

Supporting information

Elucidating Tribochemical Reaction Mechanisms: Insights into Tribofilm Formation from Hydrocarbon Adsorbates Coupled with Tribochemical Substrate Wear

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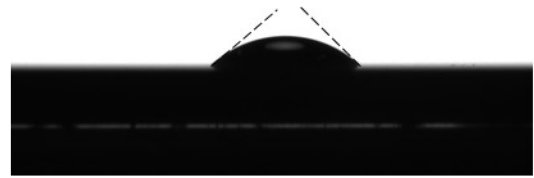
Water contact angle measured on the silicon wafer cleaned with RCA-a solution and then dehydroxylated through thermal annealing

(a) RCA-1 cleaned silica



$$\theta < 5^\circ$$

(b) Dehydroxylated silica



$$\theta = 42 \pm 1^\circ$$

Figure S1. Water contact angle measured on (a) RCA-1 cleaned silica on Si wafer and (b) thermally dehydroxylated silica on Si wafer. The silicon wafer was cleaned with the RCA-1 solution (water:27% NH_4OH : 30% H_2O_2 = 5:1:1) at 75-80 °C for 20 mins, followed by rinsing with deionized water. The RCA-1 cleaned wafer was heated at 450 °C in dry N_2 for 15 hr (heating rate 5 °C/min, cooling rate 1 °C/min). The measurement was taken right after the treatment. Standard deviation is from 3 different measurements.

Friction coefficient measured on dehydroxylated silica in the presence of $P/P_{\text{sat}}=30\%$ of organic precursors at shear stress (τ) ranging from 0.057-0.103 GPa or P_{avg} (average Hertzian contact pressure) ranging from 0.23-0.42 GPa

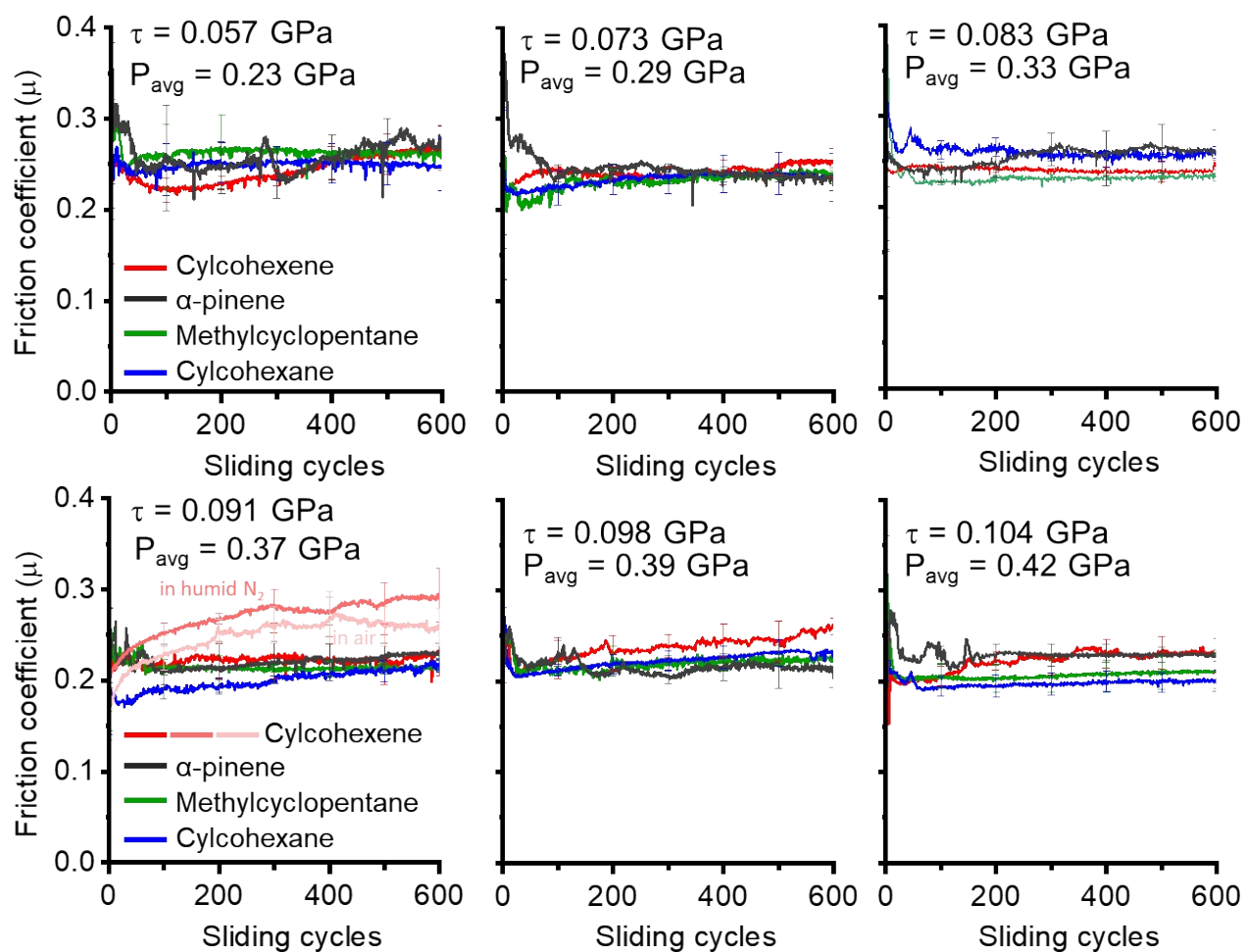


Figure S2. Friction coefficients were measured on dehydroxylated silica in a dry N₂ environment containing $P/P_{\text{sat}} = 30\%$ of cyclohexene, α -pinene, methylcyclopentane, and cyclohexane. Error bars represent standard deviations calculated from 3-4 measurements.

Representative friction loops from each precursor molecule measured at shear stress = 0.091 GPa

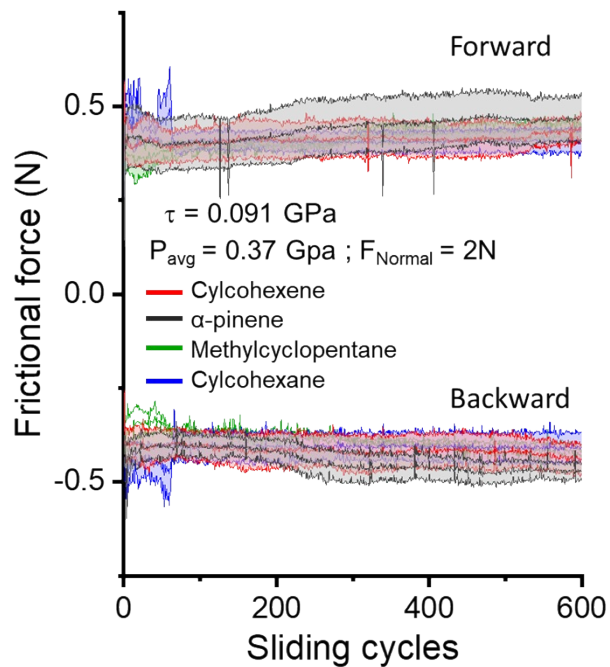


Figure S3. Representative friction loops from each precursor molecule measured at shear stress = 0.091 GPa (Normal force $F_{Normal} = 2$ N; average Hertzian contact pressure $P_{avg} = 0.37$ GPa).

Semi-log plot of the normalized yield vs. shear stress for the tribopolymers produced in VPL of cyclohexene, α -pinene, methylcyclopentane, and cyclohexane

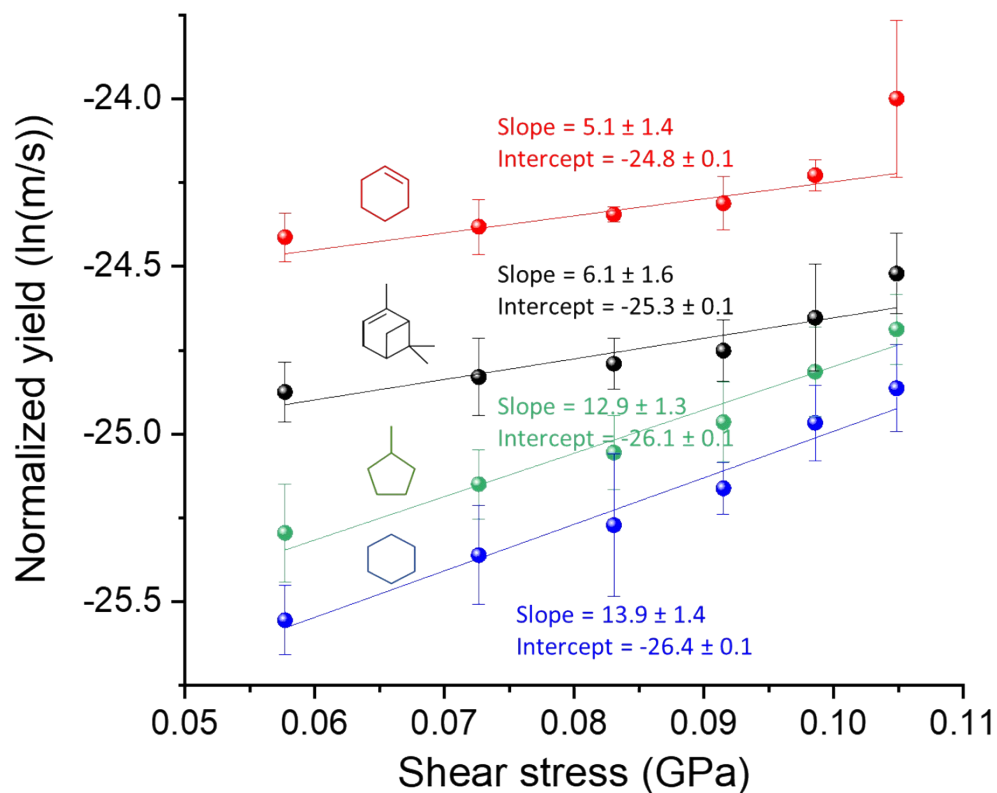


Figure S4. Semi-log plot of the normalized yield vs. shear stress for the tribopolymers produced from cyclohexene, α -pinene, methylcyclopentane, and cyclohexane vapor in N_2 . The solid lines represent linear regression of all the six data points. Error bars indicate the standard error of the mean of the reaction yield calculated from 3-4 different sliding tracks.

Analysis of sliding tracks after removal of tribofilms formed in different organic vapor environments at shear stress ranging from 0.057-0.103 GPa

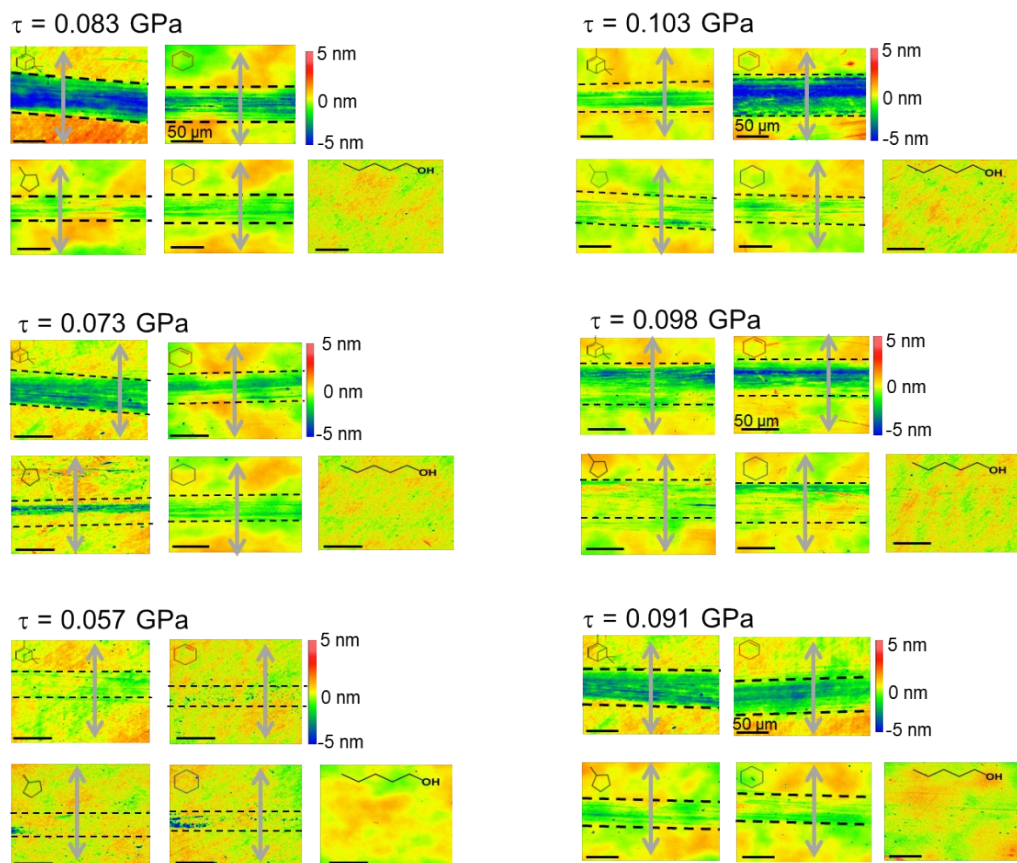
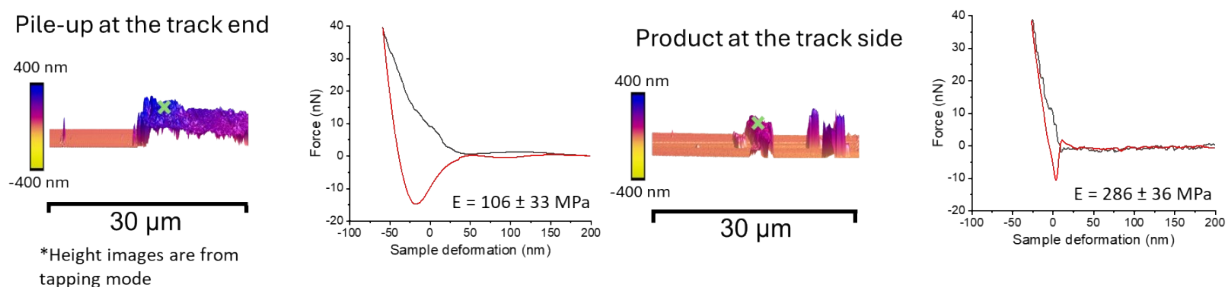


Figure S5. 3D optical profilometry images of wear track revealed after removal of tribofilms formed in dry N_2 environment with cyclohexene, α -pinene, cyclohexane, methylcyclopentane and n-pentanol vapors ($P/P_{\text{sat}} = 30\%$) at shear stress ranging from 0.057-0.103 GPa. The gray arrows in the 3D profilometry images indicate the location where the height profile in Figure 5 in the main paper was taken.

Force-sample deformation curve conducted on triboproducts produced from cyclohexene and cyclohexane by AFM in contact mode

(a) Triboproduct from cyclohexene



(b) Triboproduct from cyclohexane

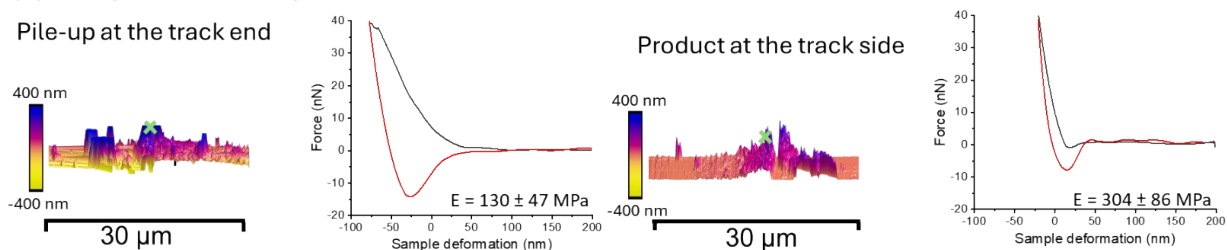


Figure S6. Force-deformation curves were measured at both the end and side of the wear track on tribo-product from (a) cyclohexene and (b) cyclohexane using AFM in contact mode. The measurement locations are marked on the height map as green cross. The spring constant of the AFM tip used is 1.72 N/m (PPP-FM; Nanosensors). For the region inside the sliding track, there was too little tribopolymer present to confidently perform force-separation measurements. Note that the height maps, as presented in the current manuscript and here, were acquired using AFM in tapping mode.

Images of tribofilms formed from cyclohexene ($P/P_{\text{sat}} = 30\%$) in dry N_2 , dry air, and N_2 with 40% relative humidity

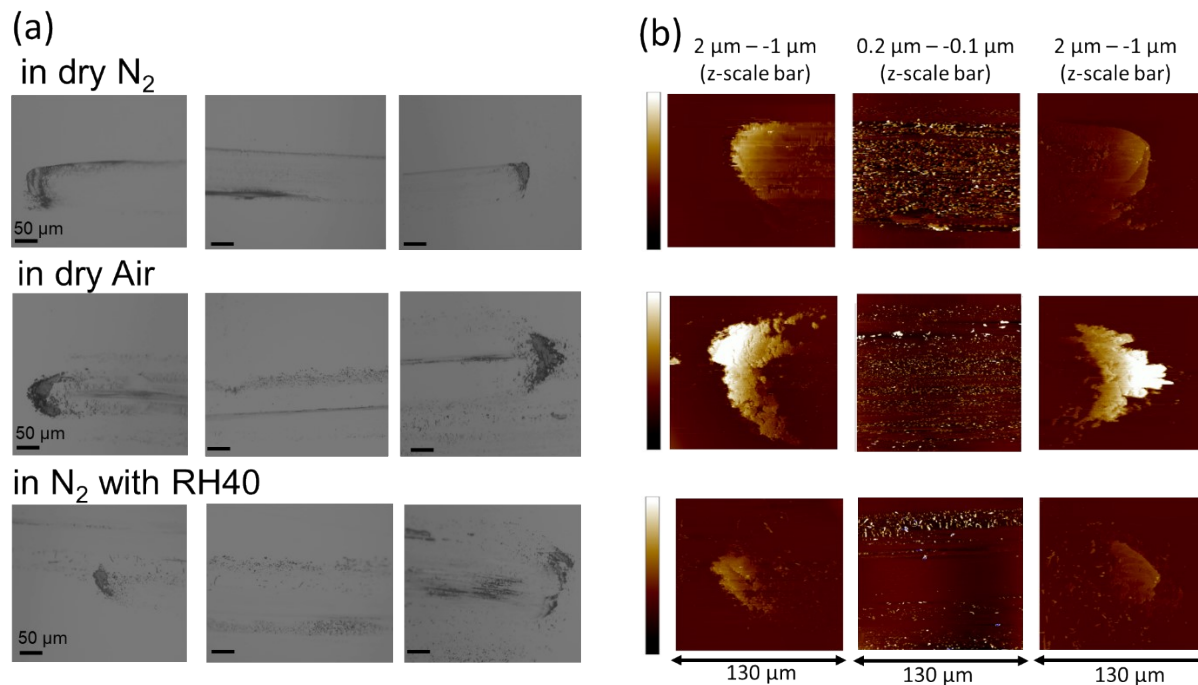


Figure S7. (a) Optical images and (b) AFM images of the sliding tracks after tribotest in cyclohexene in dry N_2 , dry air, and N_2 with relative humidity of 40%.