Supplementary Materials
$\alpha-C D$
PCL



Figure S1. ${ }^{1} \mathrm{H}$ NMR spectra of $\alpha-\mathrm{CD}$, neat PCL and PCL-CD-IC.


Figure S2. FTIR spectra of neat PCL, $\alpha-C D$ and PCL-CD-IC.


Figure S3. DSC thermal scan of PEA/PEO/PVAc/PCL-CD-IC=80/10/10/1 composite. The arrow indicates the single $\mathrm{T}_{\mathrm{g}}$ of the composite, demonstrating the miscibility of the composite.

The analysis method of isothermal crystallization using the Avrami equation
The isothermal crystallization results from neat PEA to quaternary PEA/PEO/PVAc/PCL-CD-IC composites were analyzed by the Avrami equation [1,2] showing below:

$$
\begin{equation*}
1-X_{t}=\exp \left(-k t^{n}\right) \tag{1}
\end{equation*}
$$

In equation (1), $X_{t}$ is relative crystallinity at a given time $t, k$ is the crystallization rate constant, and n is the Avrami exponent. The relevant kinetic parameters can be evaluated through the logarithmic form of the Avrami equation, such as equation (2):

$$
\begin{equation*}
\log \left[-\ln \left(1-X_{t}\right)\right]=\log k+n \log t \tag{2}
\end{equation*}
$$

Equation (2) shows that when $\log \left[-\ln \left(1-X_{t}\right)\right]$ has a linear relationship with $\log (t), k$ and $n$ are the slope and intercept of the plot, respectively. Furthermore, the crystallization half-time ( $\mathrm{t}_{0.5}$ ) can be obtained by equation (3):

$$
\begin{equation*}
t_{0.5}=\left(\frac{\ln 2}{k}\right)^{\frac{1}{n}} \tag{3}
\end{equation*}
$$

It should be noted that $t_{0.5}$ can be defined as the time when the crystallization proceeds to $50 \%$. In general, is the crystallization rate is related to the reciprocal of t 0.5 . When the crystallization rate is higher, $1 / \mathrm{t} 0.5$ is larger.

## References

1. Avrami, M. Kinetics of phase change. II transformation-time relations for random distribution of nuclei. J. Chem. Phys. 1940, 8, 212-224.
2. Avrami, M. Granulation, phase change, and microstructure kinetics of phase change. III. J. Chem. Phys. 1941, 9, 177-184.
