## Crystallization and Melting of Poly(ethylene oxide) in Blends and Diblock Copolymers with Poly(methyl acrylate)

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The volume fraction  $\varphi_1$  of PMA was calculated adopting the definition of the segment volume fraction as introduced by Flory

$$\varphi_1 = \frac{z_1 n_1}{z_1 n_1 + z_2 n_2} \tag{1}$$

where  $z_i$  is the number of segments in polymer *i* and  $n_i$  is the number of polymer molecules of type *i*. The segment number  $z_i$  is obtained from the ratio of the number-average molar mass  $M_n$  and the segment molar mass  $M_{seg}$  of the respective polymer, i.e.  $z_i = M_{n,i}/M_{seg,i}$ . Introducing this ratio and using standard relationships, Eq. (1) can be rearranged into

$$\varphi_{1} = \frac{W_{1}}{W_{1} + (1 - W_{1}) \frac{M_{seg,1}}{M_{seg,2}}}$$
(2)

where  $w_1$  is the weight fraction of PMA. Values of  $M_{seg}$  were recently determined from PVT data of identical homopolymers in the framework of the Flory-Orwoll-Vrij equation-of-state.<sup>1</sup> The corresponding values are 45.7 g/mol and 37 g/mol for PMA and PEO, respectively. Calculated volume fractions for both blends and diblock copolymers are listed in Table S1.

<b>Table S1</b> : Weight fraction w	and volume fraction $\varphi_1$	of PMA in blends and	diblock copolymers
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Blend	nds Diblock Copolymers		Copolymers
$w_1$	$\varphi_1$	$w_1$	$\varphi_1$
0.1	0.83	0.09	0.077
0.2	0.168	0.17	0.143
0.3	0.258	0.38	0.327
0.4	0.351	0.43	0.379
0.5	0.447	0.59	0.538
		0.78	0.739



**Figure S1**: Normalized one-dimensional electron density correlation function K(z) of the sample PEO*b*-PMA<sub>7.7</sub> illustrating the determination of long period *d* and thickness of the amorphous layer  $L_a$ . K(z) was calculated from the last evaluable SAXS trace close to the melting temperature.



**Figure S2**: Evolution of Lorentz-corrected SAXS intensity profiles during heating from 40  $^{\circ}$ C to the begin of the melting process of diblock copolymer PEO-*b*-PMA<sub>14.3</sub>



**Figure S3**: Evolution of Lorentz-corrected SAXS intensity profiles during heating from 40 °C to the begin of the melting process of diblock copolymer PEO-*b*-PMA<sub>37.9</sub>

References

(1) Pfefferkorn, D.; Sonntag, S.; Kyeremateng, S. O.; Funke, Z.; Kammer, H.-W.; Kressler, J. J. Polym. Sci. B: Polym. Phys. 2010, 48, 1893–1900.