[Electronic Supplementary Information]

High molecular weight Bio Furan based copolyesters for Food Packaging applications: Synthesis, Characterization and Solid-state polymerization

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Table S1. Characteristics of injection molding.

sample	Chip IV [a)] (dL/g)	Temp. (℃)	Screw rpm	Fill time (sec)	Cycle time (sec)	Preform IV (dL/g)	Δ IV [b)] (dL/g)
PEF	**0.72**	**235**	**175**	**2.7**	**27.0**	**0.65**	**0.07**
EC75	**0.94**	**285**	**170**	**2.4**	**27.8**	**0.72**	**0.22**
PCF	**0.84**	**285**	**170**	**2.2**	**27.6**	**0.54**	**0.30**
PET	**0.80**	**285**	**175**	**3.0**	**28.1**	**0.74**	**0.06**

(a) Intrinsic viscosity (dL/g); (b) Differences in IV before and after injection molding.

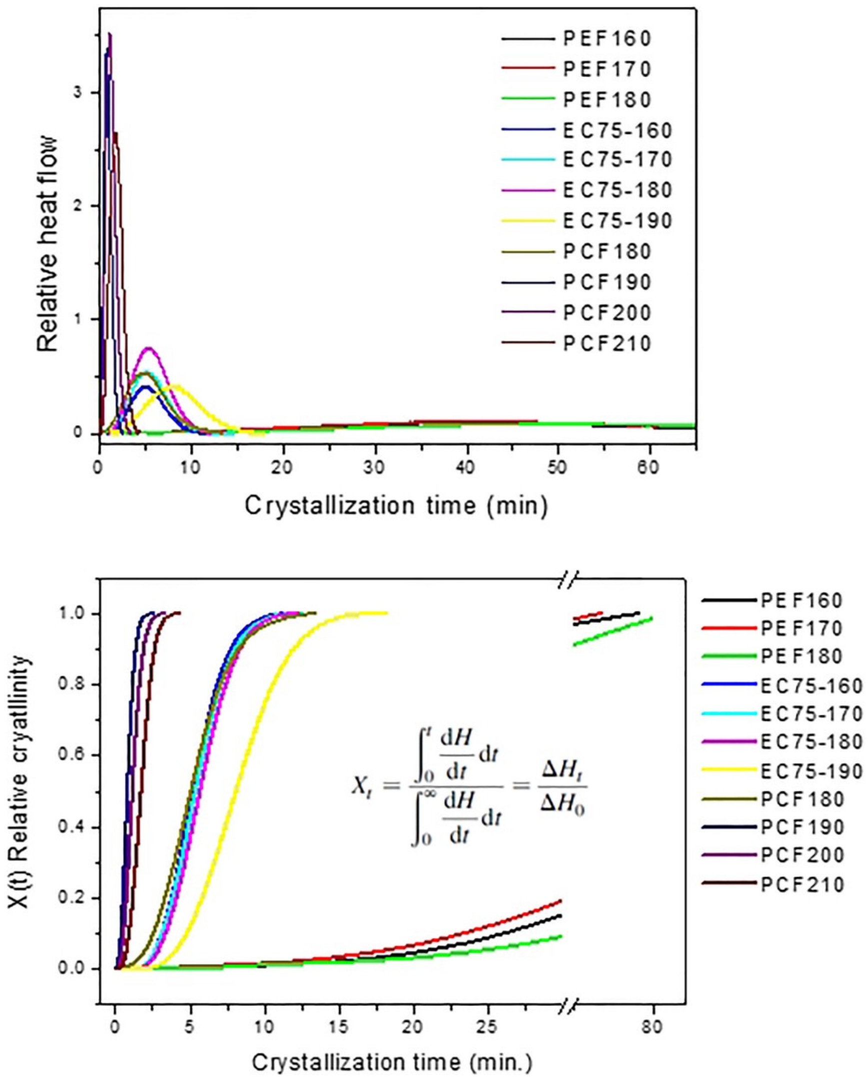


Figure S1. Isothermal crystallization behaviors of furan-based co-polyesters at different temperatures.

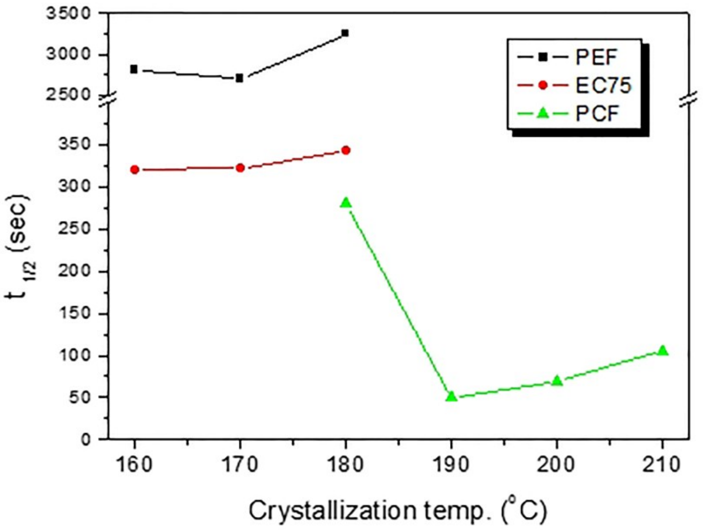


Figure S2. Crystallization half-time of furan-based co-polyesters.

Fig. S1 shows the (a) DSC thermograms and (b) relative crystallinities (X(t)) of each co-polyester isothermally crystallized from an amorphous state as a function of crystallization time. Fig. S1(b) shows that all of the curves have a typical sigmoidal shape and the crystallization rate of each sample is dependent on the isothermal crystallization temperature. PCF has the highest crystallization rate, when compared to PEF and EC75, which can also be confirmed by crystallization half-time ($t_{1/2}$) (Fig. S2). The $t_{1/2}$ is defined as the time at which the degree of crystallization reaches 50%. The fastest crystallization rates occur at 170 °C for PEF, 160 °C for EC75 and 190 °C for PCF.

Crystalline morphology was also monitored for the observation of a spherulite growth process and shape during isothermal crystallization (Fig. S3). Fig. S3 shows the crystalline morphology as a function of crystallization time. PEF showed the formation of dense spherulite 600 s after the isothermal crystallization began, which indicates that the furan unit hinders packing of the polymer chains and thus caused cessation of the spherulite growth. Incorporation of CHDM, however, expedites the spherulite growth; EC75 showed the formation of spherulite 30 s after the onset of isothermal crystallization and spherulite impingement after 60 s. PCF formed spherulite during the process of cooling and spherulite impingement occurred at 240 °C.

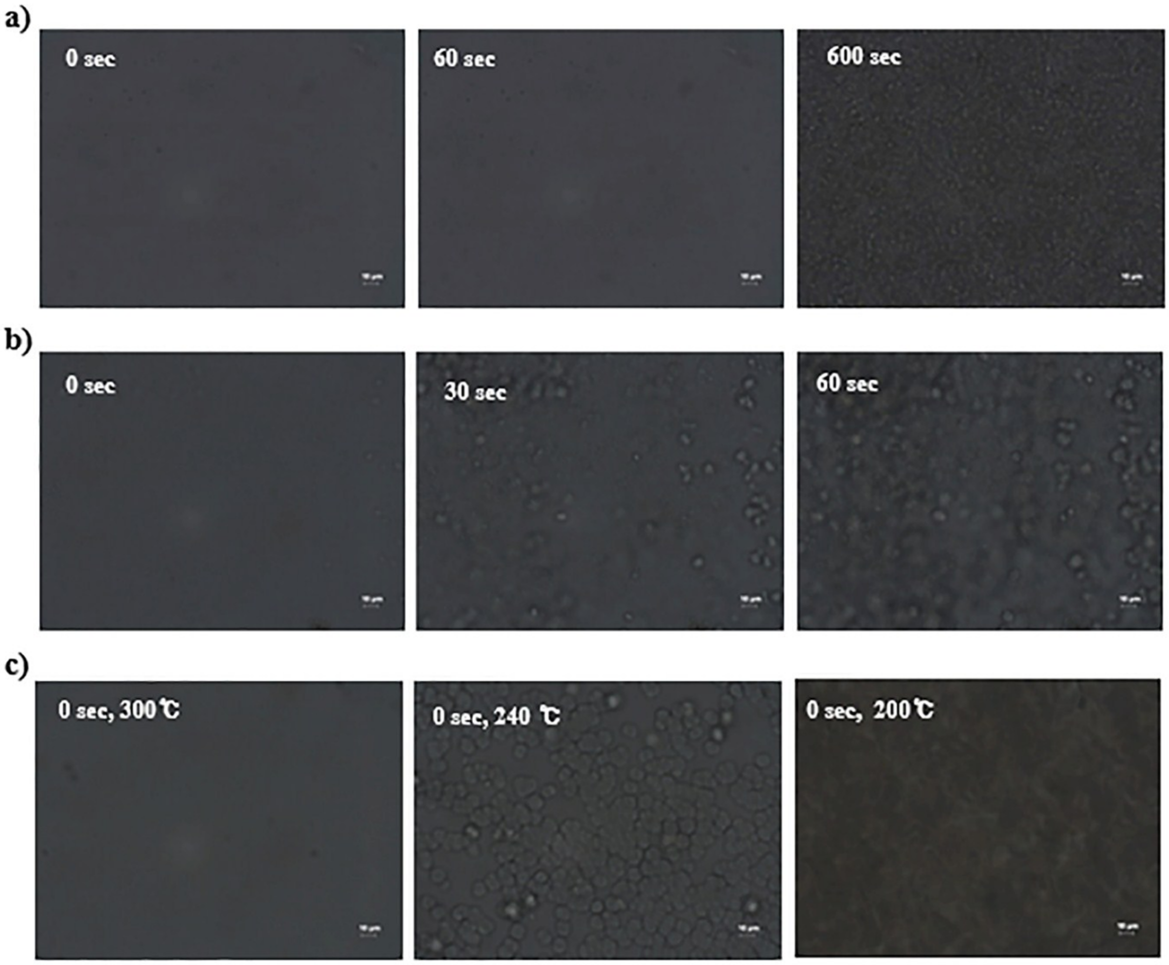


Figure S3. Polarized optical microscopy (POM) images of furan-based co-polyesters: (a) PEF isothermal crystallized at 170 °C; (b) EC75 isothermal crystallized at 170 °C; (c) PCF crystallized during the process of cooling. (Scale bar = 10 μm).

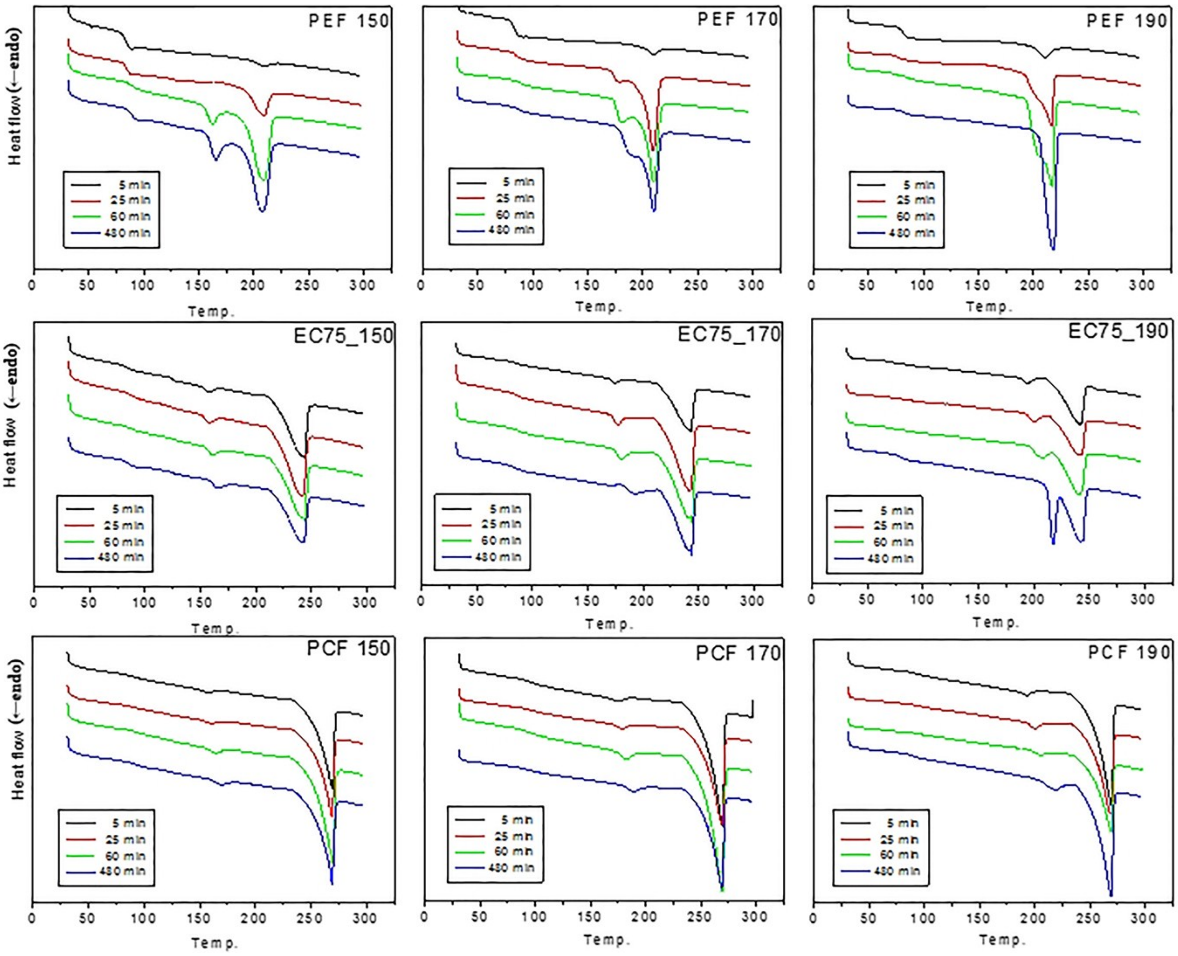


Figure S4. DSC thermograms of furan-based co-polyesters: annealed at various times and temperatures: (a) PEF, (b) EC75, and (c) PCF.

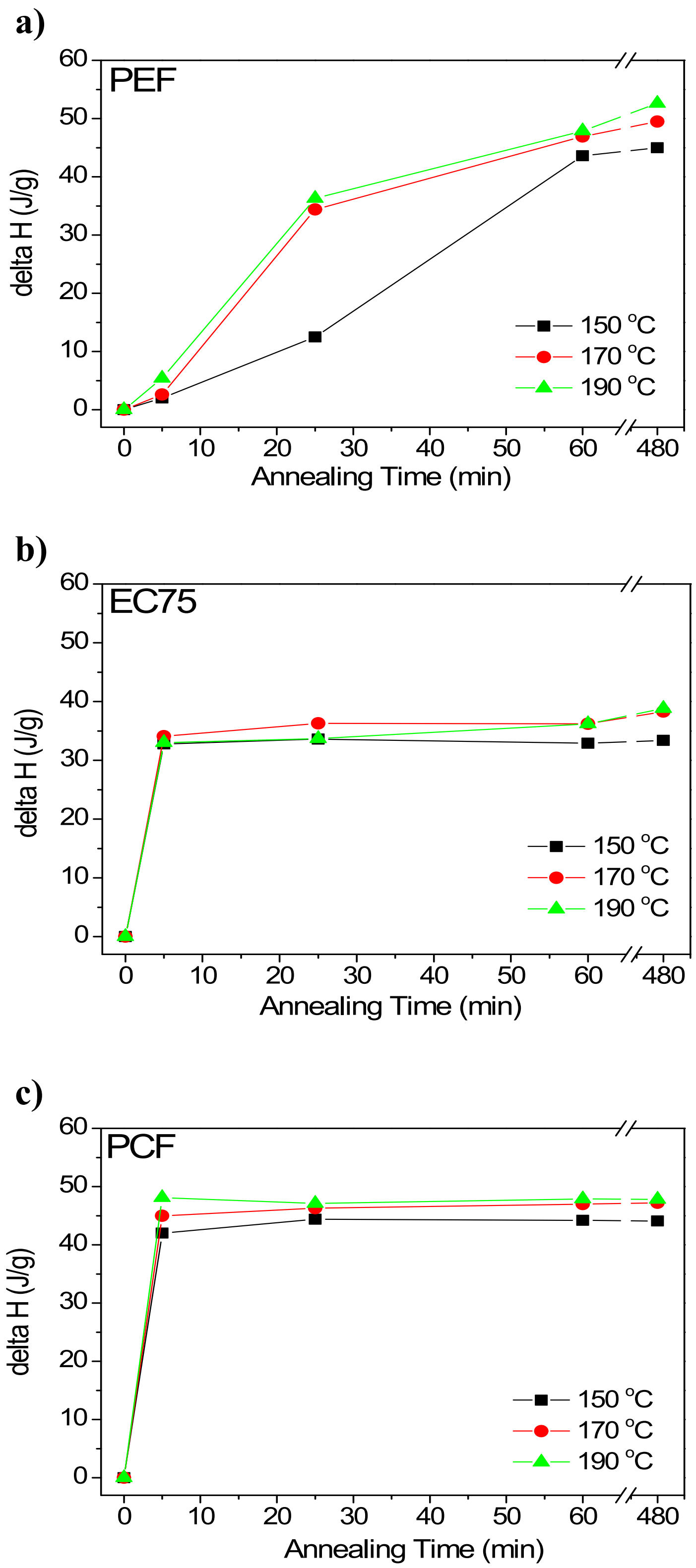


Figure S5. Changes in ΔHm of furan-based co-polyesters at various annealing times and temperatures: (a) PEF, (b) EC75, and (c) PCF.

Fig. S4 shows the DSC thermograms for (a) PEF, (b) EC75, and (c) PCF after annealing at various temperatures and over a range of time periods. Annealing treatments were performed below the melting temperatures. Each co-polyester was annealed at 150, 170, and 190 °C to provide the crystallization conditions required for SSP. Crystallinity can be observed by DSC, whereby the ΔHm correlates with time at each annealing temperature. All DSC curves exhibit two endothermal peaks, in which the lower peak is related to the melting of the crystals developed during an isothermal crystallization or annealing, and the higher peak is related to the melting of the crystals developed by gradual melting and both annealing temperature and time on the crystallinity are summarized in Fig. S5. The crystallinity of PEF continued to increase through the annealing process, and there was little difference between the annealing temperature at the start of the process and after 60 min. Both EC75 and PCF showed similar behaviors in their changes in crystallinity, in which a rapid increase in crystallinity was observed over the first 5 min of annealing, regardless of the temperature, followed by very little change as time progressed. PEF was shown to have the highest crystallinity after 480 min of annealing, followed by PCF and EC75.

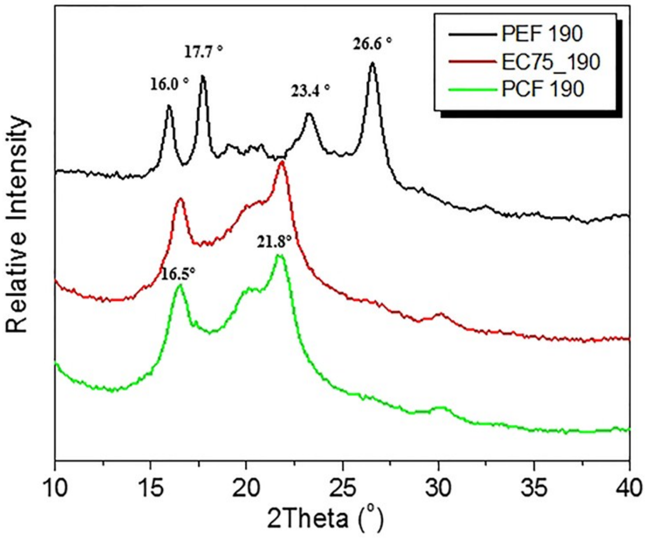


Figure S6. WAXS patterns of furan-based co-polyesters after annealing at 190 °C for 480 min.

To investigate the crystallinity of each co-polyester after sufficient annealing at 190 °C for 480 min, wide angle X-ray scattering (WAXS) was used, with the results shown in Fig. S6. PEF showed characteristic peaks at $2\theta = 16.0°$, 17.7°, 23.4° and 26.6°, which are similar to that reported in a previous study. The polyester has a triclinic unit cell, with dimensions of $a = 5.75$ Å, $b = 5.35$ Å, and $c = 20.10$ Å, and $\alpha = 133.3°$, $\beta = 90°$ and $\gamma = 112°$, with two repeating units in the asymmetric unit cell.[S1] The crystallinity of PEF was calculated by combining the integral values of the characteristic peak whose full width at half maximum (FWHM) was below 2.5, where it was found to be 45%. Both EC75 and PCF showed peaks at $2\theta = 16.5°$ and 21.8°, which indicated that they have a similar crystal structure. Crystallinity decreased, however, from 38% for PCF to 24% for EC75, as the concentration of EG in the polyester main chain of PCF from packing efficiently for crystallization. It is worthy to note that PEF exhibited the highest crystallinity when compared to EC75 and PCF, even though its rate of crystallization was especially slow.

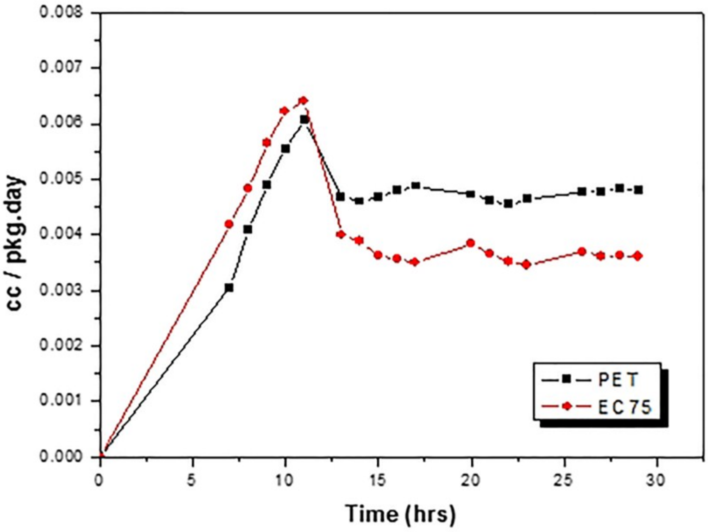


Figure S7. O_2 barrier properties of EC75.

Table S2. Permeability and fractional free volume (FFV) of furan-based co-polyesters.

Sample	Permeability (cc / pkg.day)	MW (g/mol)	Density (g/cm^3)	$\hat{V}_g$ $^{a)}$ (g/cm^3)	$\hat{V}_0$ $^{b)}$ (g/cm^3)	$\hat{V}_F$ $^{c)}$ (g/cm^3)	FFV
PEF*	-	**182.1**	**1.42**	**0.704**	**0.592**	**0.112**	**0.159**
EC75	**0.0036**	**248.7**	**1.26**	**0.794**	**0.675**	**0.119**	**0.149**
PET	**0.0048**	**192.2**	**1.34**	**0.749**	**0.651**	**0.098**	**0.130**

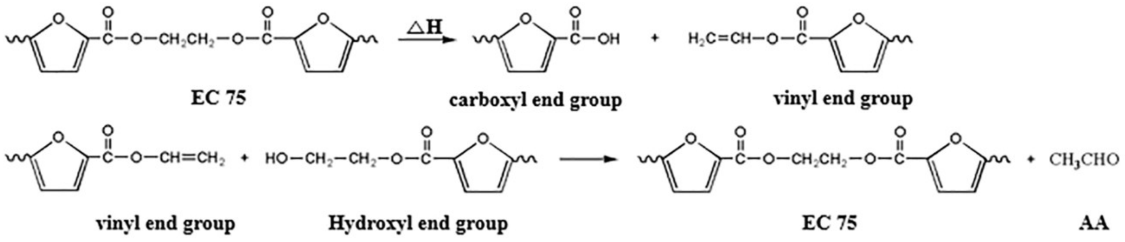
The specific free volume ($\hat{V}_f$) and fractional free volume (FFV) were calculated to confirm the results of O_2 permeability using equations (1) and (2):

$$\hat{V}_f = \hat{V}_g - \hat{V}_0 \quad (1)$$

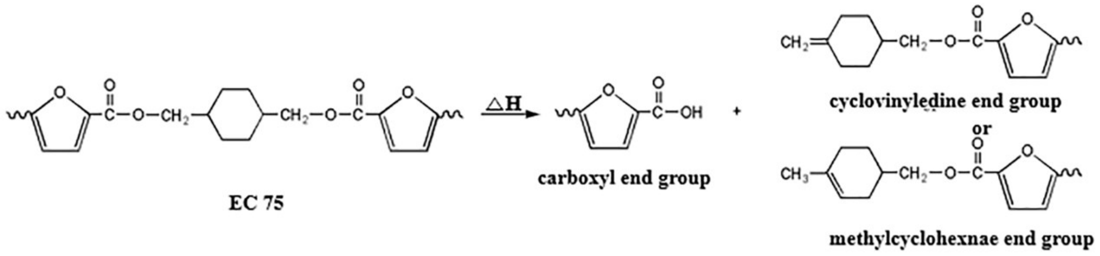
$$FFV = \frac{\hat{V}_g - \hat{V}_0}{\hat{V}_g} \quad (2)$$

These parameters indicate, however, that there is no relationship between FFV and O_2 permeability, as has been suggested in a previous report.[S2]

a) Thermal degradation of EC 75 including ester linkage between FDCA and EG



b) Thermal degradation of EC 75 including ester linkage between FDCA and CHDM



Scheme S1. Thermal degradation of EC75: (a) thermal degradation of EC75 including ester linkage between FDCA and EG; (b) thermal degradation of EC75 including ester linkage between FDCA and CHDM.

References

S1 Vasilios Tsanaktsis, Dimitrios G. Papageorgiou, Stylianos Exarhopoulos, Dimitrios N. Bikiaris†, and George Z. Papageorgiou, Cryst. Growth Des. 2015, 15, 5505−5512

S2 Besnoin, J. M. Choi, K. Y. Rev Macromol Chem Phys 1989, 29, 55-81