Electronic Supplementary Material (ESI) for Soft Matter.
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Electronic Supplementary Information (ESI)

Effect of segmental motion on hydrolytic degradation of polyglycolide in electro-spun fiber mats

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1. MATERIALS

Polyglycolide (PGA) with an inherent viscosity of 1.4 dL·g^{-1} and deuterium oxide (D_2O, 99.9 %atom D) were purchased from Merck (Darmstadt, Germany). 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP > 99.5 %) and acetonitrile (> 99.8%) were purchased from FUJIFILM Wako Pure Chemical Industries (Osaka, Japan). Tablets of phosphate-buffered saline (PBS) were purchased from Takara Bio (Kusatsu, Shiga, Japan). Ultrapure water was prepared using a Milli-Q system (Merck).

2. CHARACTERIZATIONS

2.1. Thermogravimetry (TG). Fig. S1 shows typical TG data for an S_v5.1-PGA fiber mat prepared from a 7.0 wt% PGA solution by an electrospinning method. Before the TG measurement, the sample was dried under vacuum at 353 K for 24 h. No weight loss was observed up to approximately 480 K. Taking into account that the boiling point of HFIP used for the electrospinning process is 331 K, it is clear that the solvent was fully removed from the fiber mat by drying under the above condition.

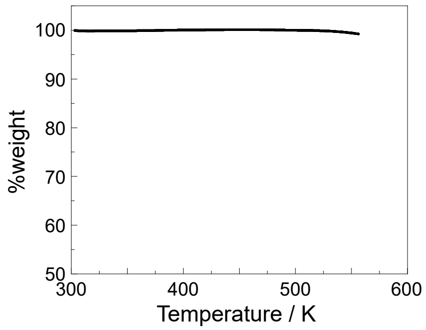

Fig. S1. TG data for an S_v5.1-PGA fiber mat.

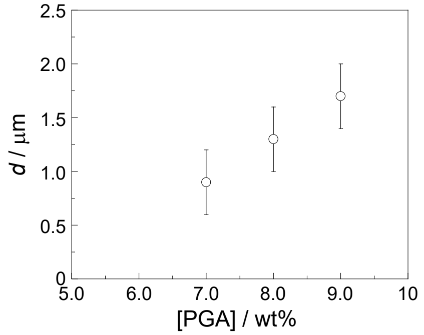

Fig. S2. The *d* value as a function of the concentration of PGA solutions.

2.2. Scanning Electron Microscopy (SEM). Fig. S2 shows the diameter (*d*) of PGA fibers as a function of the concentration of PGA solutions employed.

2.3. ^{1}H Nuclear Magnetic Resonance (^{1}H NMR) Spectroscopy. After the degradation test of an S_v5.1-PGA fiber mat in PBS for a given time, a small amount of the solution was diluted with D_2O, and then analyzed by ^{1}H NMR spectroscopy. Panels (a, b) of Fig. S3 show (a) spectra for the solutions as a function of the immersion time and (b) enlarged views. A peak observed at approximately 4.3 ppm was assignable to methylene groups of HO–$(CH_2COO)_n$–H (n = 2~6).[S1]

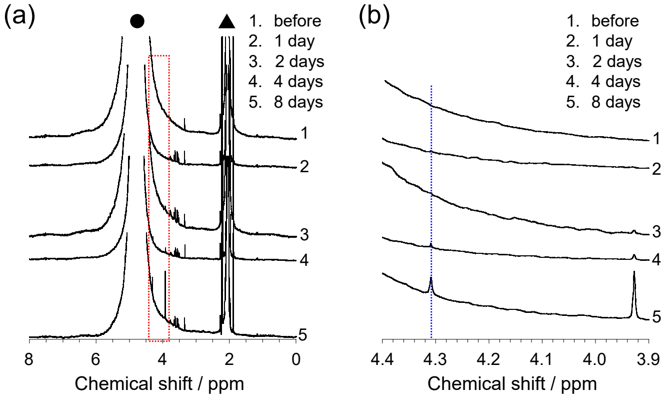

Fig. S3. (a) ^{1}H NMR spectra for PBS solutions used for the degradation tests of an S_v5.1-PGA fiber mat as a function of the immersion time. The filled circle and triangle represent peaks arisen from H_2O in PBS and CH_3CN used as an internal standard, respectively. (b) Enlarged spectra of (a) in the range from 4.4 to 3.9 ppm surrounded with a red dotted rectangle in (a).

2.4. Small Angle X-ray Scattering (SAXS) Analysis. One-dimensional scattering intensity profile was obtained by circularly integrating a two-dimensional SAXS pattern. To estimate the average thickness of crystalline (L_c) and amorphous (L_a) regions, the electron density correlation function, $K(z)$, derived from the inverse Fourier transformation of the experimental intensity distribution, $I(q)$, was used as follows,[S2]

$$K(z) = \frac{\int_0^\infty I(q)q^2\cos(qz)\,dq}{\int_0^\infty I(q)q^2 dq} \tag{S1}$$

where z and q are the location measured along a trajectory normal to the lamellar surface and the scattering vector, respectively.

Panels (a, b) of Fig. S4 show $K(z)$ for an S_v5.1-PGA fiber mat as a function of immersion time at (a) 310 and (b) 280 K. Panels (c, d) of Fig. S4 show L_c, L_a, and L_0 values, where L_0 is a long period corresponding to (L_c + L_a), for the S_v5.1-PGA fiber mat as a function of immersion time at (c) 310 and (d) 280 K.

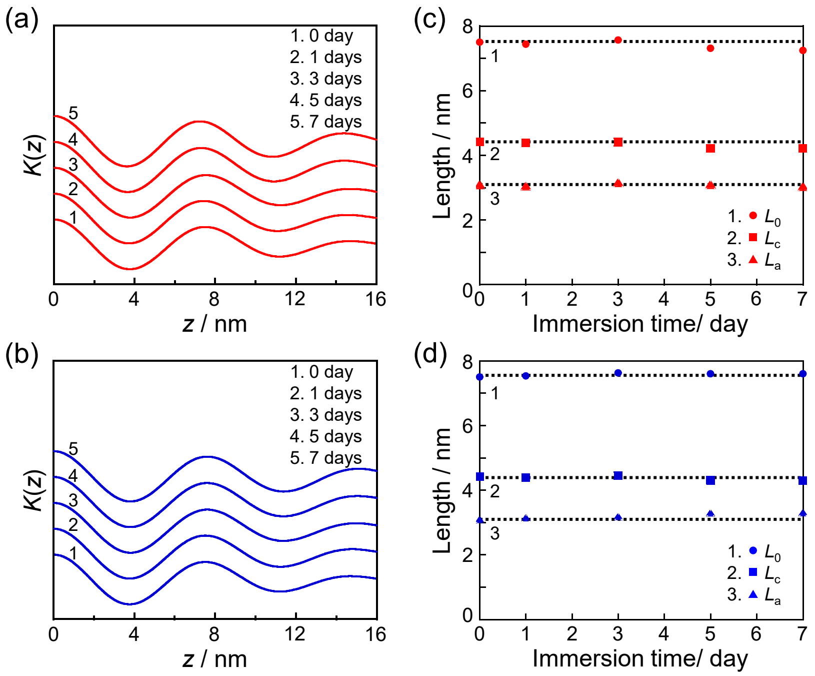

Fig. S4. (a, b) Electron density correlation function ($K(z)$) for an S_v5.1-PGA fiber mat as a function of immersion time treated at (a) 310 and (b) 280 K. (c, d) L_c, L_a, and L_0 values for the S_v5.1-PGA fiber mat as a function of immersion time treated at (c) 310 and (d) 280 K.

2.5. Dynamic Mechanical Analysis (DMA). The fragility index (m) for the PGA fiber mats after the degradation was examined by DMA. Fig. S5 shows log(τ/s) as a function of T^{-1} scaled by $T_{g\alpha}$ for the Sv5.1-PGA fiber mats. Here, τ represents the relaxation time, and T and $T_{g\alpha}$ are the absolute temperature and dynamic glass transition temperature, respectively. Solid curves are the best fitting to the results by the following equation.[S3,S4]

$$m = \left[\frac{\partial\{log(\tau/s)\}}{\partial(T_{g\alpha}/T)}\right]_{T = T_{g\alpha}} \qquad \text{(S2)}$$

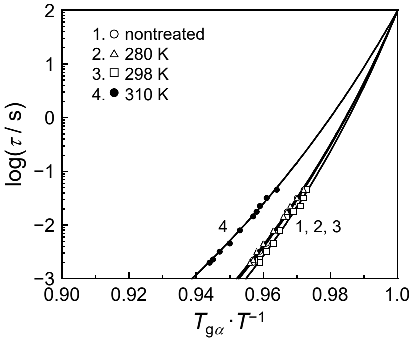

Fig. S5. Relationships between log(τ/s) and T^{-1} for the α-relaxation process of the S_v5.1-PGA fiber mats nontreated and treated in PBS at different temperatures.

Table S1 summarizes the *m* value for the three PGA fiber mats before and after the PBS immersion treatment at different temperatures for 7 days. Before the treatment, the *m* was in the range of 149 to 146, meaning that the PGA fiber mats were classified as a fragile glass-forming liquid. Once the mat was immersed into the PBS solution at 310 K, the *m* value remarkably decreased, regardless of the S_v value.

Table S1. The *m* values of PGA fiber mats nontreated and treated in PBS at various temperatures for 7 days.

fiber mat	*m*			
	nontreated	treated		
		280 K	298 K	310 K
S_v2.5-PGA	146	144	154	111
S_v3.3-PGA	146	143	148	112
S_v5.1-PGA	149	153	159	117

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