

*Supplementary Materials*

# Effect of copolymer properties on the phase behavior of ibuprofen-PLA/PLGA mixtures

**Anton Iemtsev<sup>1</sup>, Martin Klajmon<sup>1</sup>, Fatima Hassouna<sup>2</sup>, Michal Fulem<sup>1,\*</sup>**

<sup>1</sup> Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic

<sup>2</sup> Faculty of Chemical Engineering, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic

\* Correspondence: fulemm@vscht.cz

**Table S1.**  $T_s$  values obtained for IBU–PLGA and IBU–PLA systems.

	PDLG 5004A	PDLG 7504A	PDL 02A	PDL 04A
IBU (wt. %):	$T_s$			
20	74.8	—	—	—
30	75.0	75.5	74.0	75.0
40	—	—	74.7	74.9
50	75.5	75.6	74.6	75.1
70	75.4	75.7	74.8	75.2

**Table S2(a).**  $T_g$  values obtained for IBU–PDLG 5004A system annealed at 80–150 °C.

IBU (wt. %):	10	20	30	50	70
Temperature (°C):	$T_{g1}$	$T_{g1}$	$T_{g2}$	$T_{g1}$	$T_{g2}$
80	44.7	−41.4	43.4	−42.3	45.0
90		−41.4	43.0	−41.7	44.4
100		−41.7	42.6	−41.4	43.2
110		−41.2	37.6	−41.6	40.9
120		35.2	—	36	−42.1
130		34.4	—	34.7	−42.4
140		34.9	—	34.4	−42.1
150		34.3	—	34.9	−42.4

**Table S2(b).**  $T_g$  values obtained for IBU–PDLG 7504A system annealed at 80-150 °C.

IBU (wt. %):	10	20	30		50		70	
Temperature (°C):	$T_{g1}$	$T_{g1}$	$T_{g1}$	$T_{g2}$	$T_{g1}$	$T_{g2}$	$T_{g1}$	$T_{g2}$
80	48.3	48.2	−40.7	48.2	−42.1	48.2	−43.2	32.3
90			−41.7	48.4	−41.8	48.6	−43.0	31.5
100			−39.3	46.6	−41.9	47.4	−43.0	31.0
110			40.2	−	−41.3	35.9	−42.8	29.4
120			39.3	−	−41.8	30.0	−42.9	28.5
130			39.7	−	27.5	−	−42.2	27.7
140			40.6	−	27.6	−	−43.4	27.4
150			40.6	−	28.6	−	−44.3	27.8

**Table S2(c).**  $T_g$  values obtained for IBU–PDL 02A system annealed at 80-150 °C.

IBU (wt. %):	10	20	30	40		50		70	
Temperature (°C):	$T_{g1}$	$T_{g1}$	$T_{g1}$	$T_{g1}$	$T_{g2}$	$T_{g1}$	$T_{g2}$	$T_{g1}$	$T_{g2}$
80	31.6	17.3	15.2	−44.2	12.3	−44.7	13.5	−43.3	12.7
90				−44.7	11.9	−44.3	12.5	−43.2	11.4
100				−44.1	11.0	−44.2	12.5	−43.3	11.5
110				−44.8	12.2	−43.8	13.2	−43.1	12.4
120				−44.7	10.9	−44.1	11.8	−43.1	12.1
130				−44.7	13.0	−44.3	11.1	−43.7	12.4
140				−44.6	13.2	−44.6	11.2	−43.1	11.9
150				−45.6	11.5	−44.6	11.4	−43.4	12.5

**Table S2(d).**  $T_g$  values obtained for IBU–PDL 04A system annealed at 80–150 °C.

IBU (wt. %):	10	20	30	40		50		70	
Temperature (°C):	$T_{g1}$	$T_{g1}$	$T_{g1}$	$T_{g1}$	$T_{g2}$	$T_{g1}$	$T_{g2}$	$T_{g1}$	$T_{g2}$
80	44.1	37.4	26.1	−44.8	16.4	−43.1	15.4	−42.4	17.1
90				−45.2	14.8	−44.1	15.4	−42.7	15.6
100				−44.9	16.2	−43.8	16.4	−43.6	15.8
110				−45.1	15.7	−44.4	16.6	−44.0	15.2
120				−44.8	14.9	−45.9	18.3	−44.3	14.9
130			16.0	—	16.1	—	—	−45.1	15.6
140			15.1	—	16.3	—	—	−44.5	14.5
150			16.1	—	15.8	—	—	−45.2	16.1

**Table S3.** Parameters  $k$  and  $q$  of the Kwei equation ((Equation (1) in the main article) for IBU–PLGA and IBU–PLA systems.

Polymer	$k$	$q$
PDLG 5002A	0.22025	232.97454
PDLG 5004A	0.33251	232.97454
PDLG 7502A	0.99972	14.91052
PDLG 7504A	26.72092	5.39933
PDL 02A	0.24938	117.51721
PDL 04A	0.99909	27.99866

**Table S4.** AARD ( $w_{\text{API}}$ )<sup>a</sup> values between experimental SLE data and data calculated using PC-SAFT EOS for all IBU–PLGA and IBU–PLA systems.

Polymer	All $k_{ij} = 0$	Optimized $k_{ij}$ s <sup>b</sup>
PDLG 5002A	109	27.9
PDLG 5004A	157	33.4
PDLG 7502A	93	29.7
PDLG 7504A	121	27.3
PDL 02A	95	23.3
PDL 04A	105	28.6

<sup>a</sup> AARD denotes the average absolute relative deviation:

$$\text{AARD} = 100N^{-1} \sum_{i=1}^N \left| \left( w_{\text{API}}^{\text{exp}} - w_{\text{API}}^{\text{calc}} \right) / w_{\text{API}}^{\text{exp}} \right| ; w_{\text{API}}$$

“exp” denote the experimental values and those calculated using PC-SAFT EOS, respectively, and  $N$  is the number of experimental data points.

<sup>b</sup> The respective optimized  $k_{ij}$  values are shown in Table S5.

**Table S5.** PC-SAFT EOS binary interaction parameters,  $k_{ij}$ , between the IBU and the different monomer units of PLGA/PLA polymers.

Polymer	$k_{ij}$ (LLA and DLA)	$k_{ij}$ (GA)
PDLG 5002A/5004A and 7502A/5004A	0.030	0.042
PDL 02A and 04A	0.030	-