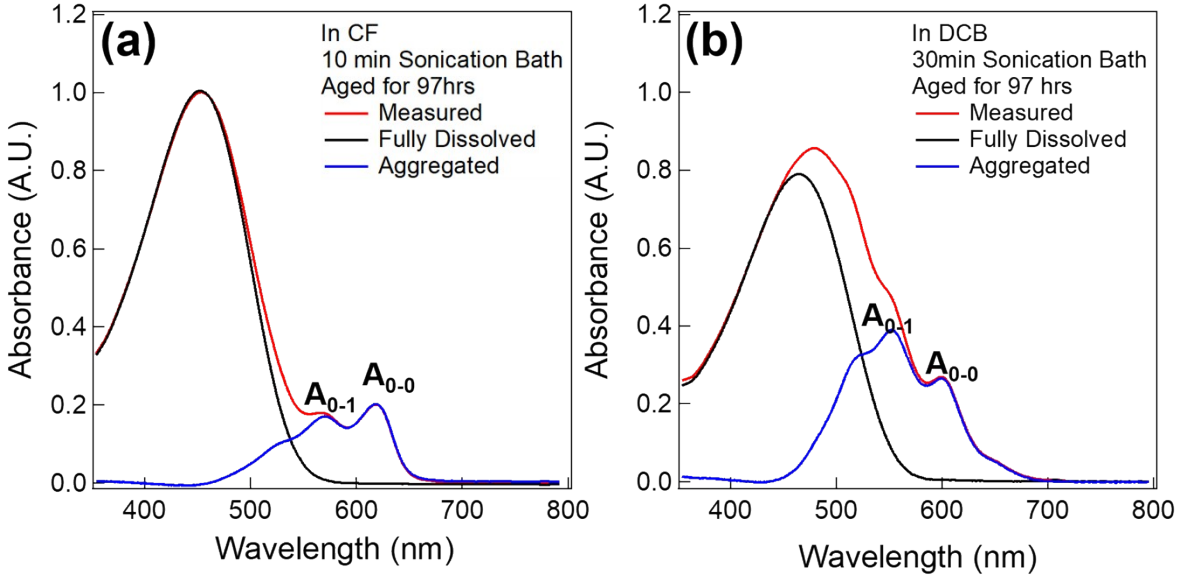

Figure S2. Measured absorption spectra of polymer solution aged 97 hrs after ultrasound application, completely dissolved P3HT solution, and subtracted absorption spectra of pure aggregates in (a) chloroform and (b) dichlorobenzene.

Description of combined model for SANS fitting of rre-P3HT

Parallelepiped model [1,2] combined with dissolved polymer model considering excluded volume effect [3,4] are used to model the P3HT system with dissolved polymers and nanofibers. The first half of Eq-S1 describes the polymer nanofibers and the second half of the model represents dissolved polymers.

$$I\,(q) = \phi_v \varphi_f \left(\Delta\rho_{PP}\right)^2 P_{PP}(q) + \phi_v (1 - \varphi_f)\left(\Delta\rho_{PExV}\right)^2 P_{PExV}(q) \qquad \text{Eq-S1}$$

Where ϕ_v is the volume fraction of P3HT in solution, φ_f is the polymer fraction in fiber form, $\Delta\rho_{PP}$ is the SLD difference between solvent and nanofibers, and $\Delta\rho_{PExV}$ is the SLD difference between solvent and fully dissolved P3HT chains. The form factors of the parallelepiped ($P_{PP}(q)$) and polymer excluded volume model ($P_{PExV}(q)$) are given by Eq-S2 and Eq-S3~ S5, respectively. In this model, only three parameters are allowed to change. These are fiber height (a), width (b), as well as polymer fractions in fiber form (φ_f). Other parameters are known or determined from fits at sonication time=0 (e.g. radius of the dissolved polymer) and kept fixed in fits at other sonication times.

$$P_{PP}(q) = \frac{2}{\pi}\int_0^{2\pi}\int_0^{2\pi}\left[\left(\frac{\sin\left(qA\sin\alpha\cos\beta\right)}{qA\sin\alpha\cos\beta}\right)\left(\frac{\sin\left(qB\sin\alpha\cos\beta\right)}{qB\sin\alpha\cos\beta}\right)\left(\frac{\sin\left(qC\cos\alpha\right)}{qC\cos\alpha}\right)\right]^2 \sin\alpha\, d\alpha d\beta \qquad \text{Eq-S2}$$

$$P_{PExV}(q) = \frac{1}{\nu U^{\frac{1}{2\nu}}}\gamma\left(\frac{1}{2\nu}, U\right) - \frac{1}{\nu U^{\frac{1}{\nu}}}\gamma\left(\frac{1}{\nu}, U\right) \qquad \text{Eq-S3}$$

$$\gamma(x,U) = \int_0^U dt\ exp(-t)t^{x-1}$$ Eq-S4

$$U = \frac{q^2 R_g^2 (2\nu + 1)(2\nu + 2)}{6}$$ Eq-S5

Regio-random P3HT show spherical shape clusters under sTEM with and without sonication.

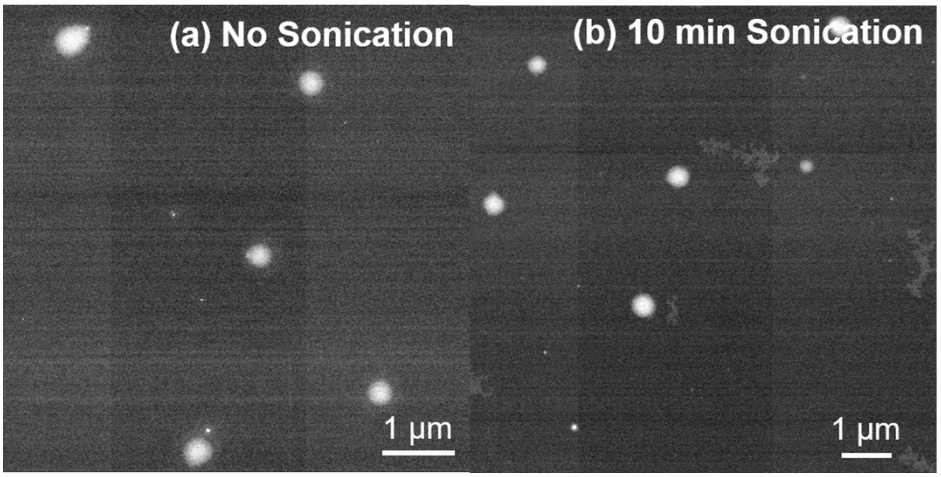

Figure S3. sTEM images of regio-random P3HT solution in 1,2-dichlorobenzene (a) without and (b) with 10 min sonication.

Description of combined model for SANS fitting of rra-P3HT

Sphere model [5] combined with dissolved polymer model is used to fit the scattering profile of regio-random P3HT (Eq-S6). The form factor of sphere model is in Eq-S7 and dissolved polymer model with excluded volume effect is shown in Eq-S3~ Eq-S5.

$$I\,(q) = \phi_v \varphi_f \left(\Delta\rho_{Sph}\right)^2 P_{Sph}(q) + \phi_v (1-\varphi_f)\left(\Delta\rho_{PExV}\right)^2 P_{PExV}(q) \qquad \text{Eq-S6}$$

$$P_{Sph}(q) = V \times \left[\frac{3(\sin\,(qr) - qr\cos\,(qr))}{(qr)^3}\right]^2 \qquad \text{Eq-S7}$$

Where $\Delta\rho_{Sph}$ is the scattering length density difference between polymer and solution and P_{Sph} is the form factor of the sphere model, which is defined in Eq-S7. V is the volume of a single polymer chain and r is the radius of the sphere. All the rest of the parameters are the same as those defined in Eq-S1. In this model, only the sphere radius and polymer fraction in sphere form are used as variables.

PQT-12 samples show fibril and fractal aggregated shape both before and after sonication.

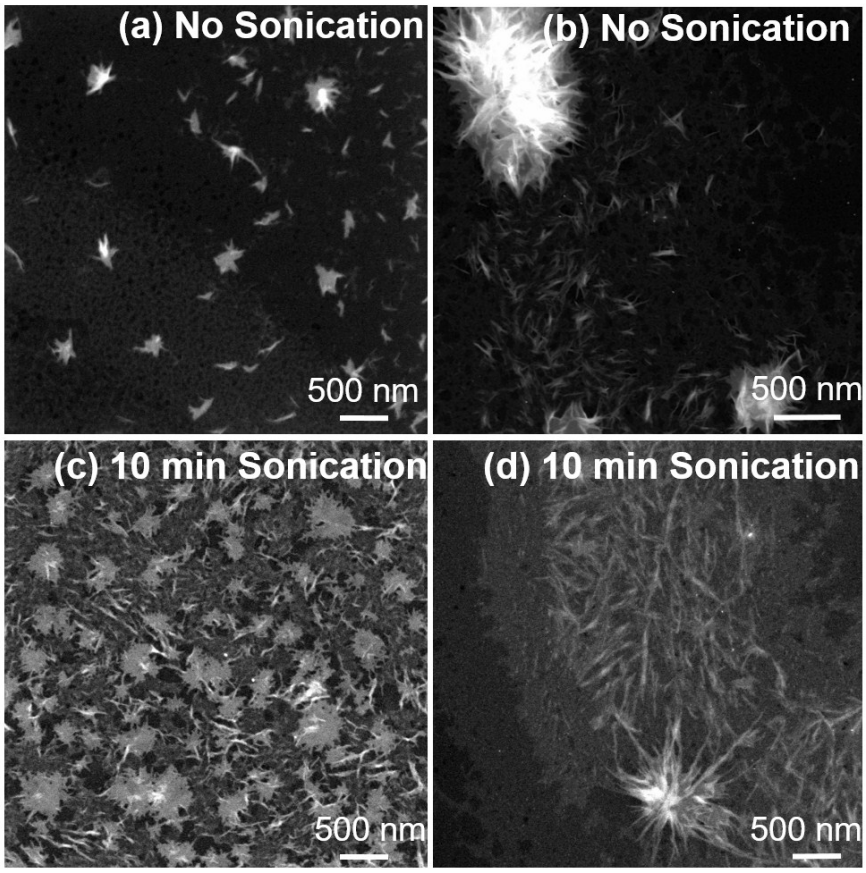

Figure S4. sTEM images of PQT-12 in 1,2-dichlorobenzene (a) (b) without and (c) (d) with 10 min sonication.

All the data was collected with 20% duty cycle using ultrasound transducer and the time labeled here are the total time. P3HT solutions in chloroform show new peaks formation at ~600nm of the absorption spectra when exposed to ultrasound with peak negative pressure larger than 4 MPa.

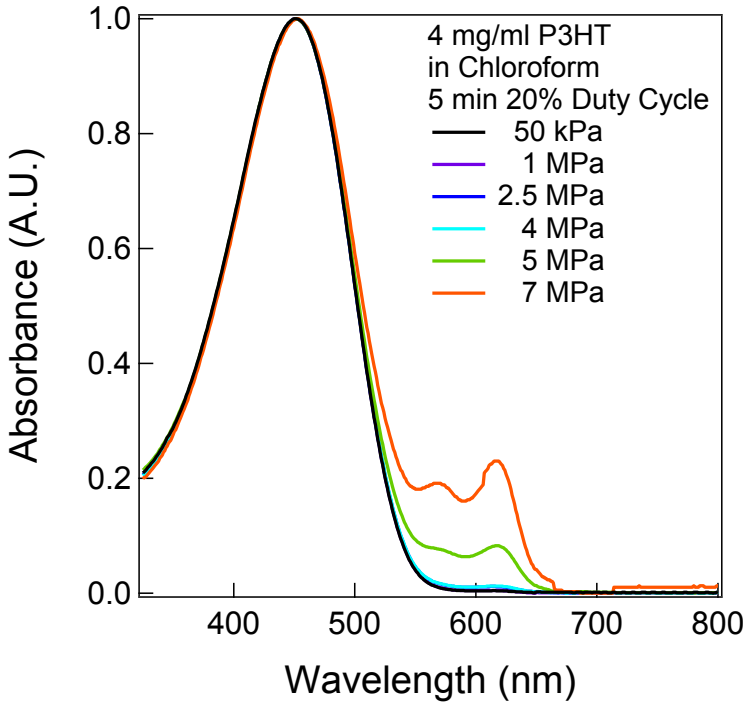

Figure S5. Normalized UV-vis spectra of P3HT solutions in chloroform after acoustic wave applied with varied peak negative pressures with pulse on for 5 min.

New peaks start to form only after 100 s ultrasound application of P3HT sample in chloroform at 7.2 MPa pressure. Up to 1500 s insonation, the longer time the ultrasound is applied, the higher the fiber fractions.

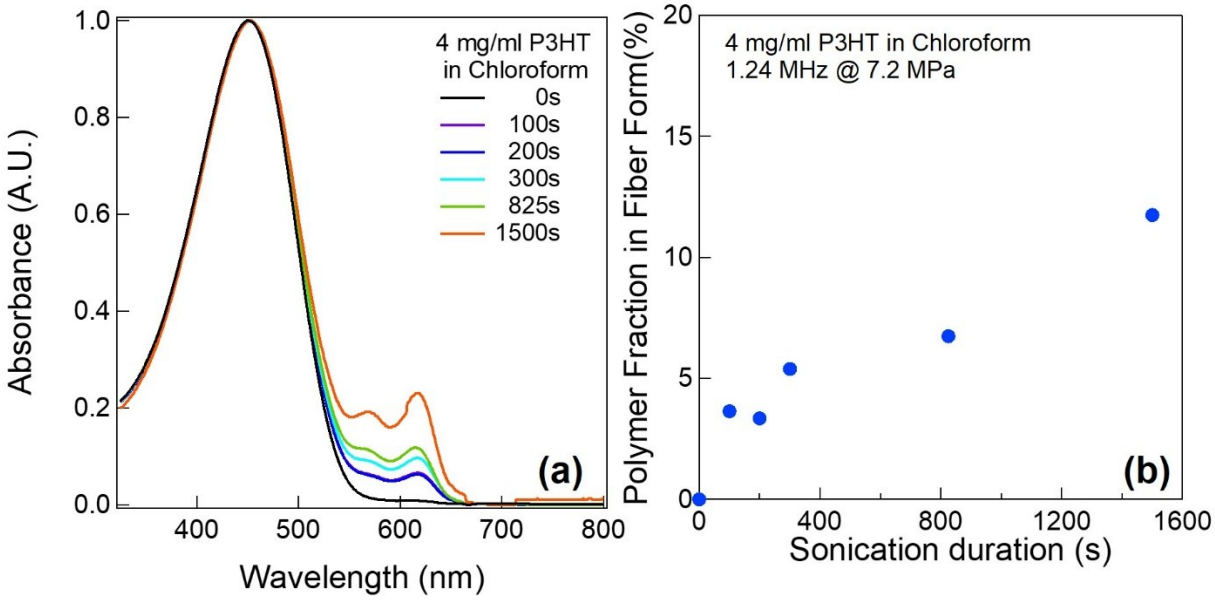

Figure S6. (a) Normalized UV-vis spectra of P3HT solutions in chloroform after acoustic wave applied with varied amount of time at 7.2 MPa peak negative pressure. (b) Fiber fraction calculated from UV-vis measurement as a function of sonication time.

When P3HT solution is exposed to a pressure lower than the cavitation threshold, 3 MPa for example, even 6000 s is not enough to induce fiber formation.

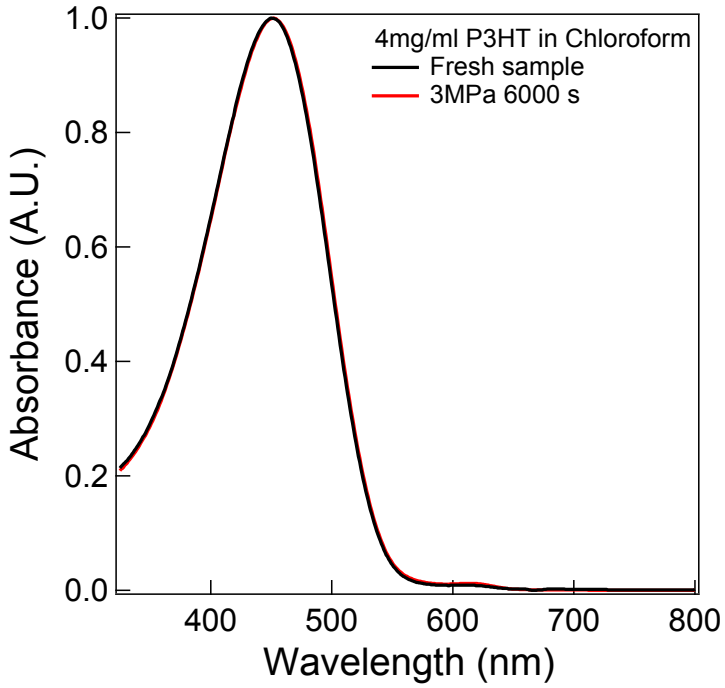

Figure S7. Normalized UV-vis spectra of P3HT solutions in chloroform with and without 3 MPa pressure for 6000 s. The duty cycle of the acoustic wave is 20%.

Dichlorobenzene requires a much higher peak negative pressure (6.8 MPa) to induce cavitation events than chloroform (~4 Mpa).

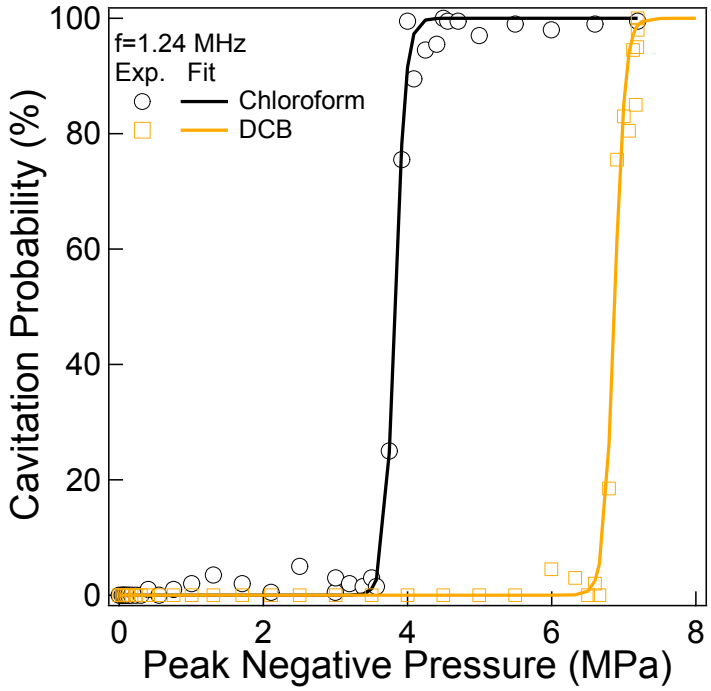

Figure S8. Cavitation probability of solvents as a function of peak negative pressure for chloroform and dichlorobenzene.

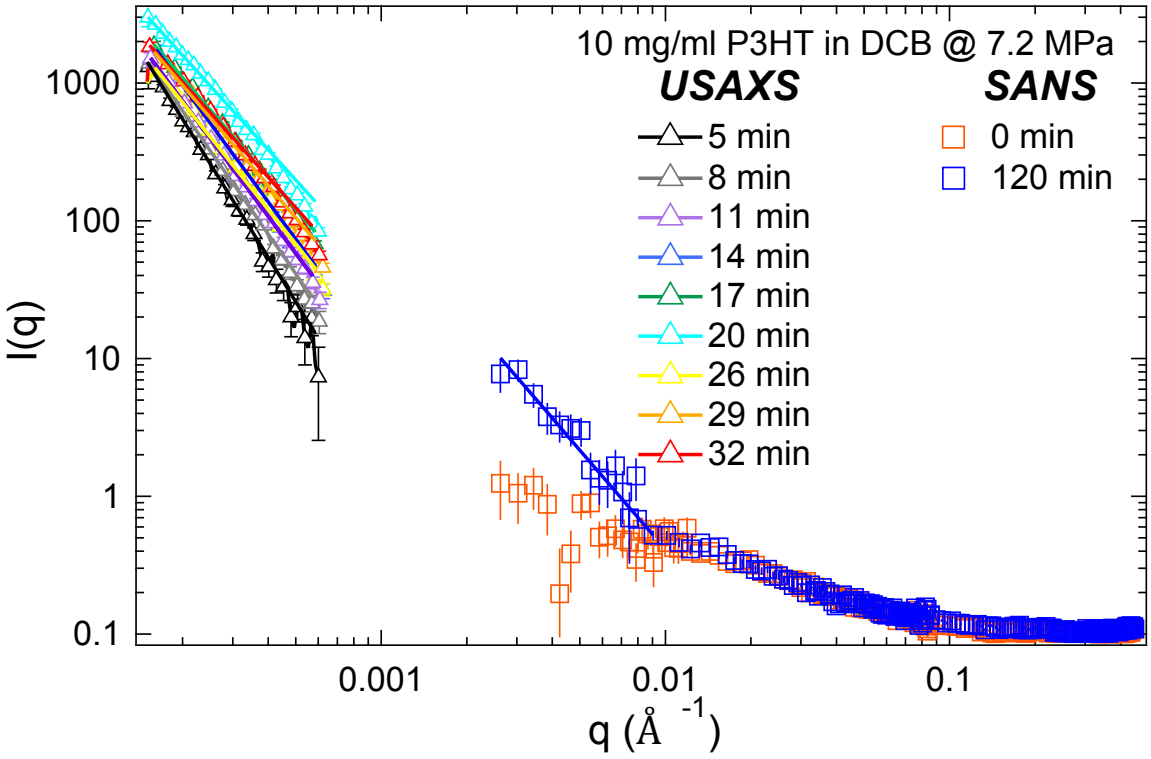

Figure S9. Power law fitting results of USAXS and SANS at low q range (< 0.01 $Å^{-1}$). The open symbols represent data points and solid lines are the corresponding power law fitting.

In DCB, no obvious optical change is observed short time after sonication. An extended aging time could induce fiber formation for samples with and without sonication. The sample exposed to ultrasound could form thin and long fibers.

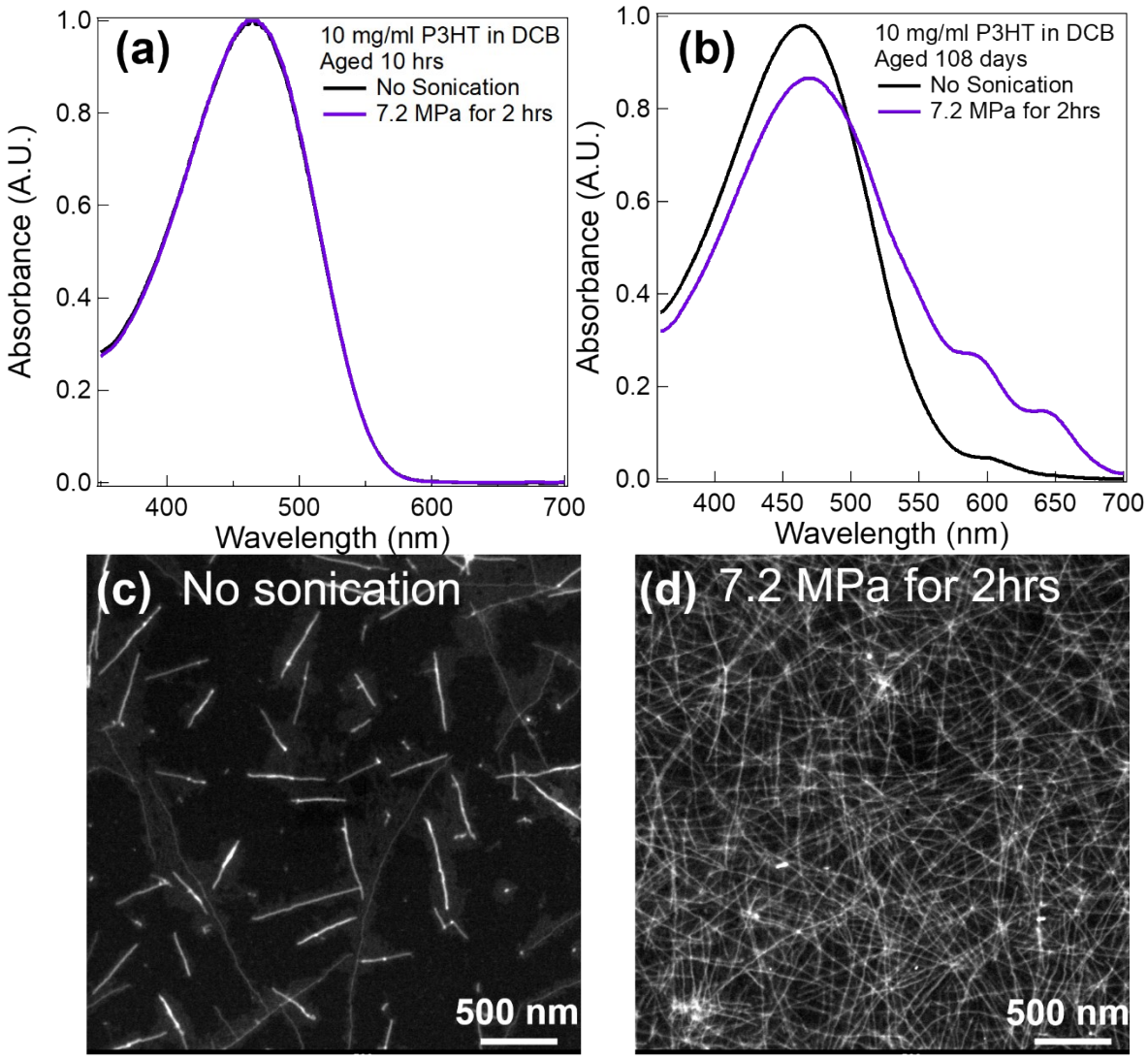

Figure S10. UV-vis measurement of 10 mg/ml P3HT in DCB (a) aged for 10 hrs and (b) aged for 180 days with and without ultrasound application in in-situ cell. sTEM image of (c) sample solution without ultrasound treatment and (d) 2hrs application of 7.2 MPa ultrasound after aging for 108 days.

Table S2. Summary of molecular weight and polydispersity index (PDI) of P3HT (Lot # BS23-49) before and after sonication. The GPC measurements used polystyrene standard and performed by dissolving P3HT in chlorobenzene.

Polymers	M_w	*Đ*
No Treatment (Rieke Value)	69k	2.3
No Treatment (Measured)	74k	2.2
30 min Sonication bath in chloroform	74k	2.3
2 hrs 7.2 MPa with 20% duty cycle in o-DCB	66k	2.6