

Electronic Supplementary Information (ESI)

**Proton Induced Aggregation of Water Soluble Isophthalic Acid  
Appended Arylene diimides: Justification with Perylene derivative**

Kausik Bag, Pradip Kumar Sukul, Dines Chandra Santra, Arkapal Roy and Sudip Malik\*

*Polymer Science Unit, Indian Association for the Cultivation of Science, 2A and 2B Raja S. C.  
Mullick Road, Jadavpur, Kolkata 700032, India, E-mail:psusm2@iacs.res.in*

**Table of Content**

1. Materials and Instrumentations	2, 3
2. Partial preparation procedure and preparation scheme of perylene derivatives.	4
3. Preparation and Characterization of NI and BI moieties.	5, 6
4. Solution and Gel preparation technique with table	7
5. Absorbance and Photoluminescence Spectra	8
6. Absorbance profile of DMSO with different amount of water content.	9
7. AFM and DLS clarification of PI aggregation in DMSO/Water	9
8. Probable scheme in DMSO/Water for perylene derivative	10
9. Calculation Table for Rheology	10
10. XRD of NI and BI dried gel	11
11. Change in the absorption profile of PBI	11
12. Temperature dependency on Gel to Sol transition table	12
11. References	12

## 1. Materials

Benzene-1,2,4,5-tetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, perylene-3,4,9,10-tetracarboxylic dianhydride, 5-aminoisophthalic acid were purchased from Aldrich Chemical. Co., USA and they were used without further purification. Triethyl amine (TEA) and dimethyl sulfoxide (DMSO) were distilled prior to use. Imidazole (pure grade) and glacial Acetic acid were purchased from Merck. For spectroscopic studies, water (18M $\Omega$ ) obtained from a Millipore Milli-Q system was used. All experiments were done at room temperature at about 25°C.

## 2. Instrumentation

<sup>1</sup>H-NMR spectra were recorded at 25°C on 300MHz and 400 MHz DPX spectrometers (Bruker). <sup>1</sup>H NMR chemical shifts ( $\delta$ ) were reported in parts per million (ppm). Splitting patterns has been designated as s (as singlet), d (as doublet), br (broad). MALDI-TOF was carried out with a Bruker Daltonics FLEX-PC using dithranol and  $\alpha$ -Cyano-4-hydroxycinnamic acid (when required) as a matrix. FT-IR spectra of the powder samples and gels were recorded using KBr pellets and CaCl<sub>2</sub> cell of samples in an FTIR- 8400S Shimadzu instrument. UV-Vis spectra of the solutions were recorded with an Agilent (model 8453) UV-Vis spectrophotometer with a quartz cell (pathlength 1cm). Photoluminescence studies of solutions were done with a Horiba Jobin Yvon Fluoromax 3 spectrometer. Power XRD analysis were performed by using a Bruker AXS diffractometer using Cu K $\alpha$  radiation ( $\lambda=1.542 \text{ \AA}$ ), scanned from 5° to 50° with a rate of

0.5s/step. pH of the solutions were measured using probe type pH-meter (IQ Scientific Instruments, Model-IQ240) calibrated with standard buffer solution of pH-10 and pH-7. FESEM instrument (JEOL, JSM 6700F) operating at 5 KV was used to understand the morphology of assembly and samples were pt-coated prior to scanning the image. Rheological measurements were studied with advance AR 2000 rheometer (TA Instruments, New Castle, DE). Experiments were carried out with plate of 40 mm diameter and a cone angle of 4 degree. Proper care was taken to ensure the absence of air bubble.

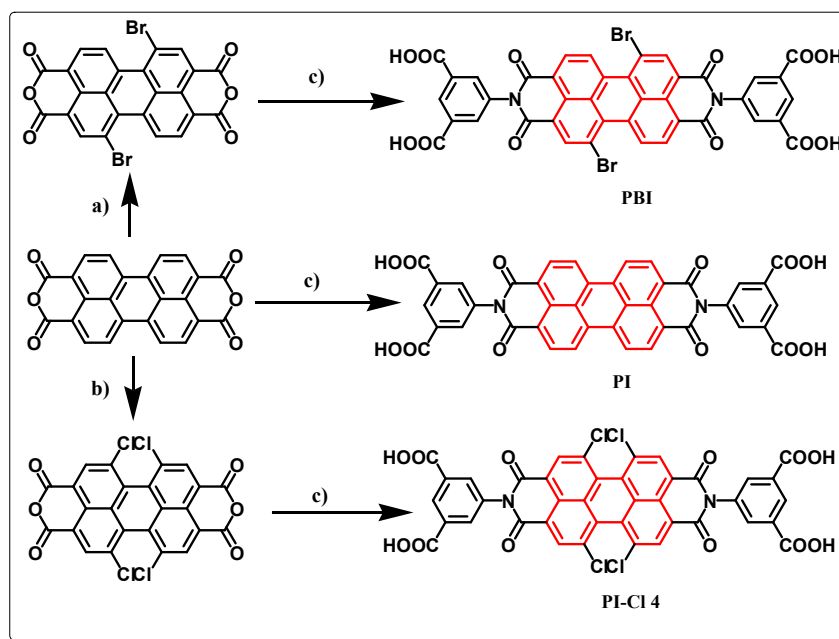
### 3. Synthesis of Compounds

#### S-1.Preparation of the Compounds

##### Preparation of Perylene Derivatives (PI, PBI and PI-PCl<sub>4</sub>)

All the derivatives are prepared by our previous reported methods <sup>S1, S2</sup>. To remove the excess imidazole completely from the system the prepared water soluble compounds were precipitated using 2N Hydrochloric acid, filtered and dried in vacuum oven at 60°C. The compounds were not soluble even in d<sub>6</sub>-DMSO at the required NMR concentration. So NMR spectra of the perylene based compounds are not clear. The formation and purity of the compounds were indirectly supported by our previous reported methods.

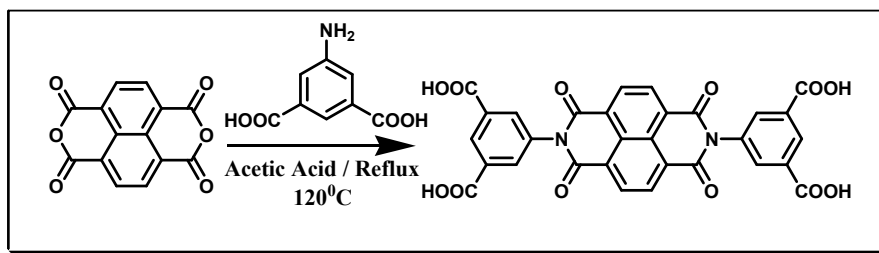
**Scheme S1.** Synthesis method of **perylene** derivatives.



**Reagents and conditions** a) Liquid Bromine, Conc. Sulphuric acid, 48 h, 85°C, Methanol wash, 80% b) Chlorosulphuric Acid, 24 h, 70°C, Water Wash, 75% c) 5-Amino Isophthalic Acid, Imidazole, 24h , 120°C, Ethanol/ Acetone mixture reflux, 2N HCl, Water Wash.

## Synthesis of N, N'-Di-(phenyl-3, 5-dicarboxylic acid)-naphthalenetetracarboxylic acid diimide (ND):

Scheme S2. Synthesis method of naphthalene derivative.



5-Aminoisophthalic acid (0.844 g, 4.66 mmol) and Naphthalene-1,2,4,5- tetracarboxylic dianhydride (0.5 g, 1.86 mmol) were placed in a round bottom flask followed by the addition of 5 ml of glacial acetic acid. The mixture was stirred and was heated at 120°C for 24 hours under reflux condition. It was cooled to RT then 20 ml water was added to it. It was filtered and washed with water and methanol. The crude product was recrystallised from DMF. Weight of the recrystallised product was 0.690 g (yield= 62%).

$^1\text{H NMR}$  (400MHz,  $d_6$  DMSO)  $\delta$  (ppm): 13.54 (br, 4H), 8.72 (s, 4H), 8.57 (s, 2H), 8.33 (s, 4H)

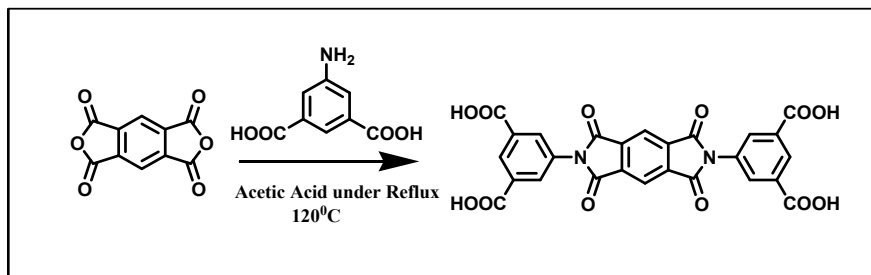
$^{13}\text{C NMR}$  (300 MHz,  $d_6$  DMSO)  $\delta$  (ppm): 165.98, 162.99, 136.44, 134.34, 132.25, 130.28, 129.89, 127.15, 126.77

FT-IR (KBr)  $\nu_{\text{max}}$ : 740,921,1199,1251,1352,1448,1581,1676,1710,2555,3080, 3422

MS (MALDI-TOF):  $m/z$  calc. for  $\text{C}_{30}\text{H}_{14}\text{N}_2\text{O}_{12}$ : 594.4, found: 617.3  $[\text{M}+\text{Na}^+]$

## Synthesis of N, N'-Di-(phenyl-3, 5-dicarboxylic acid)-benzenetetracarboxylic acid diimide (BI):

**Scheme S3.** Synthesis method of benzene derivative.



Benzene-1,2,4,5- tetracarboxylic dianhydride (0.5 g, 2.29 mmol) and 5-Aminoisophthalic acid (1.03 g, 5.73mmol) were placed in a round bottom flask. 5 ml of glacial acetic acid was added to it. The mixture was stirred and heated at 120°C for 24 hours under reflux condition. The resulting gray precipitate was filtered and washed with distilled water followed by methanol. The crude product was further recrystallised from DMF. Weight of the recrystallised product was 0.790 g (yield= 63%).

$^1\text{H}$  NMR (400MHz,  $d_6$  DMSO)  $\delta$  (ppm): 13.45 (br, 4H), 8.53 (t, 2H), 8.41 (s, 2H), 8.35 (d, 4H)

$^{13}\text{C}$  NMR (300 MHz,  $d_6$  DMSO)  $\delta$  (ppm): 165.86, 165.17, 162.32, 137.14, 132.39, 132.15, 131.82, 129.39

FT-IR (KBr)  $\nu_{\text{max}}$ : 755,834, 913, 1105, 1203,1279,1375,1430,1601,1718,1778,2546, 3088,3421

MS (MALDI-TOF):  $m/z$  calc. for  $\text{C}_{26}\text{H}_{12}\text{N}_2\text{O}_{12}$ : 544.3, Found: 545.0  $[\text{M}+\text{H}^+]$ .

## Solution and Gel Preparation for Rheology Study

For spectroscopic measurements, respective solution was made in presence requisite amount of distilled Triethylamine (TEA) in water. Most of the study at the solution phase was done at  $10^{-5}$  M concentration. In case of PI solution, a 10 ml stock solution of  $10^{-4}$  M PI solution was made by weighing 0.7mg in 10 ml milliQ water in presence of 20  $\mu$ L of TEA. The solution as prepared looked clear and red in colour (Yellow fluorescence). 0.2 M Hydrochloric acid was used to study the aggregation behavior in water. For gel preparation, 2 ml of  $10^{-2}$  M was used followed by 300 $\mu$ l of 2N HCl. Gels in case of benzene, naphthalene and unsubstituted perylene was formed within five minutes of addition of acid and the di-bromo substituted perylene moiety took about 2 hrs to form gel. The formation of the gel was defined by the “stable –to –inversion of a vial” method. The hydrogel was used for rheological measurements. The formed gel was centrifuged and washed with water to get rid of excess acid. When the supernatant of the solution was of slight acidic (pH around 5-6) the gel was dispersed in 5 ml Milli-Q water and that solution was used for morphology study.

Content of Gel	Minimum Conc. For Gelation	Hydrogel formed	Rheology Done
BI	2.3mg/ ml	Yes	Yes
NI	2.8mg/ ml	Yes	Yes
PI	5.2mg/ ml	Yes	Yes
PBI	5.4mg/ ml	Yes	Yes
PI-Cl <sub>4</sub>	8.5mg/ ml	No	No

## Absorbance and Photoluminescence Study

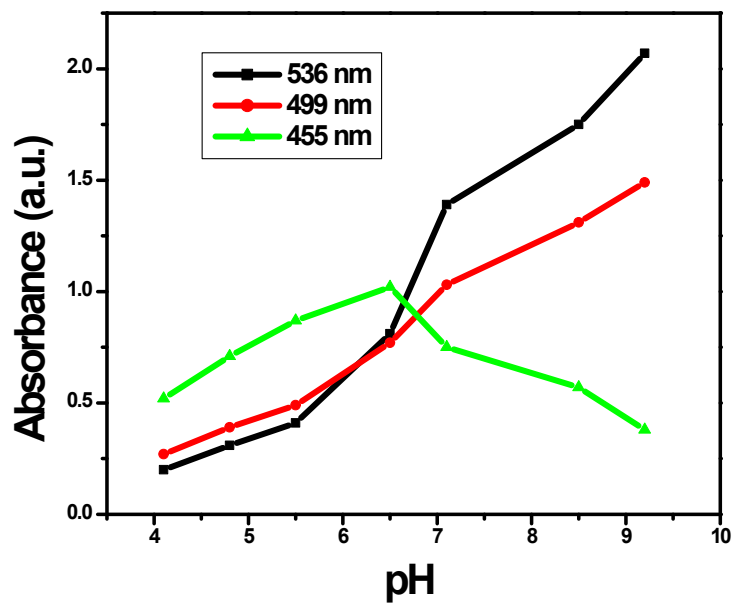


Fig. S1. Absorbance of different maxima with pH for PI molecule in aqueous solution

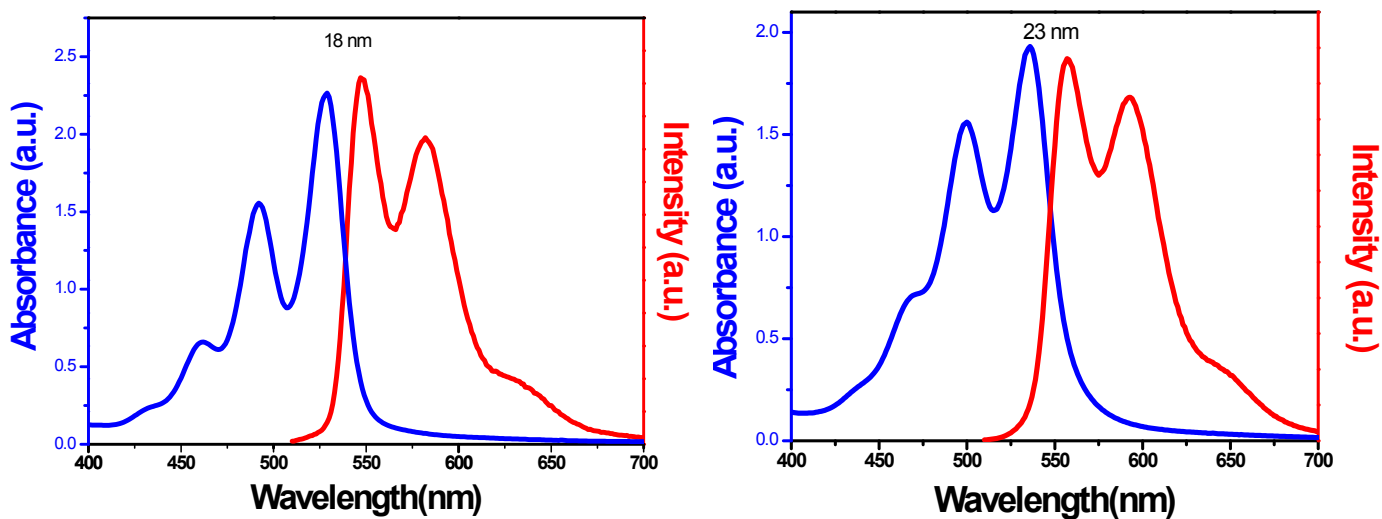
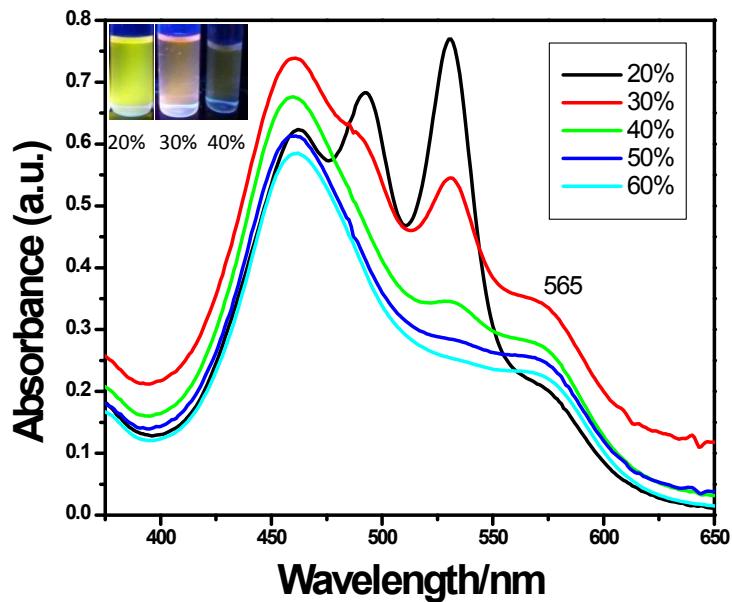


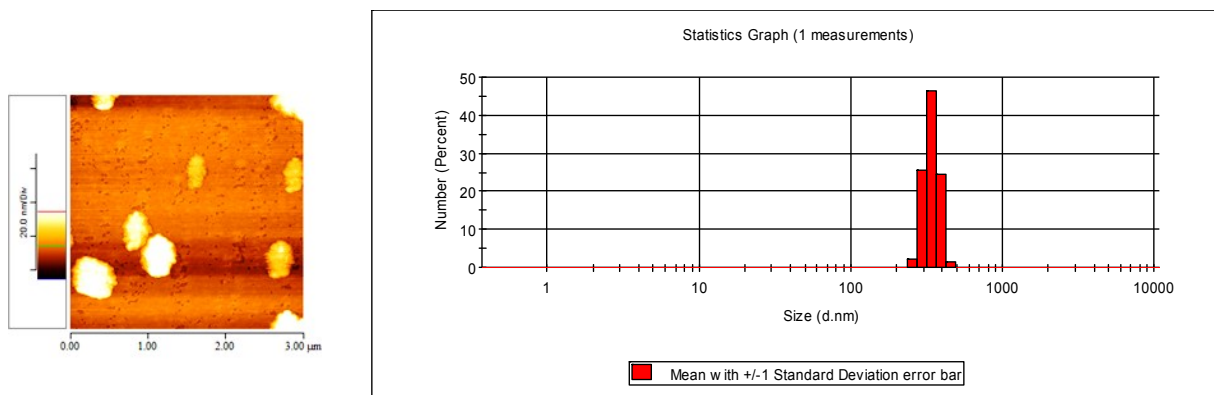
Fig. S2. Absorbance and PL spectra for (left) PI in DMSO and (right) PI in water/triethyl amine





**Fig. S3.** Absorbance Spectra of PI in DMSO with different amount of Water

### AFM and DLS study



**Fig. S4.** (Left) AFM of PI aggregate in 30% water, (right) DLS of corresponding solution

## Aggregation Scheme

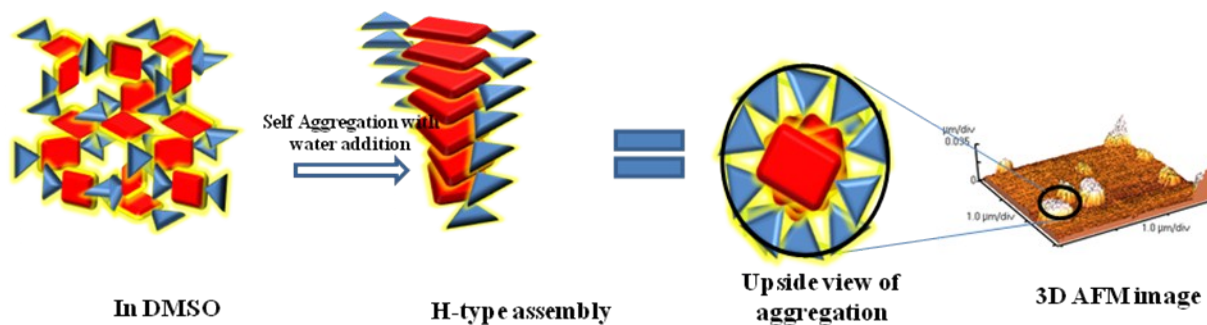


Fig. S5. Probable aggregation of PI in DMSO with Water

## Rheology parameter calculation

Gel Sample	$G'$ (Pa)	$G''$ (Pa)	$G'-G''$ (Pa)	$G'/G''$	$\sigma^*$ (Pa)
BI	1541	221	1320	6.9	0.40
NI	630	67	563	9.3	0.32
PI	497	36	461	13.8	0.12
PBI	383	45	338	8.5	0.09

Table2. Table and formula for rheological parameter calculations

XRD study.

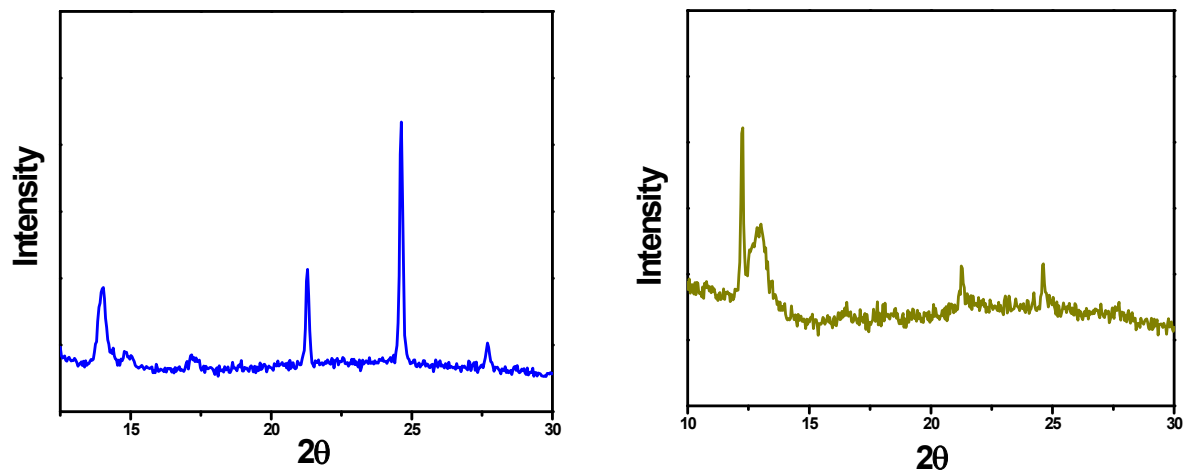


Fig. S6. WAXS pattern for (left) BI and (right) NI dried gel

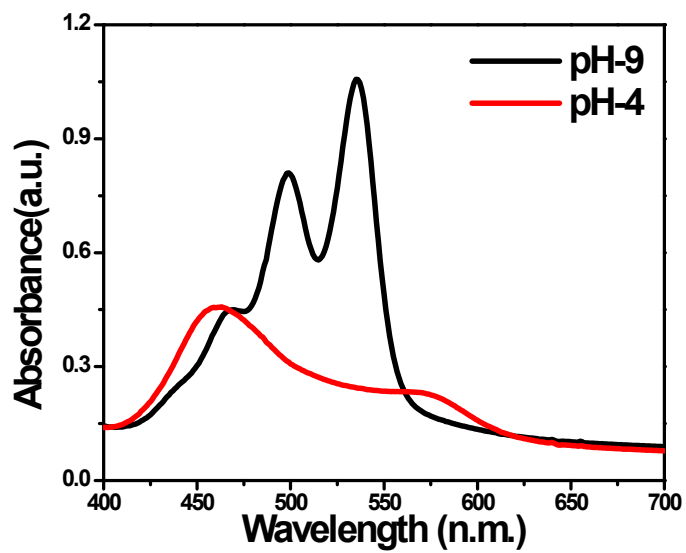


Fig. S7. Change in the Absorption Nature of PBI with pH.

### Gel to Sol Transition (Tested with Stable to Invert-bottle experiment)

Temperature (°C)	BI	NI	PI	PBI
20	gel	gel	gel	gel
30	gel	gel	gel	gel
40	gel	gel	gel	gel
50	gel	gel	gel	gel
60	gel	gel	sol	sol
70	gel	sol	sol	sol
80	sol	sol	sol	sol
90	sol	sol	sol	sol

**Table3.** Table and formula for rheological parameter calculations

#### Reference:

S1. P. K. Sukul, A. Datta and S. Malik, *Chem. Eur. J.*, 2014, **20**, 3019 – 3022.

S2. P. K. Sukul, D. Asthana, P., Mukhopadhyay., D. Summa, L. Muccioli, C. Zannoni, D. Beljonne, A. E. Rowan, S. Malik, *Chem. Commun.*, 2011, **47**, 11858–11860.