Electronic Supplementary Material (ESI) for Soft Matter. This journal is © The Royal Society of Chemistry 2023

# Electronic Supplementary Information (ESI)

# Roles of aqueous nonsolvents influencing dynamic stability of poly-(nbutyl methacrylate) thin films at biologically relevant temperatures

Jotypriya Sarkar,<sup>a</sup> Mithun Madhusudanan,<sup>a</sup> Chandni V.C.,<sup>a</sup> Shilpa Choyal<sup>b,‡</sup> and Mithun Chowdhury <sup>a,b,</sup>

<sup>a</sup>Lab of Soft Interfaces, Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai 400076, India

<sup>b</sup>Center for Research in Nanotechnology and Science, Indian Institute of Technology Bombay, Mumbai 400076, India

<sup>‡</sup>Present address: Department of Chemistry, University of Illinois Chicago, Illinois 60607, USA

\*Correspondence to: mithunc@iitb.ac.in

#### Effect of temperature and incubation media:

Dewetting dynamics of 40 nm PnBMA thin films (thickness ca. 40 nm) incubated in PBS (50 mM) and water for 1 h at different incubation temperatures are found in Fig. S1 (a) and Fig. S1 (b) where we observe that dewetting dynamics increase with incubation temperature and the nature of the incubation medium. In Fig. S1 (c), we have explained the extent of dewetting as a function of incubation temperature by plotting the radius of a hole (at dewetting time, t = 75 s) as a function of the temperature of incubation. The slope from the curve shows a steep increase in hole radius (R) for films incubated in water as compared to a less steep increase in hole radius (R) for PBS-incubated samples as a function of temperature. This indicates that thin films are selectively stable, i.e., more stable in PBS (50 mM) and less stable in water which is further explained in the paper.

### Annealing/aging or vacuum incubating PnBMA thin films:

The role of non-equilibrated polymer chains formed during preparation of the thin films is found to be one of the primary sources of molecular recoiling stress.<sup>1</sup> Studies have also shown that polymer thin film aging and

annealing causes relaxation in molecular recoiling stress as a function of aging or annealing time.<sup>1,2</sup> The absence of molecular recoiling stress was confirmed by performing an aging/annealing experiment of nonincubated PnBMA films as seen in Fig. S2. On aging or annealing the films at room temperature (25 °C) for even up to 24 hours keeping inside a vacuum oven, the radius (at 300 s of dewetting) did not change which can be found in Fig. S2 (inset). This indicates that no dominant molecular recoiling stress is relaxing upon aging it at 25 °C for aging up to 24 hours.

## **Threshold analysis:**

All the optical images recorded in the study were analyzed by using a MATLAB program to find out the percentage of dewetted area. A threshold analysis is done to achieve the data where the program converts the original image into a binary image. Further, it calculates the number of white pixels, black pixels, and the total number of pixels to give the percentage of dewetted area. An example can be found in Fig. S3.

## **Roughness of PnBMA thin films:**

Roughness of the PnBMA thin films is qualitatively examined from AFM topographic images in Fig. S5 (a), Fig. S5 (b) and Fig. S5 (c) where we can observe 30  $\mu$ m x 30  $\mu$ m area non-incubated PnBMA thin films, and PnBMA thin films incubated in PBS (50 mM) or water for 3 h. Analysis of 15  $\mu$ m x 15  $\mu$ m area (from 8 representative topographical scans) using Gwyddion software points out that the surface roughness of PnBMA thin films is increased upon incubation in water and in PBS. The increase of rms roughness of PnBMA thin film is much more prominent upon incubation in water as compared to incubation in PBS (50 mM) (Fig. S6).

#### FTIR spectra of PnBMA thin films:

PBS is an aqueous solution of potassium dihydrogen orthophosphate, potassium chloride, potassium hydrogen phosphate and sodium chloride. So, an argument can be made that PBS might react with PnBMA and causes the films to behave differently than films incubated in water. To examine if PBS reacted with the PnBMA we performed FTIR analysis of the surface of pure PnBMA thin film as well as thin films incubated in PBS up to 24 h. From the results, it can be found (Fig. S7) that there's no change in the FTIR spectra of the pure PnBMA

and incubated PnBMA films. FTIR signals found can be assigned to C-H stretching vibration of the CH<sub>3</sub> group and C-H bending vibrations of the CH<sub>2</sub> group respectively at 2965 and 2880 cm<sup>-1</sup>.<sup>3</sup> The signals at 1262 and 1060 cm<sup>-1</sup> are due to (C–O) stretching vibration and wagging vibration of C-H, respectively.<sup>3</sup> The signal 1729 cm<sup>-1</sup> is due to C=O stretching of the ester functionality from methacrylate group.<sup>3</sup> So, from Fig. S7 it can be inferred that there are no new bonds formed or modified in presence of PBS.

#### Contact angle measurement and calculation of surface energies:

The basics of the macroscopic wetting phenomenon is governed by Young's equation.

$$\gamma_{\rm lv}Cos\theta = \gamma_{\rm sv} \quad \gamma_{\rm sl}$$

where,  $\gamma_{lv}$  = liquid surface tension,  $\gamma_{sv}$  = solid surface energy,  $\gamma_{sl}$  = solid-liquid interface energy and  $\theta$  = equilibrium contact angle.

The contact angle is measured by drawing a tangent along the liquid-vapor interface as shown in Fig. S8. In that way, a contact angle close to 0° indicates complete wetting and a contact angle close to 180° indicates complete non-wetting. In the past decades, different methods are adapted to measure surface energy using contact angle measurements such as, Lewis-acid base theory, Zisman, Neumann, etc.<sup>4–6</sup> However, in this study Owens-Wendt-Kaelbel (OWK) approach is used because of its suitability for our system.<sup>4</sup> Moreover, the model also predicts separate interactions between the molecules such as polar and dispersive interractions. In this model, more than one liquids are required whose polar and dispersive surface tensions are reported in the literature to compute the solid surface energy. The OWK approach is based on the following equation-

$$\gamma_{\rm sl} = \gamma_{\rm sv} + \gamma_{\rm lv} - 2\left(\sqrt{\gamma_{\rm sv}^{\rm d}\gamma_{\rm lv}^{\rm d}} + \sqrt{\gamma_{\rm sv}^{\rm p}\gamma_{\rm sv}^{\rm p}}\right)$$

where,  $\gamma_{sv}^{d}$  and  $\gamma_{lv}^{d}$  are dispersive components and  $\gamma_{sv}^{p}$  and  $\gamma_{lv}^{p}$  are polar components of solid and liquid surface energies respectively. Putting the value of  $\gamma_{sl}$  from Young's equation and by rearranging we can get

$$\sqrt{\gamma_{\rm sv}^{\rm d}} + \sqrt{\gamma_{\rm sv}^{\rm p}} \left( \sqrt{\frac{\gamma_{\rm lv}^{\rm p}}{\gamma_{\rm lv}^{\rm d}}} \right) = \frac{\left[ \gamma_{\rm lv} (1 + Cos\theta) \right]}{2\sqrt{\gamma_{\rm lv}^{\rm d}}}$$

This equation can be represented in y = mx+c form, wherein,

$$c = \sqrt{\gamma_{sv}^d}$$
,  $m = \sqrt{\gamma_{sv}^p}$ ,  $x = \sqrt{\frac{\gamma_{lv}^p}{\gamma_{lv}^d}}$  and  $y = \frac{[\gamma_{lv}(1+Cos\theta)]}{2\sqrt{\gamma_{lv}^d}}$ 

An example of the graphical representation is shown in Fig. S9.

From Fig. S9, the dispersive counterpart of the solid surface energy can be calculated from the intercept and the polar counterpart of the solid surface energy can be calculated from slope of the curve.<sup>5</sup> The polar and dispersive values of surface tension of the liquids are tabulated below in table T1.

Probing liquid	$\gamma_{\rm lv}$ (mN/m)	$\gamma^{\rm p}_{\rm lv}$ (mN/m)	$\gamma_{lv}^{d}$ (mN/m)	Reference
Water	72.8	47.8	25	Janiszewska et al. <sup>7</sup>
PBS	69.5	41.4	28. 1	Janiszewska et al. <sup>7</sup>
Glycerol	64	34	30	Carré et al. <sup>8</sup>
Formamide	59	19.6	39.4	Carré et al. <sup>8</sup>
<b>Di-iodomethane</b>	50	2.6	47.4	Carré et al. <sup>8</sup>

Table T1 Polar and dispersive components of surface tension of the probing liquids

The polar and dispersive surface tension values of the probing liquid are used along with the experimentally measured contact angles, the OWK calculations are done to find out solid surface energies which can be found in table T2.

**Table T2** Solid surface energies and interface energies of nonincubated PnBMA thin-film (film thickness ca.40 nm) and PnBMA thin-films (film thickness ca. 40 nm) incubated in water and PBS (50 mM) at 25 °C for(0-6) h

Incubation	Incubation	$\gamma_{\rm sv}~({\rm mN/m})$	$\gamma_{sv}^{d}$ (mN/m)	$\gamma_{sv}^{p}$ (mN/m)
medium	time (h)			
As spun	0	$26.55 \pm 1.58$	$24.22 \pm 1.51$	$2.33\pm0.48$
Water	1	$28.21 \pm 2.48$	$25.42 \pm 2.35$	$2.78\pm0.8$
Water	2	$30.08 \pm 2.67$	$27.75 \pm 2.56$	$2.33\pm0.77$
Water	3	$32.62 \pm 2.04$	$27.96 \pm 1.88$	$4.66\pm0.79$
Water	6	$33.27 \pm 1.35$	$26.09 \pm 1.16$	$7.18 \pm 0.68$
PBS	1	$27.5 \pm 1.58$	$25.59 \pm 1.52$	$1.91\pm0.43$

PBS	2	$29.59 \pm 1.64$	$28.28 \pm 1.6$	$1.36\pm0.36$
PBS	3	$30.15 \pm 1.82$	$28.90 \pm 1.78$	$1.24\pm0.38$
PBS	6	$30.66 \pm 1.45$	$29.54 \pm 1.43$	$1.11 \pm 0.23$

Table T3 Characteristic decay time values from modulus and viscosity as a function of incubation time data

Sample	Temperature of	$ au_E$ (s)	$ au_{\eta}$ (s)
	incubation (°C)		-
PBS (50 mM)	4	$14976\pm3096$	$17208 \pm 4920$
PBS (50 mM)	16	$11880 \pm 1224$	$8280\pm1080$
PBS (50 mM)	20	$8172\pm900$	$7560\pm720$
PBS (50 mM)	25	$8028\pm2376$	$6680\pm600$
PBS (50 mM)	28	$6048\pm288$	$5724 \pm 324$
PBS (50 mM)	32	$5256 \pm 180$	$4536\pm36$
PBS (50 mM)	37	$4068 \pm 108$	$3924\pm108$
Water	4	$6984\pm396$	$9612\pm2052$
Water	16	$5364 \pm 396$	$6408 \pm 432$
Water	20	$4140\pm36$	$6120\pm828$
Water	25	$3096 \pm 432$	$5400\pm396$
Water	28	$2880\pm432$	$4788\pm360$
Water	32	$2772 \pm 108$	$3816 \pm 216$
Water	37	$1980\pm108$	$3372\pm324$



**Fig. S1** (a) Hole radius (R) vs dewetting time for PnBMA thin films (film thickness ca. 40 nm) incubated in PBS (50 mM) for 1 h, (b) Hole radius (R) vs dewetting time for PnBMA thin films (film thickness ca. 40 nm) incubated in water for 1 h and (c) Hole radius (R) at the dewetting time (t=75 s) vs temperature of incubation (T) profiles of PnBMA thin films (film thickness ca. 40 nm) incubated in PBS (50 mM) and in water for 1 h to denote the extent of dewetting



**Fig. S2** Hole radius (R) vs dewetting time for PnBMA thin films (film thickness ca. 40 nm) aged/annealed in a vacuum oven at room temperature [(Inset) Hole radius (R) at dewetting time (t=300 s) vs aging time]



Fig. S3 Threshold analysis of a PnBMA thin film (film thickness ca. 40 nm) by converting a 2D-optical image in a binary format and calculating the percentage of white pixels and black pixels using a MATLAB program to denote the extent of dewetting of the films (Dimension of each image is 260  $\mu$ m x 340  $\mu$ m)



**Fig. S4** Optical microscopy images of PnBMA thin films (film thickness ca. 40 nm) incubated in PBS (50 mM) and in water for 1 h at temperatures of incubation: 4 °C, 25 °C and 37 °C upon annealing them for 25 s, 100 s, and 225 s at  $T_{dew} = 85$  °C respectively. (Size of each image is 260 µm x 340 µm)



**Fig. S5** (a) AFM topography images of nonincubated PnBMA thin film (film thickness ca. 40 nm), (b) PnBMA thin film incubated in PBS (50 mM) at 25 °C for 3 h and (c) PnBMA thin film incubated in water at 25 °C for 3 h. All the PnBMA films have a film thickness of ca. 40 nm.



**Fig. S6** (a) RMS roughness of PnBMA thin films (film thickness ca. 40 nm) incubated in PBS (50 mM) at 4 °C, 25 °C and 37 °C for (0-6) h and (b) RMS roughness of PnBMA thin films (film thickness ca. 40 nm) incubated in water at 4 °C, 25 °C and 37 °C for (0-6) h



**Fig. S7** FTIR spectra of nonincubated PnBMA thin film (film thickness ca. 40 nm) and PnBMA thin films (film thickness ca. 40 nm) incubated in PBS (50 mM) at 25 °C for (0-24) h



**Fig. S8** Schematic of a liquid drop on a solid surface representing liquid surface tension ( $\gamma_{lv}$ ), solid surface energy ( $\gamma_{sv}$ ), solid-liquid interfacial tension ( $\gamma_{sl}$ ) and  $\theta$  is the equilibrium contact angle.



**Fig. S9** Standardisation curve to calculate the dispersive and polar components of PnBMA thin film (film thickness ca. 40 nm) using different probing liquids (water, PBS, di-iodomethane, glycerol and formamide) using Owens-Wendt-Kaelbel (OWK)<sup>4</sup> approach. Here,  $\gamma_{lv}^d$  and  $\gamma_{lv}^p$  are dispersive and polar components of liquid surface tension ( $\gamma_{lv}$ ) and  $\theta$  as the equilibrium contact angle.



**Fig. S10** Dispersive component of surface energy ( $S^d$ ) (signifying long-range forces acting on a thin film) of a multilayer thin film system as a function of PnBMA film thickness (d). [(Inset) Schematic of multilayer thin film system studied in this work]



**Fig. S11** Dewetting hole radius (R) vs dewetting time for nonincubated PnBMA thin films (film thickness ca. 40 nm) and PnBMA thin films incubated for (0-6) h in water and PBS of three different concentrations (25 mM, 50 mM and 100 mM). Temperature of incubation was maintained 25 °C. Temperature of measurement,  $T_{\text{measurement}} = T_{\text{dew}} = 85$  °C.



**Fig. S12** Surface energy calculated from OWK method as a function of incubation time for PnBMA thin films (film thickness ca. 40 nm) incubated for (0-6) h in water and methanol. The temperature of incubation was maintained at 25 °C.

![](_page_10_Figure_2.jpeg)

**Fig. S13** Dewetting hole radius (R) vs dewetting time for nonincubated PnBMA thin films (film thickness ca. 40 nm) and PnBMA thin films incubated for (0-6) h in water and methanol. Temperature of incubation was maintained at 25 °C. Temperature of measurement,  $T_{measurement} = T_{dew} = 85$  °C.

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