

Efficient exchange in a bioinspired dynamic covalent polymer network via a cyclic phosphate triester intermediate.

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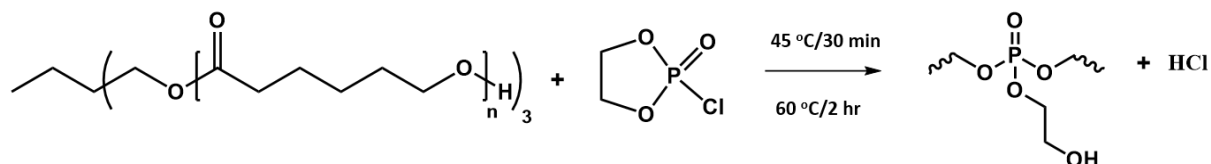
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Materials

All reagents and solvents were used as obtained without further purification unless specifically mentioned. Polycaprolactone triol (~ 1934 g/mol) was obtained from Perstorp (CAPA 3201). **2-Chloro-2-oxo-1,3,2-dioxaphospholane** was purchased from Sigma Aldrich. Toluene and tetrahydrofuran were purchased from Biosolve. Toluene was maintained dry with 3 Å molecular sieves.

Synthesis

Synthesis of polycaprolactone phosphate triester network (PCL-PX)



25.58 g (13.22 mmol) polycaprolactone triol (1934 g/mol) was dried by coevaporation with toluene. The polymer was then re-dissolved in 15 ml of dry toluene. 1.82 ml (19.79 mmol) 2-chloro-1,3,2-dioxaphospholane-2-oxide was added dropwise under vigorous stirring at room temperature. The reaction was then set at 45 °C for 30 mins under slow stirring and then at 60 °C for 2 hr. The reaction medium gelled. The temperature was brought down to room temperature and vacuum was applied to extract the hydrogen chloride which was formed as a reaction byproduct. The temperature was again gradually raised to 45 °C to facilitate the process. The gel was then taken out and dried off toluene at 100 °C in a vacuum oven for 18 hr.

Material Characterization

Gel fraction and swelling ratio analysis

The gel fraction was determined by using tetrahydrofuran (THF) as the extracting solvent. The dry sample was weighed (m_{initial}) and then allowed to swell in tetrahydrofuran (THF) for 24 hr. The swollen gel was then washed with excess THF and then dried in vacuum oven for 8 h at 100 °C. The dried material was then weighed (m_{dry}), and gel fraction was calculated using equation S1a.

$$\% \text{ gel fraction} = \frac{m_{\text{dry}}}{m_{\text{initial}}} \times 100 (\%) \quad (\text{S1a})$$

For swelling ratio analysis, a dry compression molded sample was weighed (m_{initial}). The sample was then allowed to swell in THF for 24 hr. The swollen sample was then removed, gently tap dried on a filter paper and weighed (m_{swollen}). Swelling ratio based on weight (w) was measured using equation S1b.

$$\text{Swelling ratio } (w) = \frac{m_{\text{swollen}}}{m_{\text{initial}}} \quad (\text{S1b})$$

Variable temperature solid state ^{31}P NMR spectroscopy

Variable temperature solid state ^{31}P NMR (^{31}P SSNMR) measurements were performed using an 11.7 Tesla Bruker Avance Neo 500 MHz spectrometer operating at ^{31}P resonance frequency of 202 MHz. The measurements were performed under static condition, with no Magic angle spinning, using a one pulse sequence with a 90° pulse of 5 μs and an inter-scan delay of 5 s. 0.0485 M triphenyl phosphate solution in CDCl_3 (17.70 ppm) was used as a chemical shift reference. The variable temperature experiment was performed from 60 °C to 120 °C at intervals of 15 °C. The system was allowed to equilibrate for 15 min at each temperature.

Determination of ΔH^o for dissociation from ^{31}P SSNMR spectra

In PCL-PX, there is a dynamic equilibrium between ring opened phosphate esters and cyclic phosphate esters. The ring opened phosphate triester represents a chain extension link and the cyclic phosphate triester represents a chain dissociation. The rate of the dissociation process depends on the concentration of phosphate triester links with β -hydroxyl functionality ([OP]) whereas the association step depends on the concentration of cyclic phosphate triester ([CP]) and -OH functionality. The equilibrium constant (K) can thus be represented as in (Eq. S2)

$$K = \frac{[\text{CP}][-\text{OH}]}{[\text{OP}]} \quad (\text{S2})$$

According to the stoichiometry that was used for network synthesis, the end material contains one -OH functionality per phosphate ester moiety. Therefore, the association reaction between the cyclic phosphate ester and -OH functions occurs in a large excess of OH functionality (>60 times, Figure S2) and so, it can be considered as a pseudo first order reaction. Moreover, both the association and dissociation process is a transesterification reaction and thus the OH content in the network remains unaltered and is temperature independent. The concentration ratio between the cyclic phosphate ester and ring opened phosphate ester can be calculated from ^{31}P SSNMR spectra (Figure S2). K can be used to determine ΔH^o using van't Hoff equation (Eq.S3). In this case, since [-OH] is a temperature independent constant, van't Hoff equation can be used to determine ΔH^o based on [CP]/[OP] (Eq.S4).

$$\ln K = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (\text{S3})$$

$$\ln\left(\frac{[\text{CP}]}{[\text{OP}]}\right) = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} - \ln([\text{-OH}]) \quad (\text{S4})$$

Thermogravimetric analysis (TGA)

Thermal stability of the material was analysed using a TGA Q500 (TA instruments) under N_2 flow (Figure S3). The temperature ramp was performed from 30 °C to 600 °C at 10 °C/min. Isothermal TGA was also performed for 1 h at 100 °C and 160 °C. Temperature calibration was performed using the Curie points of high purity aluminum, nickel and perkalloy standards.

Differential scanning calorimetry (DSC)

DSC was performed in a Q2000 DSC (TA instruments). Measurements were performed using standard aluminium pans. The temperature range used, was -70 °C to 140 °C. The material was heated to 60 °C to erase thermal history and then slowly cooled to -70 °C at 1 °C/min. The heating run was performed from -70 °C to 140 °C at 10 °C/min. The glass transition and melting temperature was determined from the second heating run (Figure S4).

Dynamic mechanical thermal analysis (DMTA)

DMTA was performed on rectangular shaped compression molded samples using film tension setup in a DMA Q850 (TA instruments). The temperature ramp was performed from -80 °C to 150 °C at a heating rate of 3 °C/min under an oscillatory strain of 0.1% and a frequency of 1 Hz. A preload force of 0.01 N and a force track of 110% was used. The storage and the loss modulus were recorded as a function of temperature.

DMTA with heating and cooling cycles were performed on compression molded circular disks under plate-plate geometry in a Discovery HR 20 (TA instruments). The temperature cycling was performed between 100 °C and 140 °C at 0.5 °C/min. The measurement was performed under 0.5 N axial force, at an oscillatory frequency of 1Hz and 1% strain. The sample was first heated to 140 °C to remove

thermal history, and then cooled to 100 °C. The data was acquired for the second heating and the cooling cycle.

Rheology

All rheology studies were performed using Discovery HR 20 (TA instruments) and parallel-plate geometry. The samples were compression molded at 100 °C for 25 mins and then slowly cooled to obtain disks with diameter of 8 mm and thickness of 0.8 mm. All experiments were performed with an axial force range of 1 ± 0.2 N (unless stated otherwise). The samples have been equilibrated at the temperature of measurement by performing oscillatory shear for 20 mins prior to the experiments. All strain controlled experiments have been performed under 1% strain which is within the linear visco-elastic regime of the material.

Stress relaxation experiments

Stress relaxation experiments were performed with temperature variation from 80 °C to 160 °C. The relaxation modulus ($G(t)$) was followed over different time periods for a constant applied strain of 1%. All the stress relaxation plots have been normalised at 1 s to be able to compare the relaxation rates based on bond exchange kinetics (Figure S5).

All the normalized stress relaxation plots were fitted with a stretched exponential function normalized to 1 s (equation S5) and the characteristic relaxation times (τ), obtained, have been plotted in an Arrhenius plot. The activation energy for flow can be derived from the slope of the Arrhenius plot according to equation S6.

$$\frac{G(t)}{G(1s)} = \frac{e^{-\left(\frac{t}{\tau}\right)^\beta}}{e^{-\left(\frac{1}{\tau}\right)^\beta}} \quad (S5)$$

$$\ln(\tau) = \ln(\tau_0) + \frac{E_a}{RT} \quad (S6)$$

Stress relaxation experiments were also performed to study differences in dynamic properties on prolonged exposure at high temperatures. Repeated stress relaxation experiments up to 5 cycles were performed at 160 °C and 100 °C. The experiments were performed under 1% strain.

Frequency sweep experiments

Frequency sweep experiments from 10^{-2} rad/s to 10^2 rad/s were performed on PCL-PX at different temperatures. The oscillation amplitude was set to 1% strain. The storage modulus, loss modulus and $\tan \delta$ were followed as a function of frequency.

Creep-Recovery experiments

Creep-recovery experiments were performed on PCL-PX at 25 °C, 60 °C and 100 °C under 10000 Pa imposed shear stress and 10 N axial force. Both creep and the recovery step were executed for 1000 s.

Oscillatory time sweep experiments

Oscillatory time sweep experiments were performed before and after stress relaxation experiments at the same temperature to ensure that the relaxation is brought about by network rearrangement and not network degradation. The oscillatory experiments were performed with 1% oscillatory strain and a frequency of 1 Hz. The storage modulus was followed with time.

Oscillatory time sweep experiment was performed at 160 °C for 3000 s under 1% strain and 1 Hz frequency to study the effect of prolonged material exposure at high temperatures.

Reprocessing via extrusion

Reprocessing of the material was performed in a Xplore micro compounder MC 15 HT, with a twin screw (CO-rotating) setup. ~15 g of PCL-PX, in granular form, was loaded at 50 °C. The torque was measured from 70 °C to 120 °C at a screw speed of 50 rpm. Extrusion was performed at 120 °C under 50 rpm screw rotation and 7.2 N.m torque. The extrudate was sonicated in THF for 30 mins to check the extent of sintering (Figure S7).

Results

³¹P SSNMR study

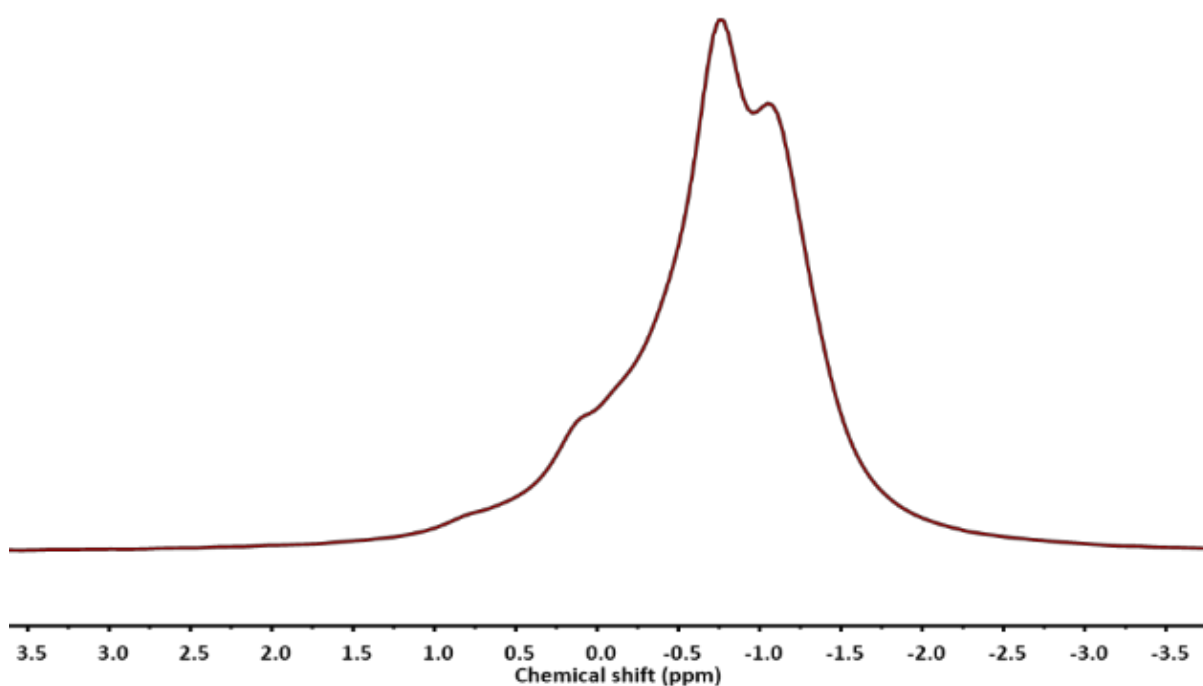


Figure S1. Solid state ³¹P NMR static spectrum acquired at 75 °C shows much resolved phosphate triester peaks in PCL-PX.

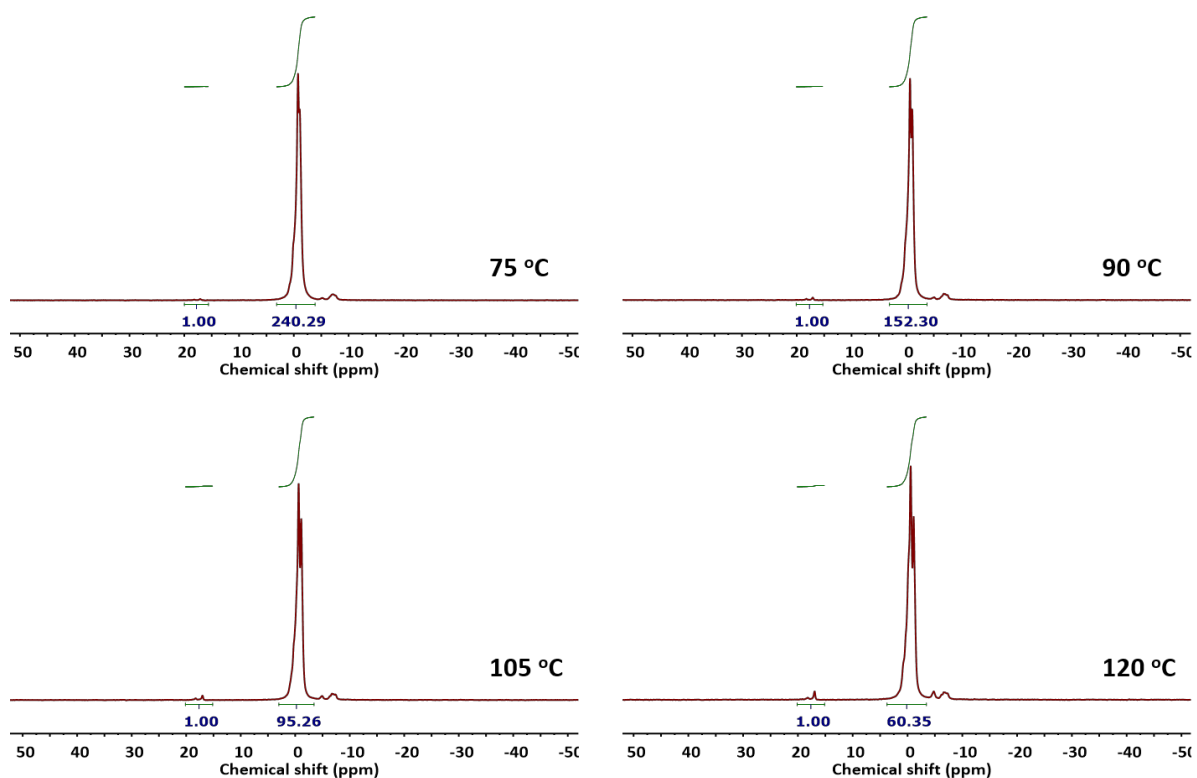


Figure S2. Peak integrals of phosphate triester peaks at different temperatures for equilibrium constant calculation from VT ^{31}P SSNMR study on PCL-PX.

TGA plots

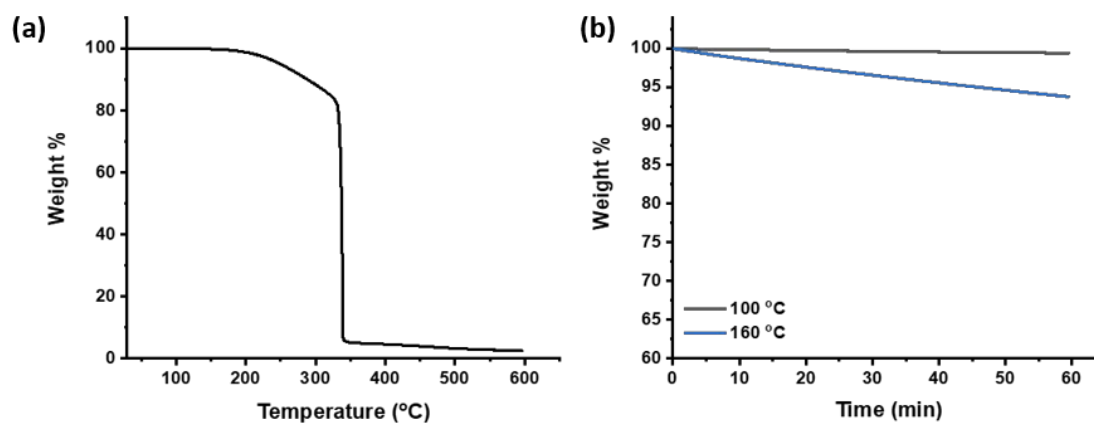


Figure S3. TGA on PCL-PX a) temperature ramp from 30 °C to 600 °C at a heating rate of 10 °C/min, b) Isothermal measurements at 100 °C and 160 °C.

DSC thermogram

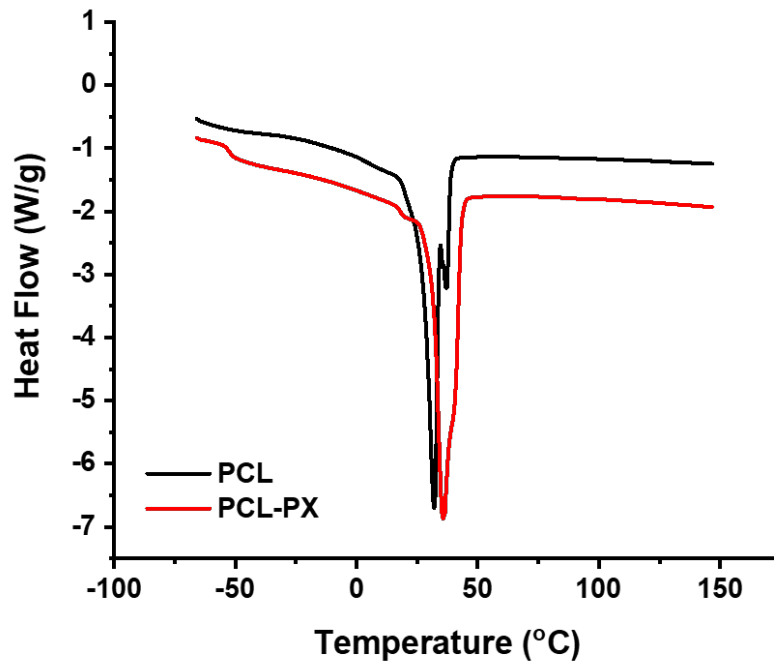


Figure S4. DSC on PCL and PCL-PX at a temperature ramp of 10 °C/min.

Rheology data: Stress relaxation and frequency sweep

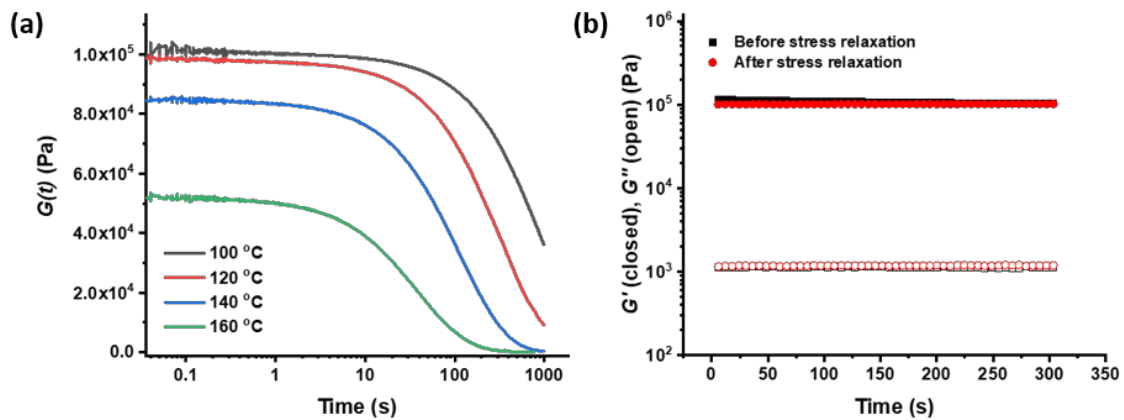


Figure S5. a) Unnormalized stress relaxation plots of PCL-PX at different temperatures under 1% step strain. b) Oscillatory shear experiment before and after stress relaxation experiment at 120 °C showing that the storage modulus of PCL-PX remains unaltered signifying that the relaxation occurs by bond exchange process and not network degradation.

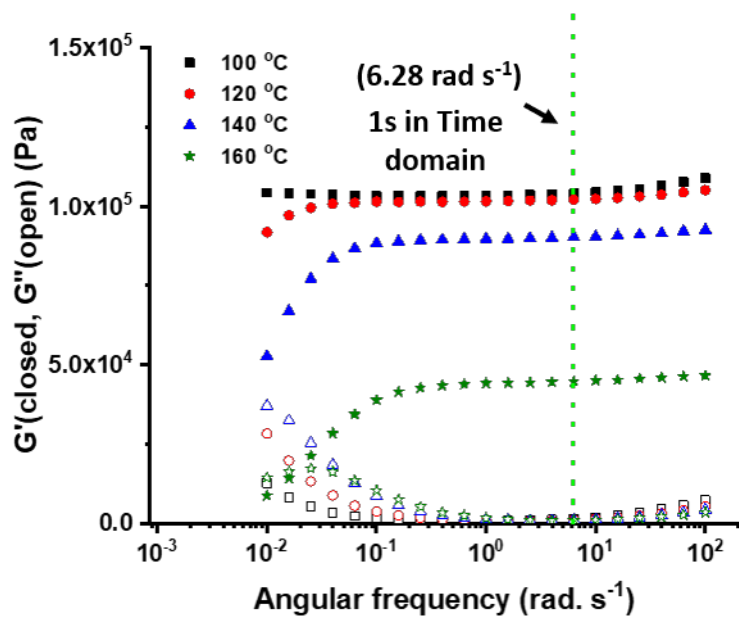


Figure S6. Frequency sweep experiments on PCL-PX show a steady rubbery plateau at 6.28 rad. s^{-1} (1 s in time domain) for all temperatures which signifies that relaxation from free chains in the network occurs within 1 s under these conditions. Therefore, at higher times the viscous flow is limited by bond exchange process.

Material reprocessing: Compounding and extrusion

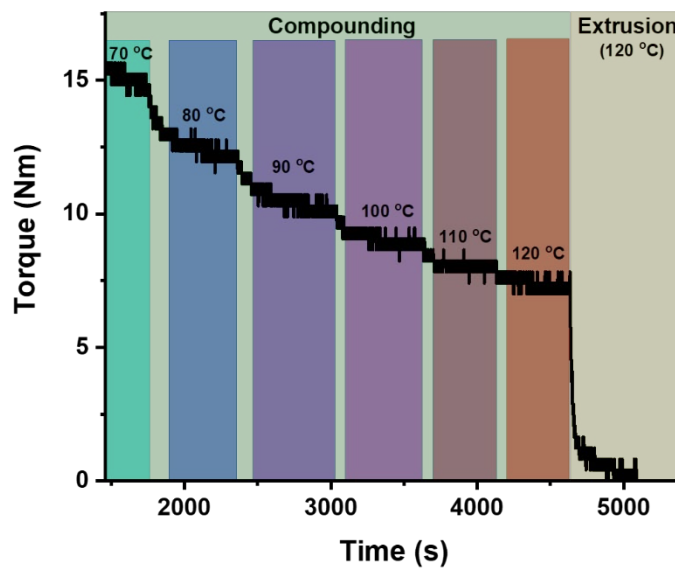


Figure S7. Experiment timeline, torque measured in Xplore micro compounder MC 15 HT at different temperatures during PCL-PX reprocessing.