

Supplemental Information: Micro/Nanoplastic Formation by Polymer Processing

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Extrusion protocol

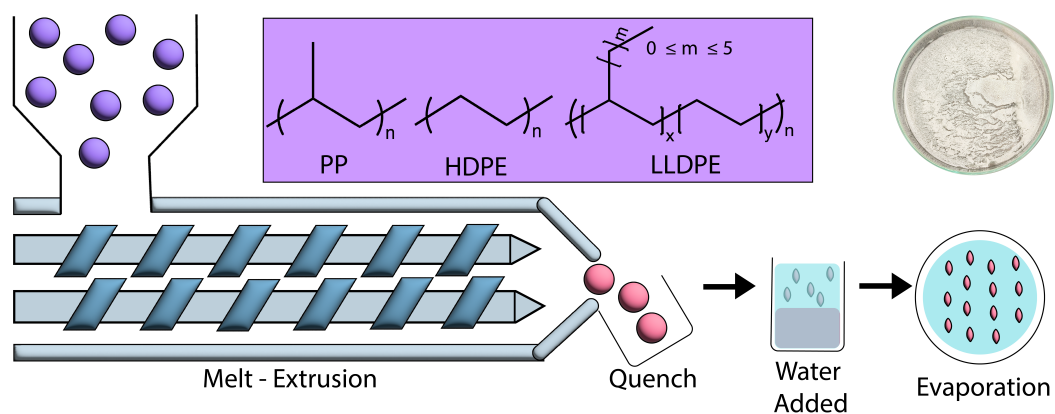


Figure S1: Extrusion protocol for the recovery of MNPL.

MNPL recovered from short residence time extrusions

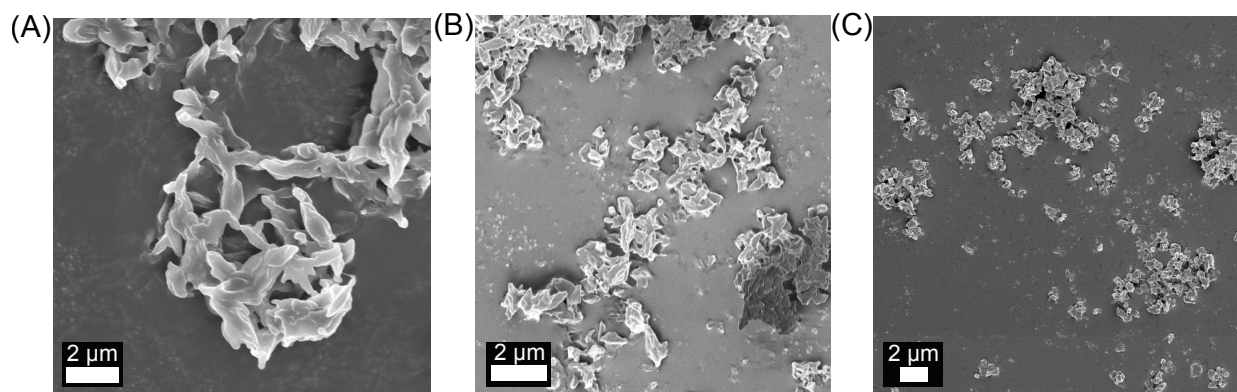


Figure S2: SEM micrographs of MNPL recovered from the extrusion of PP for 5 min at 200 °C at (A) 21 rad/s (B) 26 rad/s and (C) 31 rad/s.

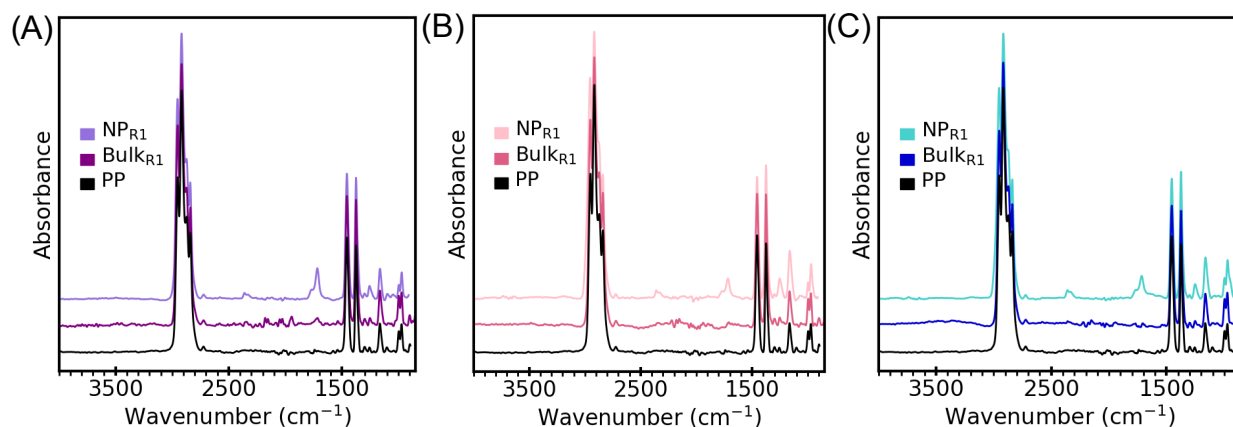


Figure S3: ATR-FTIR of bulk PP matrix and MNPL recovered from the extrusion of PP for 5 min at 200 °C at (A) 21 rad/s, (B) 26 rad/s and (C) 31 rad/s.

Light scattering count rates of water contacting extruded PP

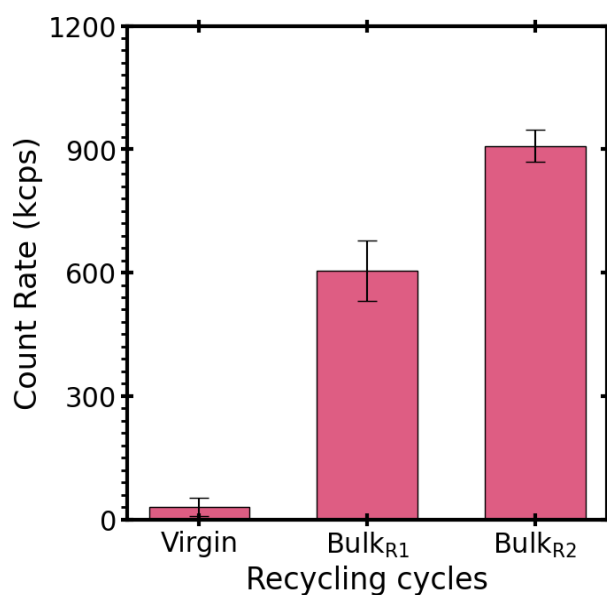


Figure S4: Light scattering count rates from water contacted with PP in the virgin state, after the first (Bulk_{R1}), and the second extrusion (Bulk_{R2}). The error bar represent the standard deviation of three measurements.

MNPL dispersion on other solvents contacting extruded PP

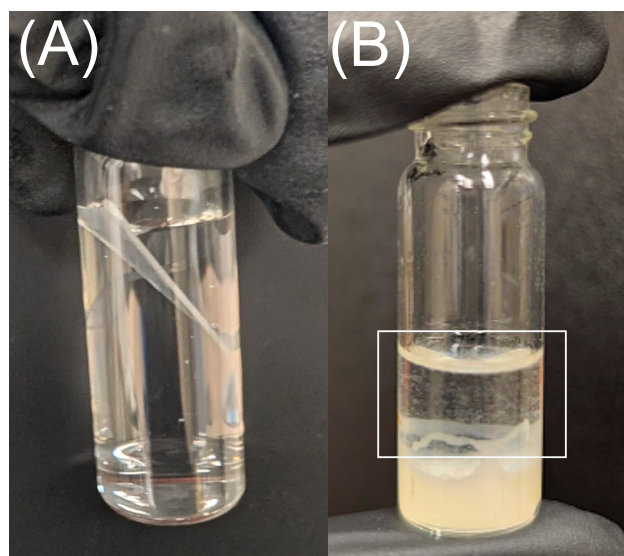


Figure S5: (A) No dispersion of particles observed on the addition of dichloromethane to virgin PP even after 24 h. (B) Dispersion of MNPL particles observed on the addition of dichloromethane to Bulk_{R1} after a short contact period of < 1 min.

EDS of the MNPL collected from extrusion of PP

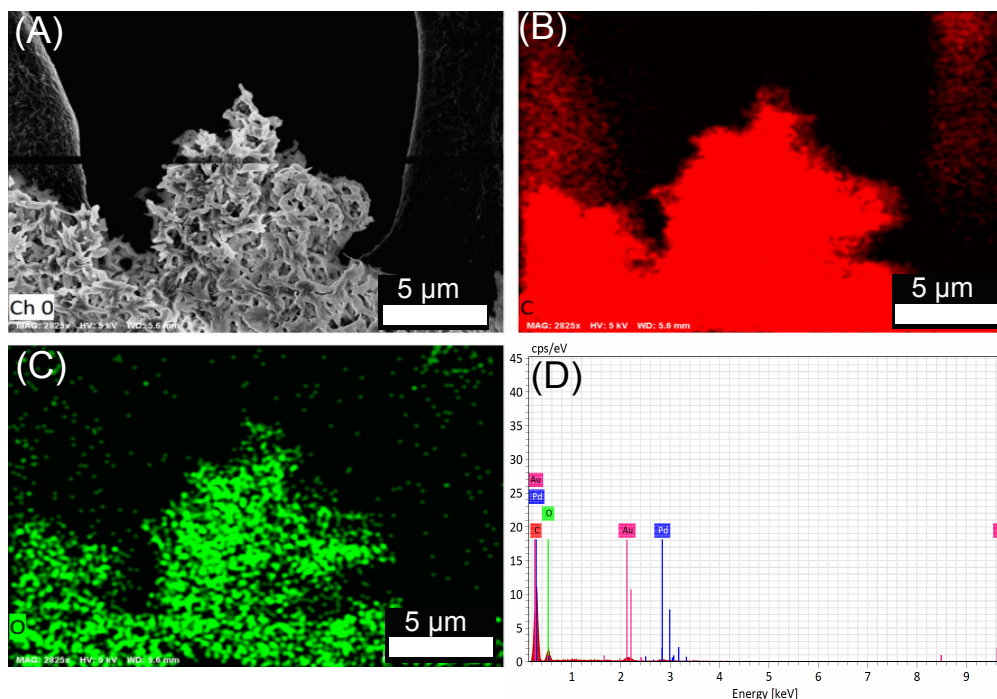


Figure S6: (A) SEM micrographs of MNPL collected from the first extrusion of PP, along with corresponding EDS elemental mapping images showing (B) carbon and (C) oxygen distribution across the sample. (D) EDS spectrum showing the elemental composition. Note: the Au and Pd signals arise from sputter coating of the sample.

Table S1: ATR-FTIR assignments of the PP backbone

Band Position (cm^{-1})	Band Assignment
2955	Asymmetric methyl stretching vibration
2920	Asymmetric methylene stretching vibration
2870	Symmetric methyl stretching vibration
2841	Symmetric methylene stretching vibration
1650 to 1800	C=O stretching vibration
1600 to 1650	C=C stretching vibration
1500 to 1600	C=C conjugation stretch
1462	CH ₃ asymmetric bending vibration
1373	CH ₃ symmetric bending vibration
1173	CH ₂ twisting and CH wagging vibration
998	CH bending and wagging vibration and CH ₃ rocking vibration
973	CH ₃ rocking, CH ₂ wagging and CH bending vibrations.

Table S1: ATR-FTIR assignments for PP backbone (1).

FTIR spectrum of oxidized PP

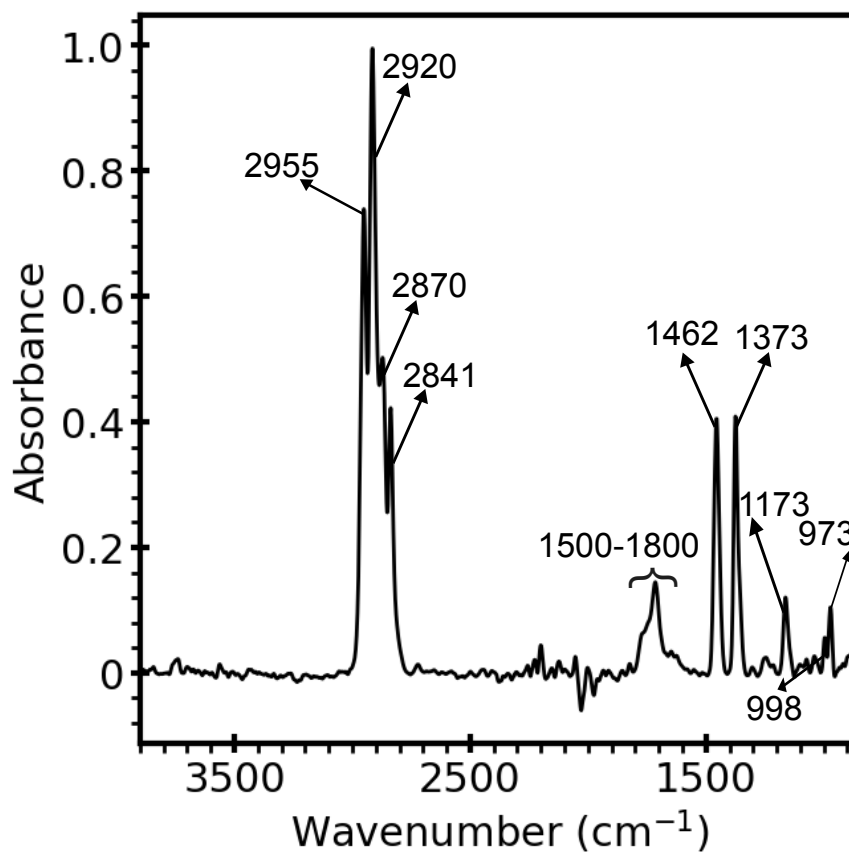


Figure S7: ATR-FTIR absorbance spectra of oxidized PP. Assignments for each of these peaks is noted in Table S1.

Table S2: ATR-FTIR assignments of the PE backbone

Band Position (cm^{-1})	Band Assignment
2910	Asymmetric methylene stretching vibration
2830	Symmetric methylene stretching vibration
1650-1800	C=O stretching vibration
1460	CH ₂ scissoring vibration
720	CH ₂ rocking vibration

Table S2: ATR-FTIR assignments for PE backbone (2).

ATR-FTIR spectrum of oxidized PE

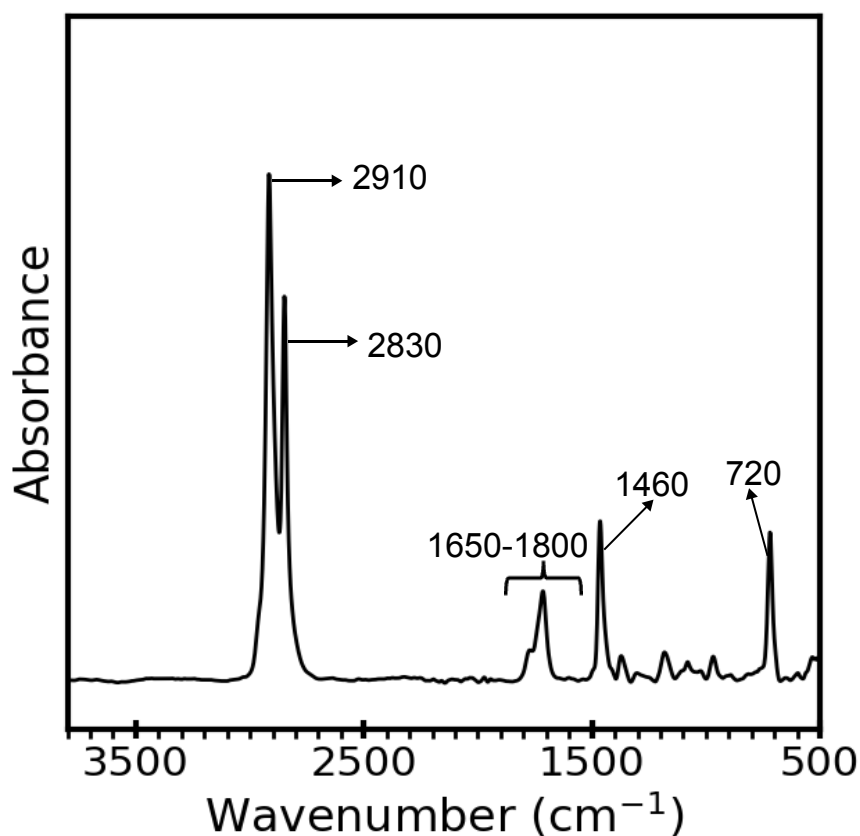


Figure S8: ATR-FTIR absorbance spectrum of oxidized HDPE. Assignments for each of these peaks is mentioned in Table S2.

MNPL collected from the first extrusion of HDPE

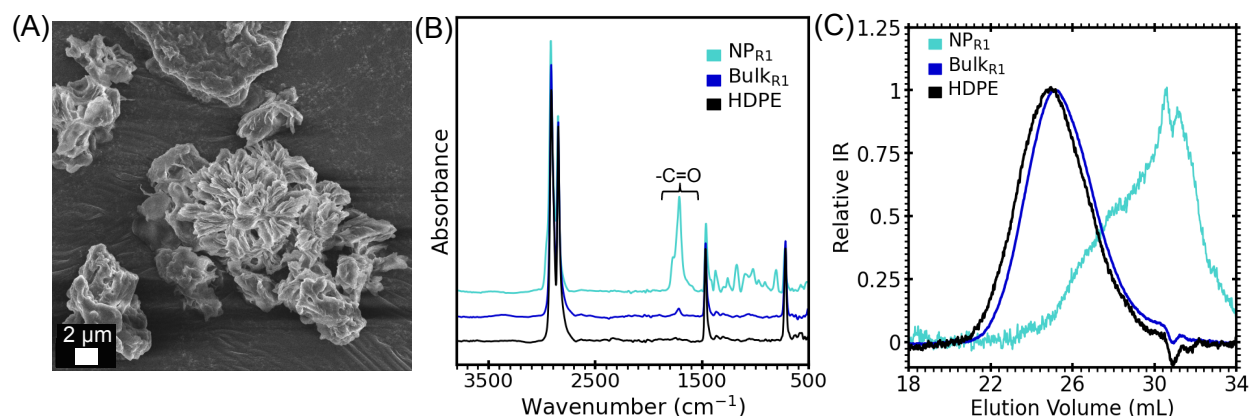


Figure S9: (A) SEM micrographs of MNPL collected after the first extrusion cycle of HDPE. (B) ATR-FTIR spectra of virgin HDPE (HDPE), bulk HDPE (Bulk_{R1}), and MNPL (NP_{R1}). Characteristic hydrocarbon HDPE peaks are observed in both bulk and MNPL samples, confirming that MNPL are primarily polyolefin-derived rather than additive leachates (3) (Table S2 and Figure S8). The band between 1600 cm⁻¹ to 1800 cm⁻¹ corresponds to carbonyl-containing functional groups, (4–7) indicating higher oxidative functionalization in MNPL relative to bulk material. (C) Molar mass distributions of virgin HDPE, bulk HDPE, and MNPL. A consistent negative peak at 30.9 mL is observed across all samples, suggesting the presence of an additive with lower IR absorption relative to the 1,2,4-trichlorobenzene (TCB)/Irganox HT-SEC solvent. This feature is more pronounced in MNPL, indicating enrichment of a certain additive fraction in the MNPL.

MNPL collected from the first extrusion of LLDPE

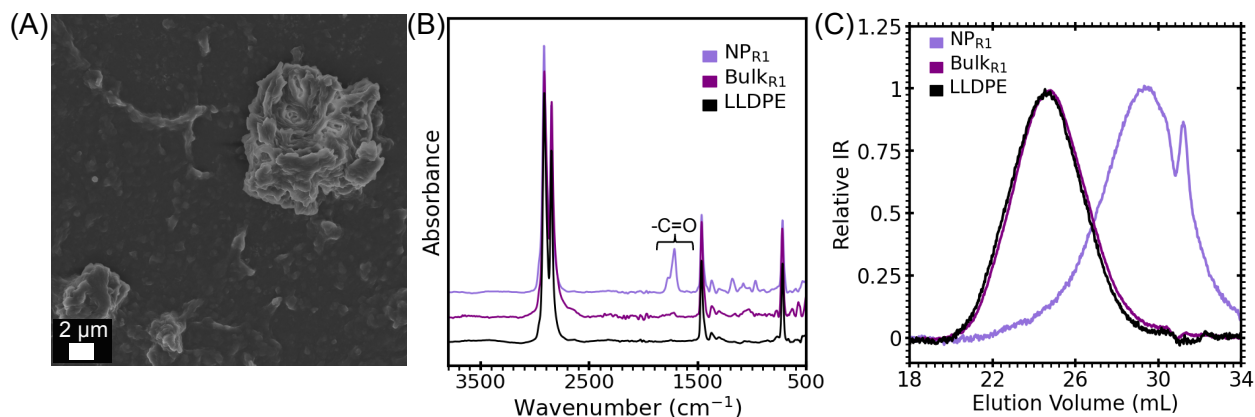


Figure S10: (A) SEM micrographs of MNPL collected after the first extrusion cycle of LLDPE. (B) ATR-FTIR spectra of virgin LLDPE (LLDPE), bulk LLDPE (Bulk_{R1}), and MNPL (NP_{R1}) collected after the first extrusion cycle. Characteristic hydrocarbon LLDPE peaks are observed in both bulk and MNPL samples, confirming that the MNPL are primarily polyolefin-derived rather than additive leachates (3) (Table S2 and Figure S8). The carbonyl band between 1600 cm⁻¹ to 1800 cm⁻¹ indicates greater oxidative functionalization in the MNPL than in the bulk material. (4–7) (C) Molar mass distributions of virgin LLDPE, Bulk_{R1}, and NP_{R1}. Similar to HDPE, a negative peak is observed at an elution volume of 30.9 mL in all samples, with greater intensity in the MNPL, suggesting enrichment of certain species responsible for this feature.

MNPL from additive free PP

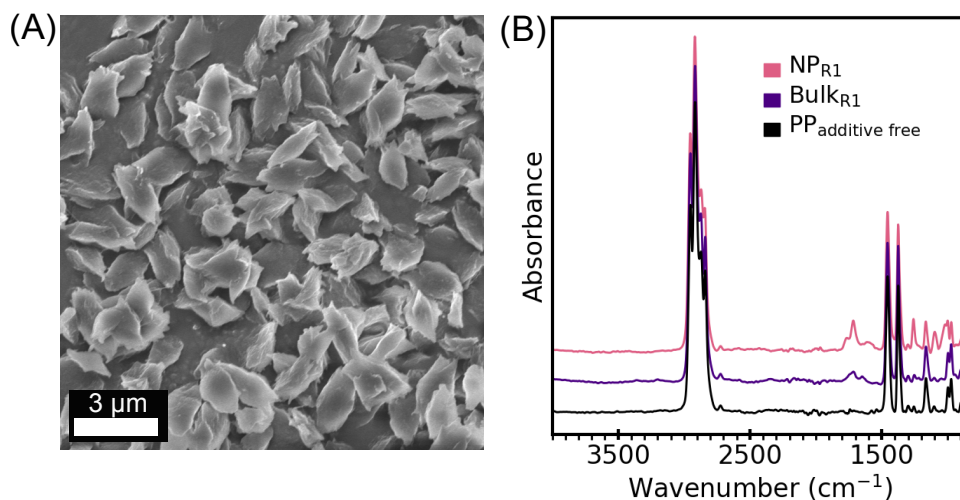


Figure S11: (A) SEM micrograph of MNPL collected from the first extrusion of additive-free PP. (B) ATR-FTIR absorbance spectra of virgin PP (labeled $\text{PP}_{\text{additive free}}$), bulk PP after the first extrusion (Bulk_{R1}), along with MNPL collected after the first extrusion (NP_{R1}).

MNPL collected from extrusion of PP - first and second extrusion

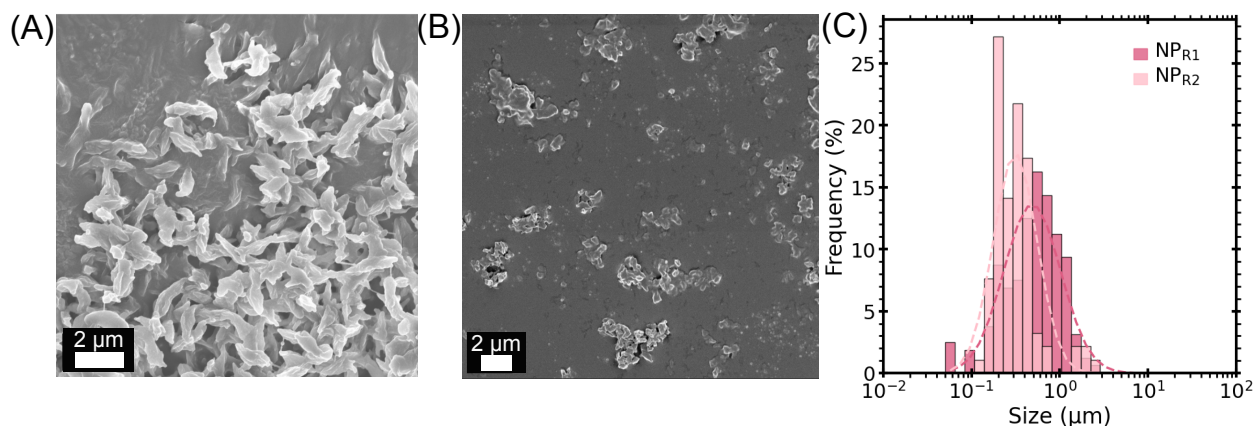


Figure S12: SEM images of the MNPL collected from the (A) first (NP_{R1}) and (B) second extrusion (NP_{R2}) of PP. (C) Size distribution histograms after ImageJ analysis of over 200 MNPL particles collected from over 20 samples. Note: The size reported is that of the longest particle dimension. The particle size distributions were fit to log-normal distributions, resulting in R^2 values of 0.843 and 0.843 for NP_{R1} and NP_{R2} , respectively.

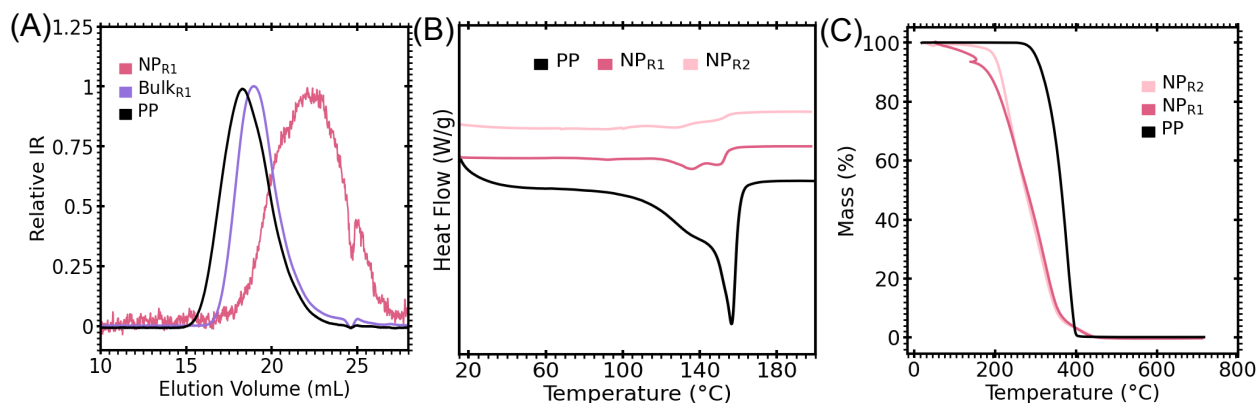


Figure S13: (A) Molar mass distributions of virgin PP (PP), bulk PP (Bulk_{R1}), and MNPL (NP_{R1}) collected after the first extrusion cycle. Similar to LLDPE and HDPE, a negative peak is observed at an elution volume of 24.7 mL in all PP samples, with greater intensity in the MNPL, suggesting enrichment of the species responsible for this feature. (B) DSC second heating curve of virgin PP with the MNPL collected from the first (NP_{R1}) and second extrusion (NP_{R2}) of PP. (C) TGA curves of virgin PP with MNPL collected from the first and second extrusion when heated at the rate of 20 °C/min, up to 700 °C in a nitrogen environment with a flow rate of 25 mL/min.

Dispersity of the bulk and MNPL collected

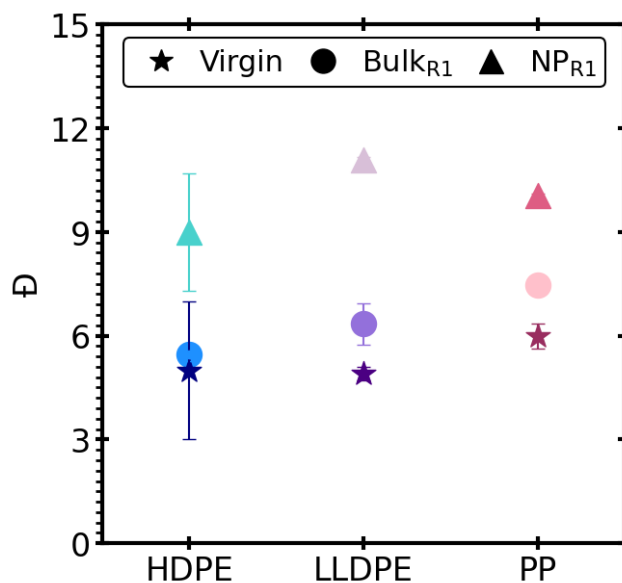


Figure S14: Dispersity of virgin, Bulk_{R1}, and NP_{R1} collected from the first extrusion of PP, LLDPE and HDPE. The error bar (some smaller than the symbols) are the standard deviations of three measurements.

Table S3: The molar mass distribution summary

Polymer	Sample	M_w (kDa)	$\bar{D}$
5*PP	Virgin	369 ± 1	5.9 ± 0.2
	Bulk _{R1}	152 ± 5	7.5 ± 0.1
	Bulk _{R2}	58.4 ± 0.6	6.5 ± 0.7
	NP _{R1}	23 ± 2	10.05 ± 0.05
	NP _{R2}	10 ± 2	7 ± 1
3*LLDPE	Virgin	100 ± 1	4.9 ± 0.2
	Bulk _{R1}	81 ± 5	6.3 ± 0.6
	NP _{R1}	9.7 ± 0.3	11.09 ± 0.08
3*HDPE	Virgin	70 ± 1	5 ± 2
	Bulk _{R1}	49 ± 2	5.5 ± 0.2
	NP _{R1}	6 ± 1	9 ± 2

Table S3: Molar mass summary of extruded polymers with the corresponding MNPL collected.

Surface cracking of the samples after quiescent oxidation.

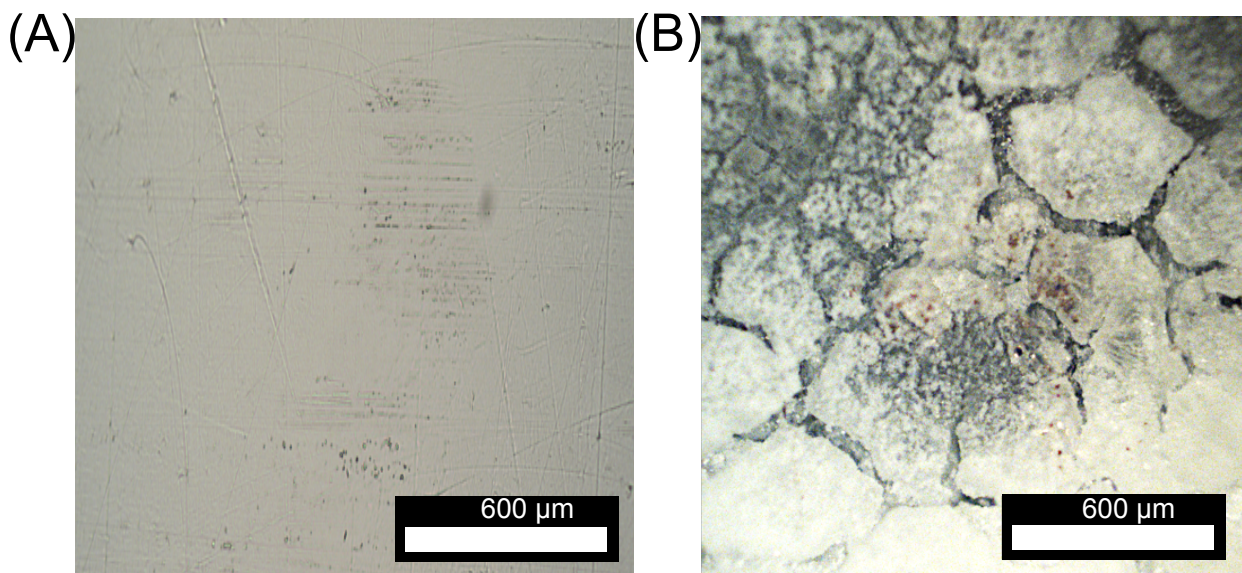


Figure S15: The optical microscope images of the surface of PP (A) unoxidized and (B) oxidized at 240 °C for 24 h. These images were obtained on an Amscope metallurgical microscope with long-range 10x and 50x objectives were used in transmission.

VOC and MNPL yield

Yield of the total MNPL and VOCs production was monitored via mass loss, using Equation S1.

- $mass_i$ = mass of the bulk oxidized polymer matrix after MNPL extraction.
- $mass_0$ = initial mass of the virgin polymer.

$$\text{Yield} = \frac{mass_i - mass_0}{mass_0} \times 100 \quad (\text{S1})$$

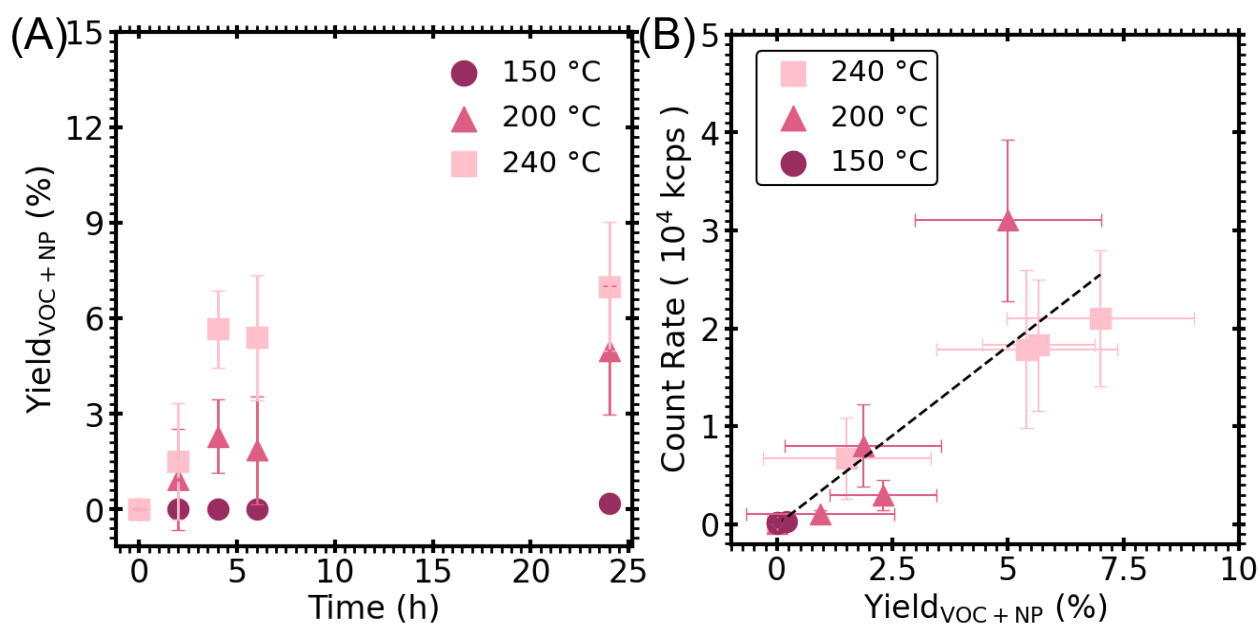


Figure S16: (A) Yield of VOC and MNPL produced during quiescent oxidation of PP at 150 °C, 200 °C and 240 °C for up to 24 h. (B) Count rate vs yield of VOC and MNPL. Regardless of the temperature or reaction time, the data points collapsed into a linear curve, $y = 3655x - 88.5$, $R^2 = 0.83$. The error bar (some smaller than the symbols) are the standard deviations of three measurements.

Size distribution of MNPL collected from PP oxidation at 150 °C

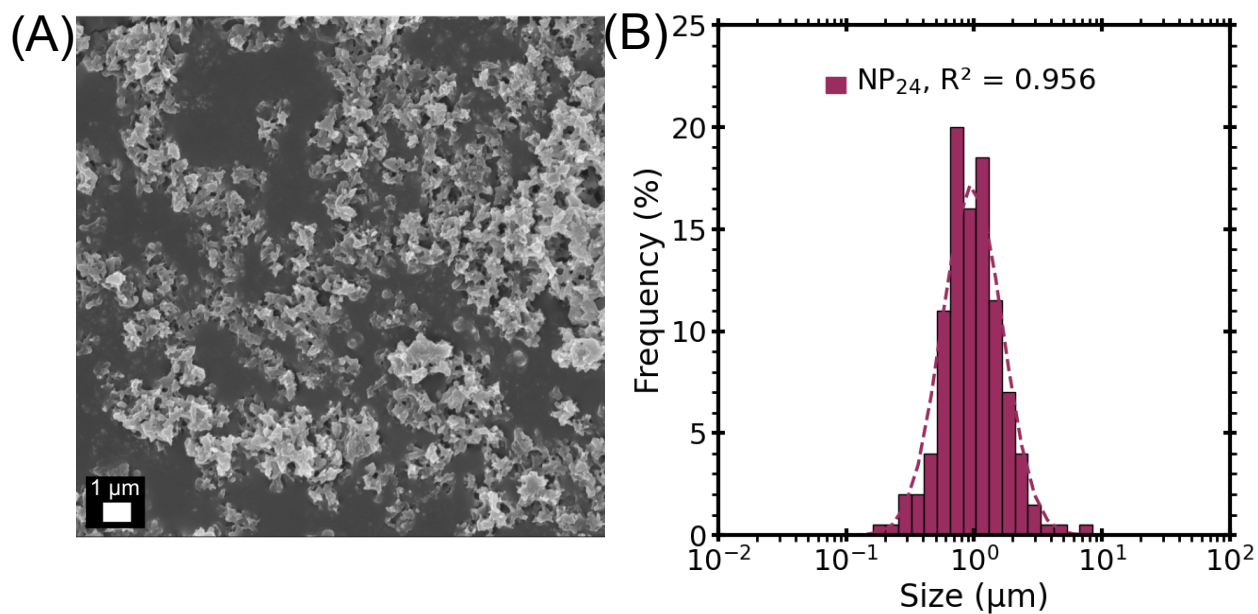


Figure S17: (A) SEM micrographs of the MNPL collected from the quiescent oxidation of PP at 150 °C for 24 h. (B) Histogram with size distribution after ImageJ analysis of over 200 MNPL particles collected from over 20 samples. Note: the largest size dimension is reported. The histogram was fit to a log-normal distribution with R^2 as reported in the figure label.

Size distribution of MNPL collected from PP oxidized at 200 °C up to 24 h

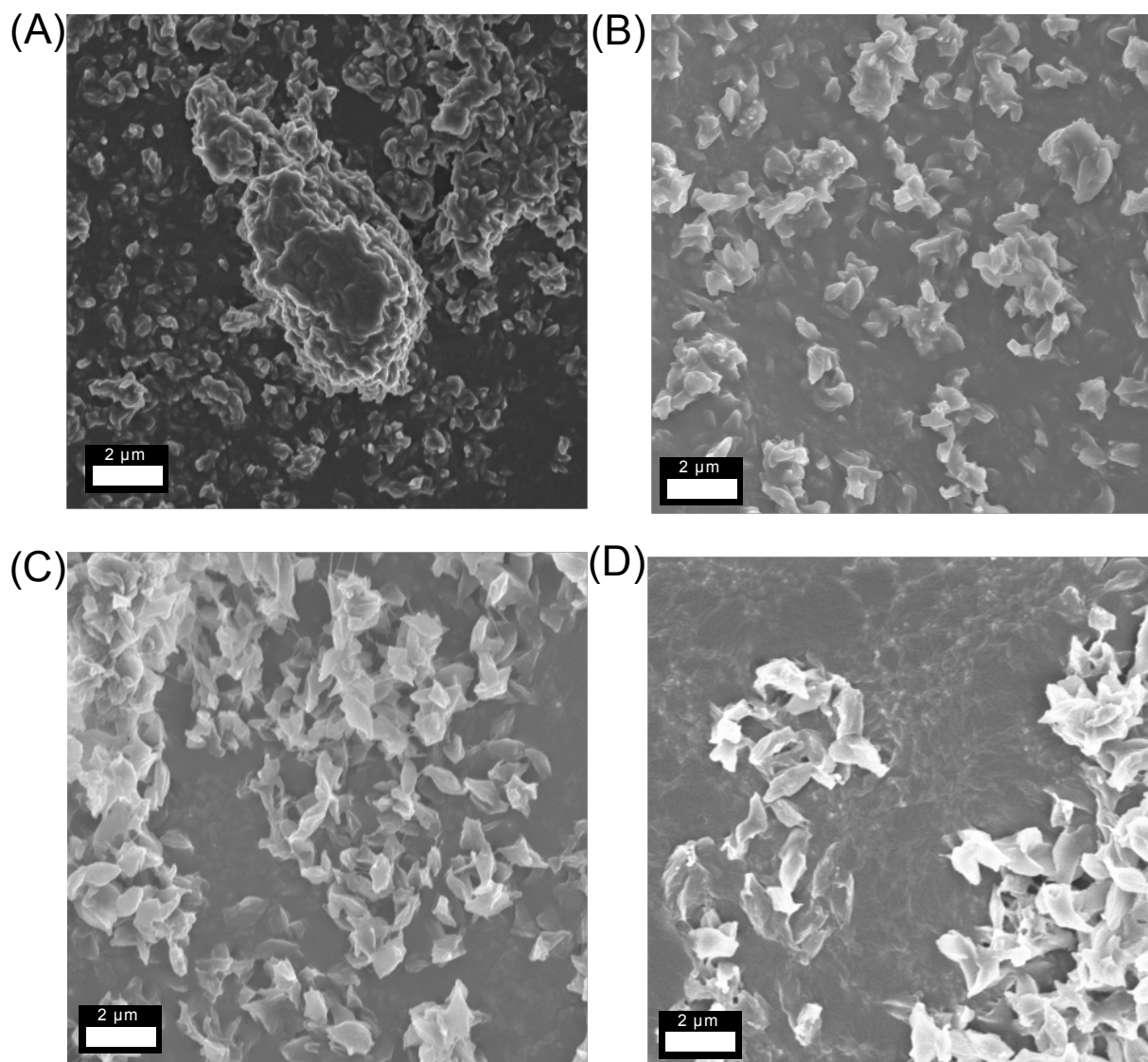


Figure S18: SEM micrographs of MNPL collected from the quiescent oxidation of PP at 200 °C at (A) 2 h (B) 4 h (C) 6 h (D) 24 h.

Size distribution histograms of MNPL collected from PP oxidized at 200 °C up to 24 h

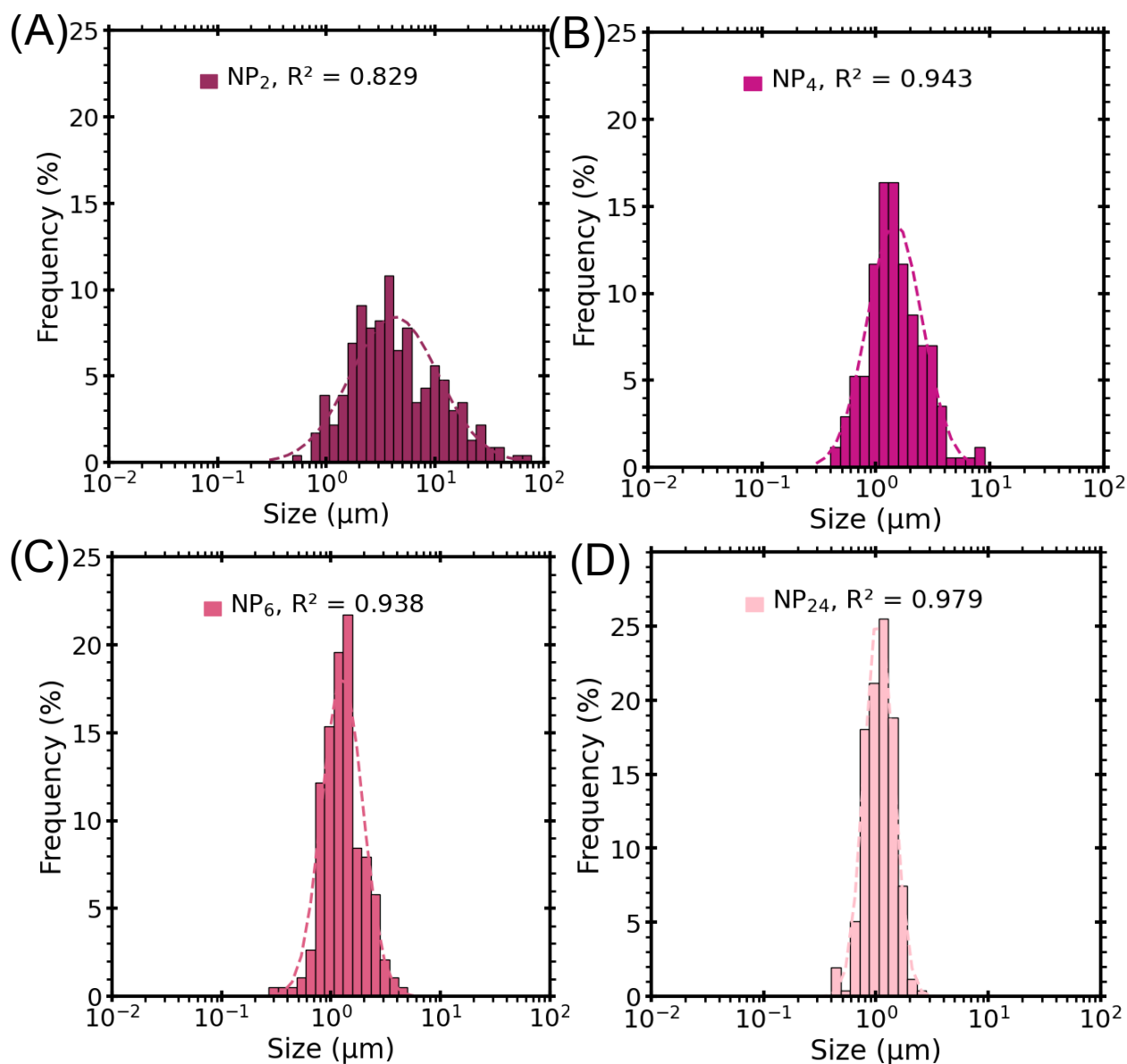


Figure S19: Histograms of the MNPL collected from the quiescent oxidation of PP at 200 °C for (A) 2 h (B) 4 h (C) 6 h (D) 24 h. These size distribution histograms are obtained after ImageJ analysis of over 200 MNPL particles collected from over 20 samples. Note: The size reported is that of the longest particle dimension. The particle size distributions were fit to log-normal distributions and the resulting R^2 values are reported in the figure labels.

Size distribution of MNPL collected from PP oxidation at 240 °C up to 24 h

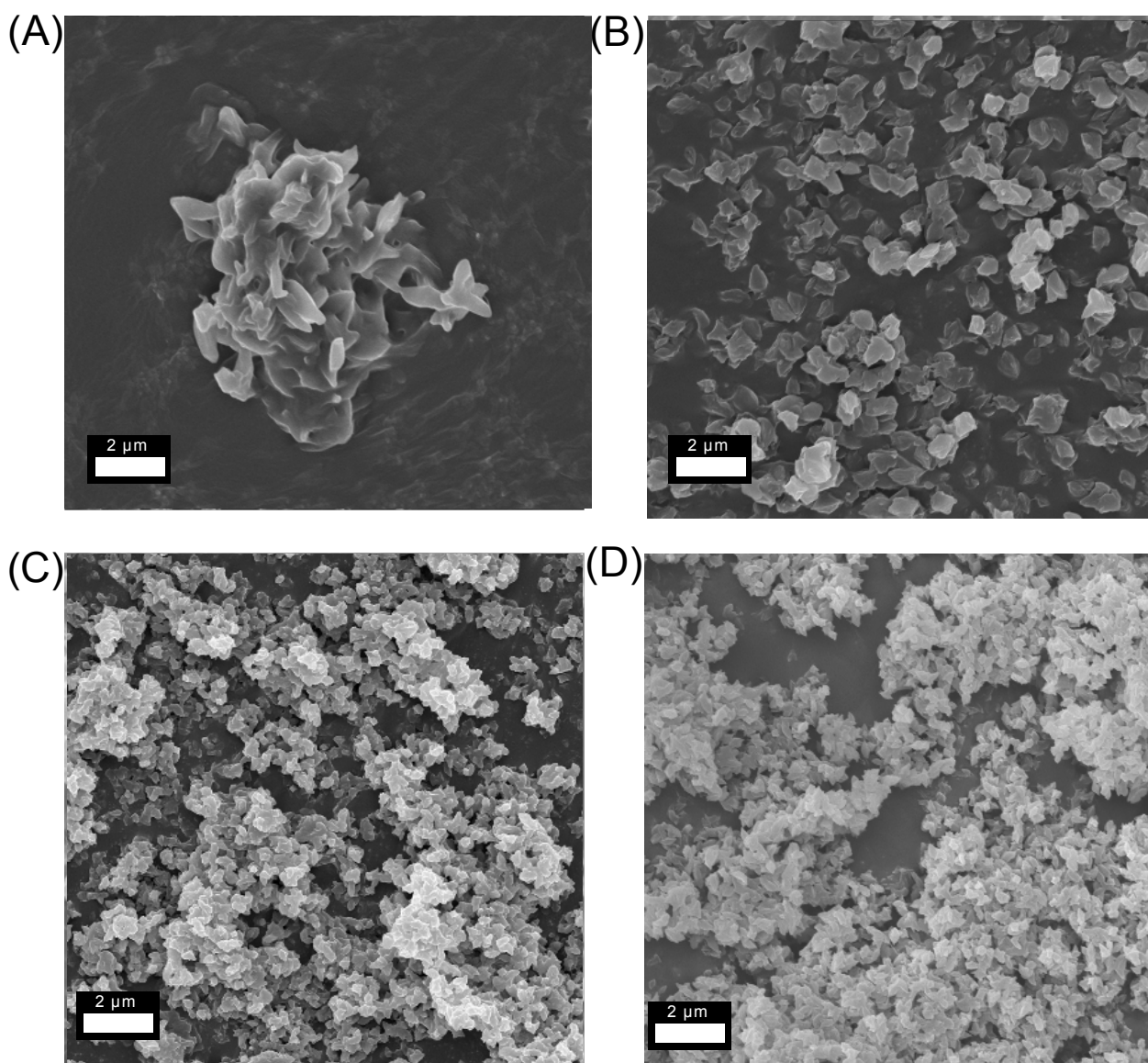


Figure S20: SEM micrographs of the MNPL particles collected from the quiescent oxidation of PP at 240 °C for (A) 2 h (B) 4 h (C) 6 h (D) 24 h.

Size distribution histograms of MNPL collected from PP oxidized at 240 °C up to 24 h

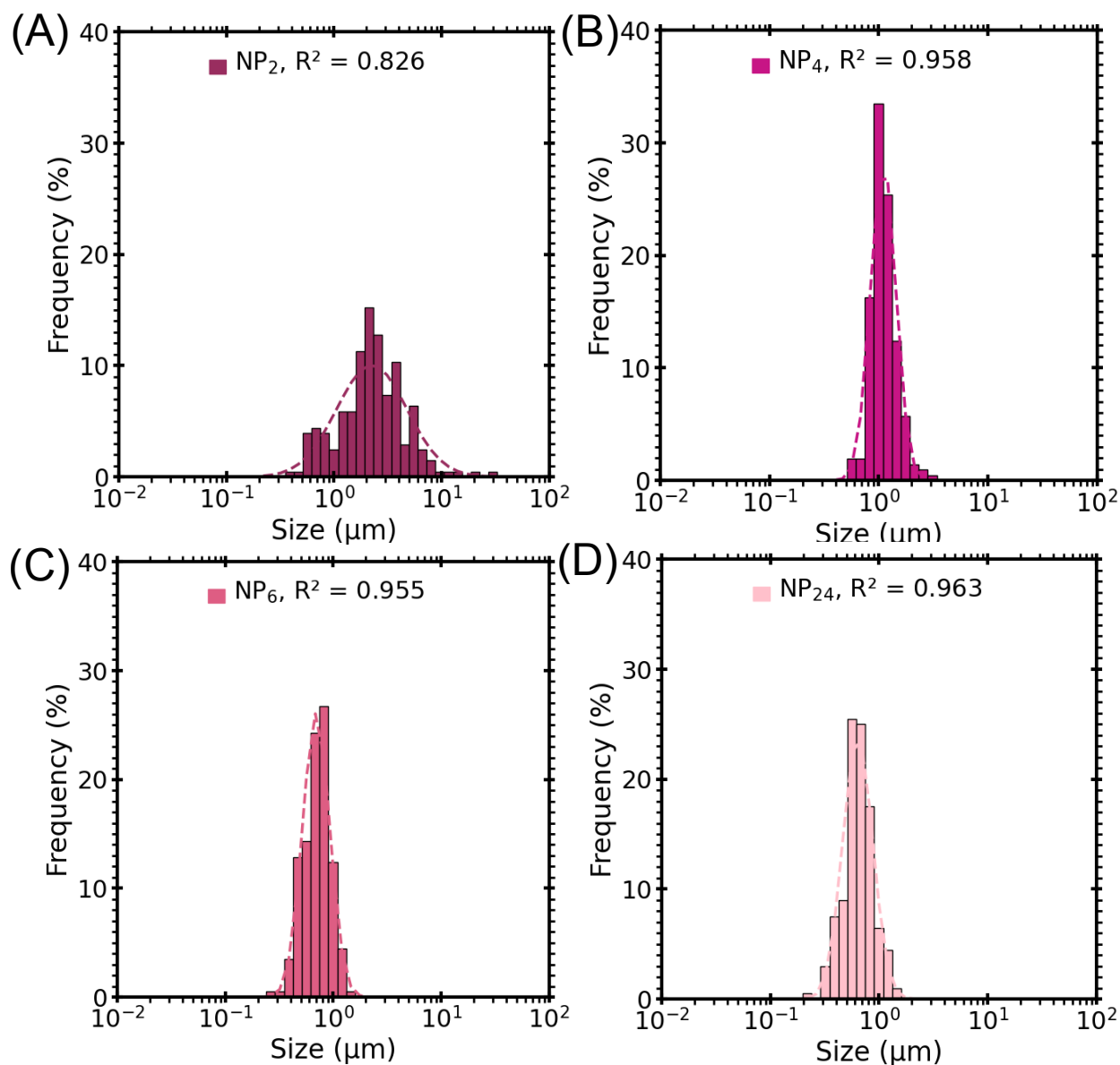


Figure S21: Histograms of the MNPL collected from the quiescent oxidation of PP at 240 °C for (A) 2 h (B) 4 h (C) 6 h (D) 24 h. These size distribution histograms are obtained after ImageJ analysis of over 200 MNPL particles collected from over 20 samples. Note: The size reported is that of the longest particle dimension. Each histogram was fit to a log-normal distribution with R^2 as reported in the figure labels.

Size distribution analysis

The mean and the 25th and 75th percentile values of each size distribution were calculated using Equations S2–S5.

$$f_X(x) = \frac{1}{x \sigma \sqrt{2\pi}} \exp \left[-\frac{(\ln x - \mu)^2}{2\sigma^2} \right], \quad x > 0 \quad (\text{S2})$$

$$\text{Mean}(X) = e^{\mu + \frac{\sigma^2}{2}} \quad (\text{S3})$$

$$X_{25} = e^{\mu + \sigma \Phi^{-1}(0.25)} = e^{\mu - 0.6745 \sigma} \quad (\text{S4})$$

$$X_{75} = e^{\mu + \sigma \Phi^{-1}(0.75)} = e^{\mu + 0.6745 \sigma} \quad (\text{S5})$$

$$IQR = X_{75} - X_{25} \quad (\text{S6})$$

where X is the particle size (the largest dimension), x is a specific value of X , $f_X(x)$ is the probability density function of X , μ and σ are the mean and standard deviation of $\ln(X)$, X_{25} and X_{75} are the 25th and 75th percentiles of X , IQR is the inter-quartile range, and $\Phi^{-1}(p)$ is the inverse cumulative distribution function of the standard normal distribution.

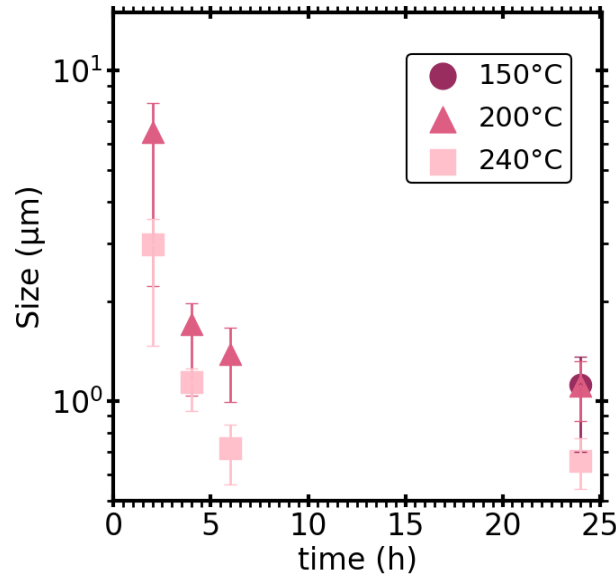


Figure S22: Size distribution of MNPL collected from the quiescent oxidation of polypropylene (PP) at 150 °C, 200 °C, and 240 °C for up to 24 h. The plots show the mean particle size, with the upper and lower error bars representing the 75th and 25th percentile sizes, respectively, obtained from log-normal distribution histograms using Equations S3 to S6.

ATR-FTIR spectra of MNPL recovered from quiescent oxidation of PP

The carbonyl and vinyl index is calculated based on the works complied by Gomes et al.(8). To capture the complexity of the different oxidative products formed, the index is calculated using the area integration methodology. The most common integration limits reported for calculating carbonyl index (CI) is from 1650 cm^{-1} to 1850 cm^{-1} . To account both for carbonyl and vinyl growth, the lower bound was extended to 1500 cm^{-1} , consistent with our previous work (4).

The carbonyl and vinyl index is calculated using equation S7.

- CVI = Carbonyl and Vinyl Index.
- $A_{1500\text{ cm}^{-1} \text{ to } 1850\text{ cm}^{-1}}$ = Area under the convoluted peak between 1500 cm^{-1} to 1850 cm^{-1} . The integration limits were kept constant across all samples.
- $A_{973\text{ cm}^{-1}, PP}$ = Area under the deconvoluted peak at 973 cm^{-1} in PP. The deconvolution was performed by fitting the peak between 950 cm^{-1} to 1020 cm^{-1} to two Gaussian curves.

$$\text{CVI} = \frac{A_{1500\text{ cm}^{-1} \text{ to } 1850\text{ cm}^{-1}}}{A_{973\text{ cm}^{-1}}} \quad (\text{S7})$$

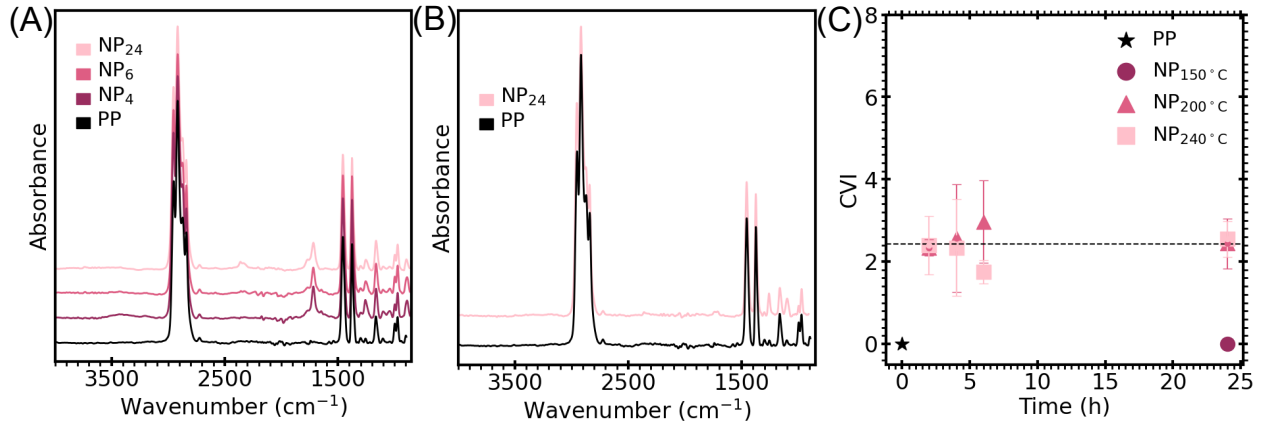


Figure S23: ATR-FTIR absorbance spectra of virgin PP along with MNPL collected from the quiescent oxidation of PP at (A) $240\text{ }^{\circ}\text{C}$ and (B) $150\text{ }^{\circ}\text{C}$ for reaction times up to 24 h. (C) CVI is calculated using Equation S7 for the MNPL collected. The error bar (some smaller than the symbols) are the standard deviations of three measurements.

Table S4: NMR limits

Functional group	Chemical Shift (ppm)	n_i^*
Aldehyde	9.59 to 9.74	1
Internal alkene	4.93 to 5.02	1
Terminal vinylidene (TVD)	4.50 to 4.78	1
Ketone	2.10 to 2.20	3
CH ₃ , CH ₂	0.90 to 1.03	4
CH ₂	1.29 to 1.39	1
CH	1.60 to 1.73	1

Table S4: Functional groups identified with ^1H NMR. (*) Number of protons per polymer repeat unit associated with the NMR peak used in quantification of this functional group.

^1H NMR spectrum of virgin PP

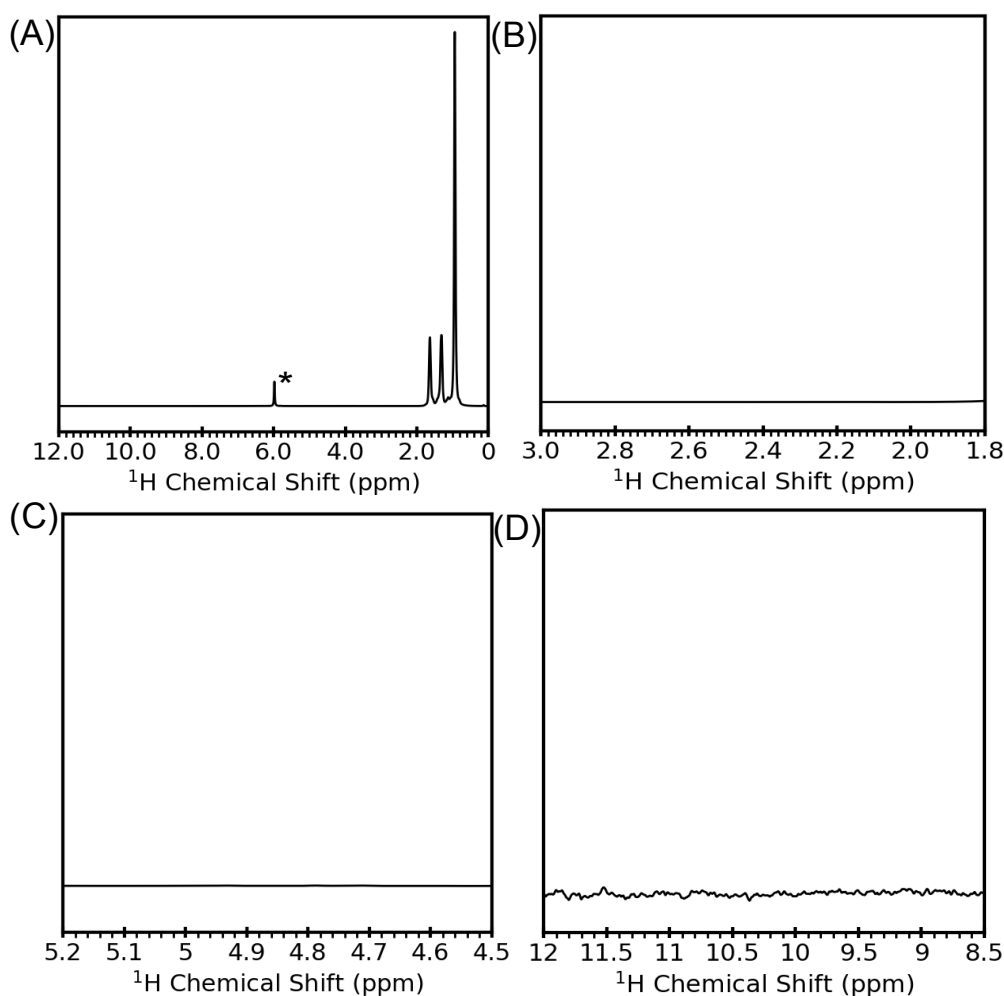


Figure S24: ^1H NMR spectrum of virgin PP. (A) Complete NMR spectrum. (B) Zoom in spectrum from 1.8 ppm to 2.8 ppm. (C) Zoom in spectrum from 4.5 ppm to 5.2 ppm (D) Zoom in spectrum from 8.5 ppm to 12.0 ppm. The peak at 6 ppm (*) is the solvent (TCE- d_2) peak.

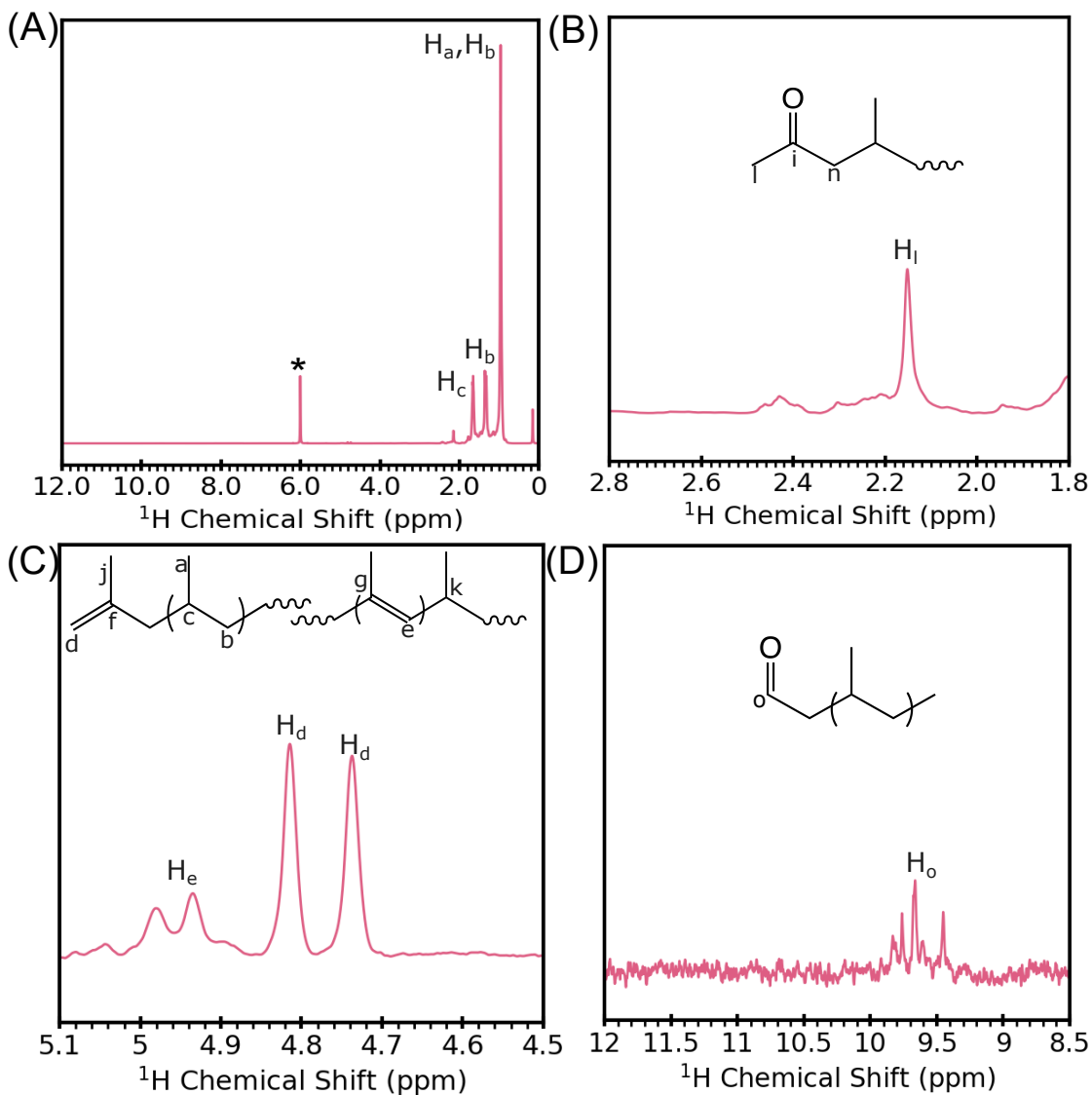
¹H NMR spectrum of MNPL collected from quiescent oxidation

Figure S25: ^1H NMR spectrum of MNPL collected from quiescent oxidation of PP at 200 °C for 24 h. (A) Complete NMR spectrum. (B) Zoom in spectrum from 1.8 ppm to 2.8 ppm with the peak assignment for methyl ketones. (C) Zoom in spectrum from 4.5 ppm to 5.2 ppm with the peak assignment for the internal alkenes and TVD. (D) Zoom in spectrum from 8.5 ppm to 12.0 ppm with the peak assignment for the aldehyde. Assignments are based on our past work, and the work of several other authors (4, 9–11). The peak at 6 ppm (*) is the solvent (TCE-d_2) peak.

Functionalization quantification

The number of terminal vinylidene, ketone, and aldehyde groups per chain were quantified using the following Equations S8, Equations S9, and Equations S10 respectively, based on our past work (4). The total number of carbonyl groups per chain were calculated using Equation S11.

$$\frac{f_{\text{TVD}}}{\text{chain}} = \frac{A_{4.50 \text{ to } 4.78 \text{ ppm}}/1}{A_{0.9 \text{ to } 1.6 \text{ ppm}}/6} \cdot \frac{M_{n,i}}{M_M} \quad (\text{S8})$$

$$\frac{f_K}{\text{chain}} = \frac{A_{2.10 \text{ to } 2.20 \text{ ppm}}/3}{A_{0.9 \text{ to } 1.6 \text{ ppm}}/6} \cdot \frac{M_{n,i}}{M_M} \quad (\text{S9})$$

$$\frac{f_A}{\text{chain}} = \frac{A_{9.59 \text{ to } 9.74 \text{ ppm}}/1}{A_{0.9 \text{ to } 1.6 \text{ ppm}}/6} \cdot \frac{M_{n,i}}{M_M} \quad (\text{S10})$$

$$\frac{f_C}{\text{chain}} = \frac{f_K}{\text{chain}} + \frac{f_A}{\text{chain}} \quad (\text{S11})$$

where $A_{4.50 \text{ to } 4.78 \text{ ppm}}$, $A_{2.10 \text{ to } 2.20 \text{ ppm}}$, and $A_{9.59 \text{ to } 9.74 \text{ ppm}}$ are the integrated areas corresponding to the terminal vinylidene peak at 4.74 ppm, the $\alpha\text{-CH}_3$ ketone peak at 2.15 ppm, and the aldehyde peaks between 9.59 ppm and 9.74 ppm, respectively. $A_{0.9 \text{ to } 1.6 \text{ ppm}}$ is the combined integrated area of the polypropylene backbone peaks at 0.9 ppm, 1.3 ppm, and 1.6 ppm. The factors of 1, 3, and 6 account for the number of protons contributing to the respective peaks. $M_{n,i}$ is the number-average molar mass of the sample, M_M is the molar mass of a polypropylene repeat unit (42.08 g/mol), and $M_{n,i}/M_M$ corresponds to the degree of polymerization.

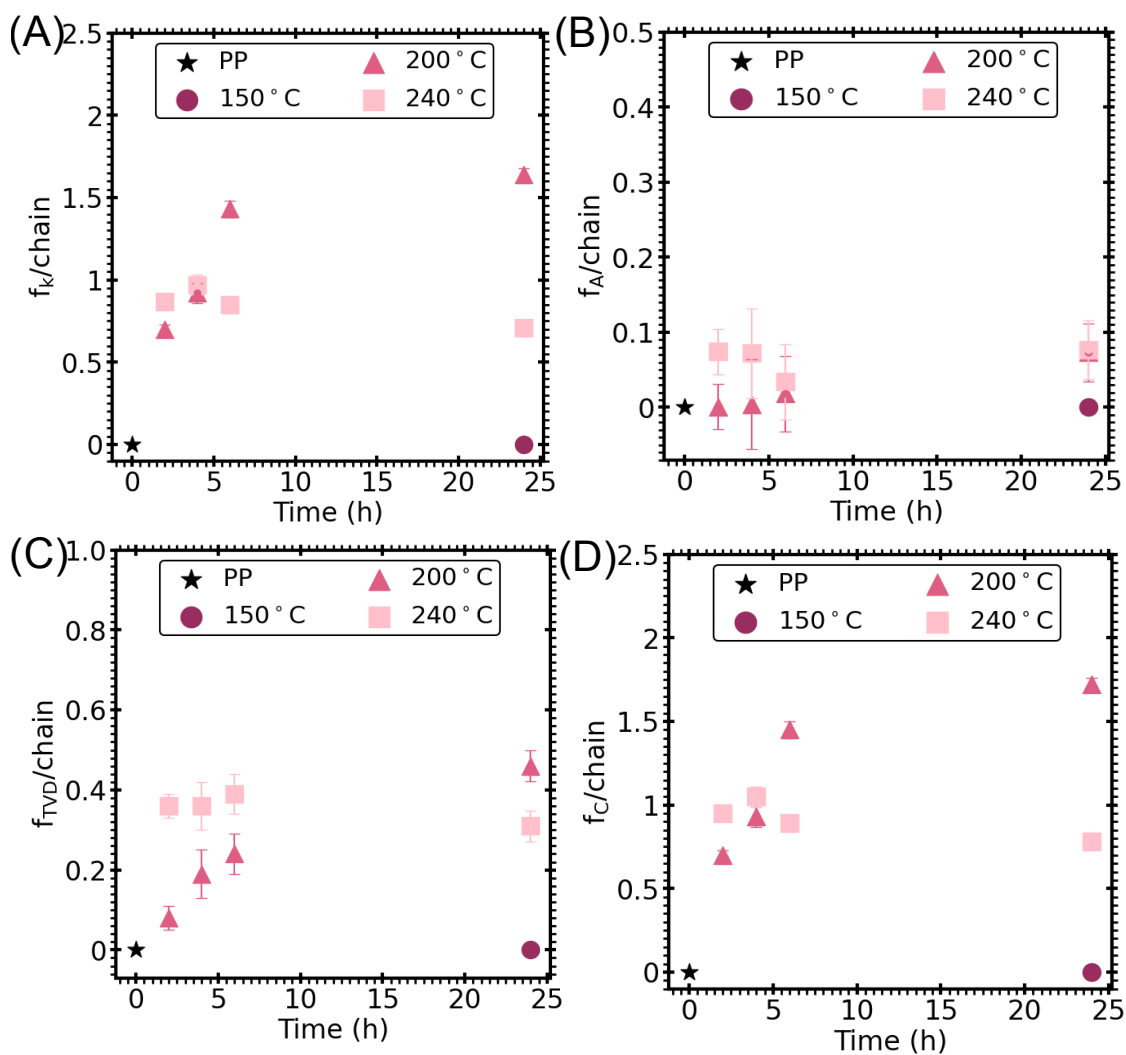


Figure S26: Functional groups per chain present in the MNPL collected from the quiescent oxidation of PP at 150 °C, 200 °C, and 240 °C with respect to reaction time up to 24 h. (A) f_K/chain (B) f_A/chain . (C) $f_{TV D}/\text{chain}$. (D) Total carbonyl chain-end functional groups per chain ($f_C = (f_K + f_A)/\text{chain}$). f_C reaches a value of ≈ 2 by 24 h, implying that both the chain-ends are functionalized with carbonyl groups. Error bars (some smaller than the symbols) are the standard deviation of at least 3 sample measurements.

Molar mass distribution of the bulk and MNPL collected from quiescent oxidation of PP

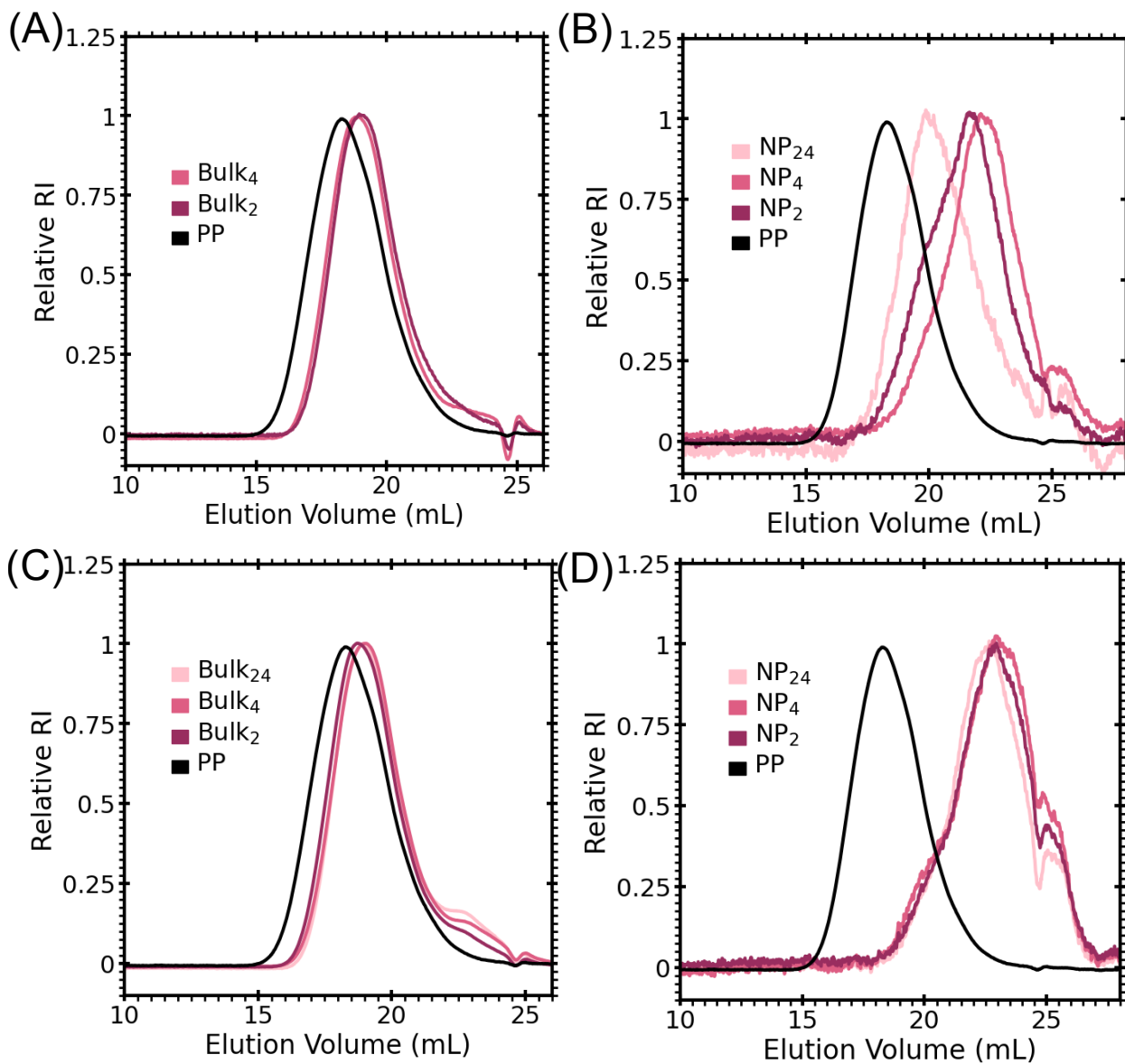


Figure S27: HT-SEC curves of the virgin, bulk and MNPL collected from the quiescent oxidation of PP up to 24 h at (A, B) 200 °C and (C, D) 240 °C. Similar to the extruded MNPL samples, a negative peak is observed at an elution volume of 24.7 mL in all samples, with greater intensity in the MNPL, suggesting enrichment of the species responsible for this feature.

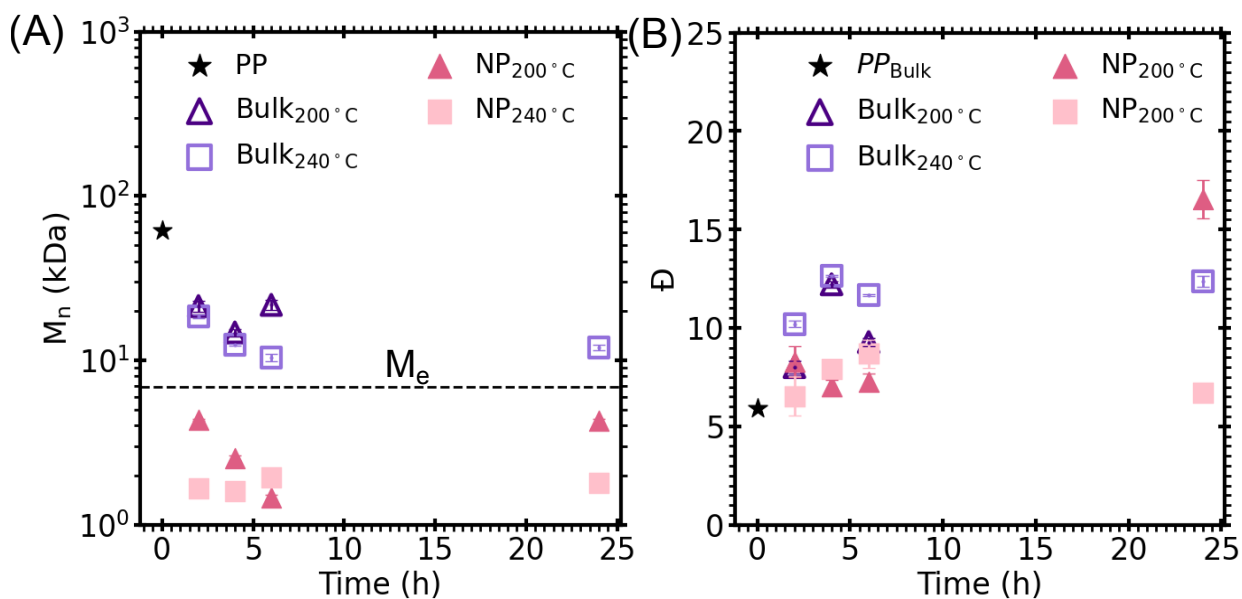


Figure S28: (A) The number average molar mass (M_n) and (B) $\bar{D}$ for MNPL and their corresponding bulk samples collected from the quiescent oxidation of PP at 200 °C, and 240 °C up to 24 h. The dotted curve at M_e represents the entanglement molar mass of PP. The peak boundary for the analysis was set at an elution volume of no more than 26.6 mL, which corresponded to the elution volume of the lowest molar mass polystyrene standard (266 g/mol). The error bar (some smaller than the symbols) are the standard deviations of three measurements.

WAXS peak assignment

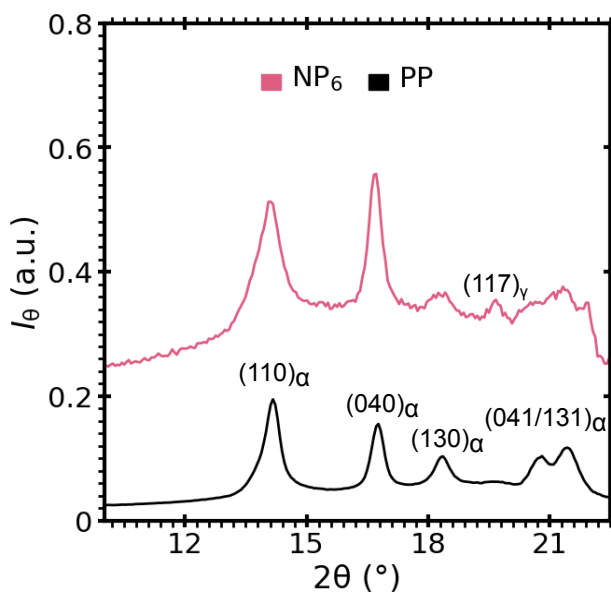


Figure S29: WAXS peak assignment for virgin PP and MNPL recovered from the quiescent oxidation of PP.

SAXS and WAXS of MNPL collected from quiescent oxidation of PP

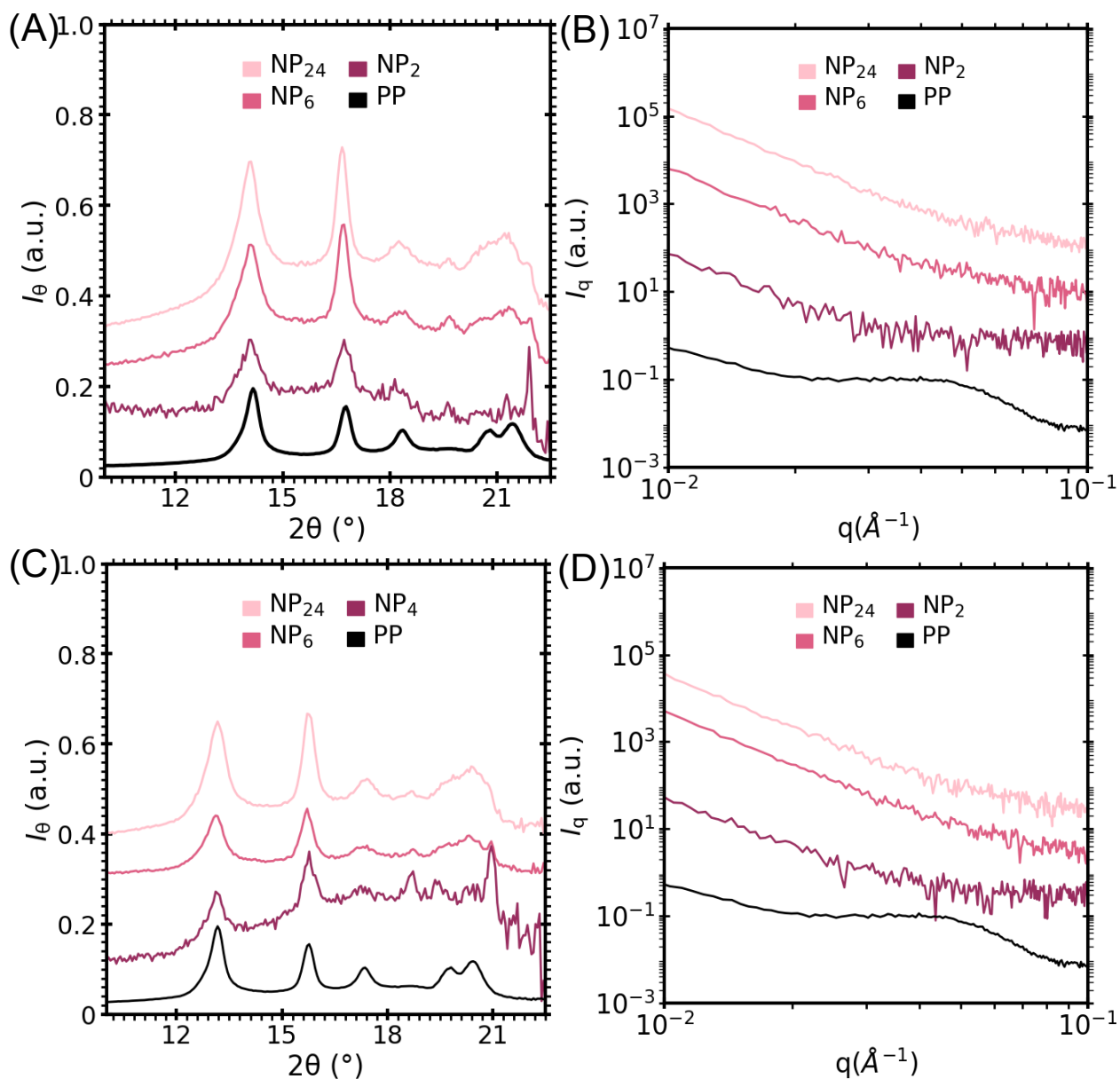


Figure S30: (A) WAXS and (B) SAXS scattering curves of virgin PP with MNPL collected from the quiescent oxidation of PP up to 24 h at 200 °C. (C) WAXS and (D) SAXS scattering curves for MNPL collected from quiescent oxidation of PP up to 24 h at 240 °C.

Crystallinity and melting point of MNPL collected from quiescent oxidation of PP

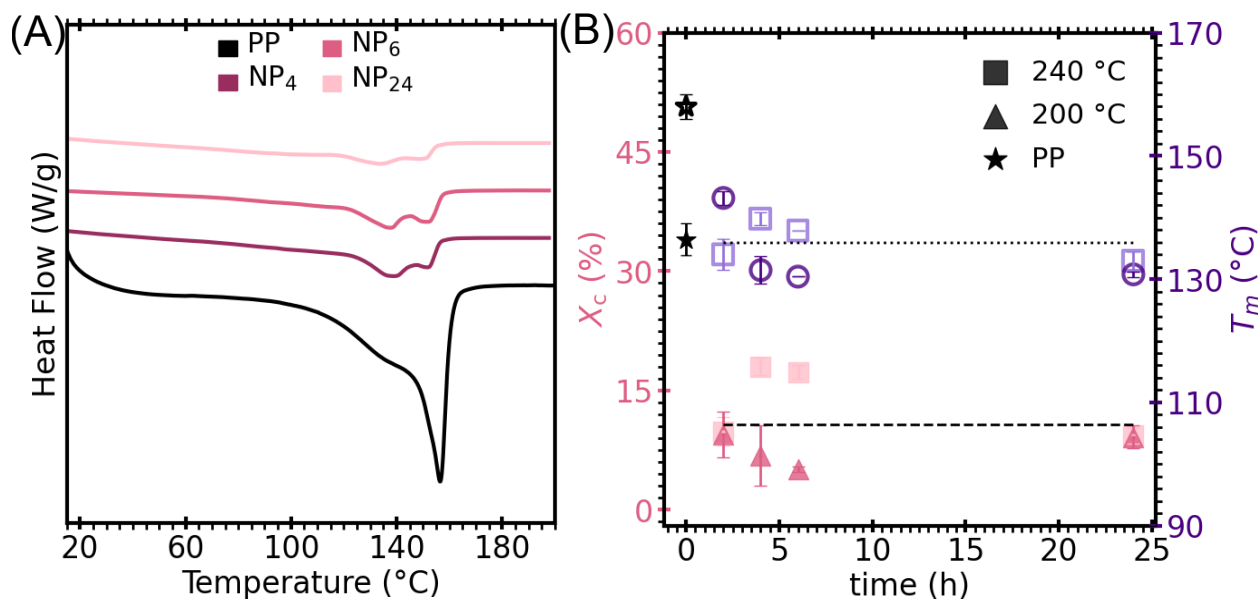


Figure S31: (A) DSC second heating scans conducted under nitrogen at a 10 °C/min ramp rate for virgin PP and MNPL collected from quiescent oxidation of PP at 240 °C up to 24 h. (B) Crystallinity and melting temperature calculated for the MNPL collected from quiescent oxidation of PP at 200 °C and 240 °C up to 24 h. The error bar (some smaller than the symbols) are the standard deviations of three measurements.

TGA curves of MNPL collected from quiescent oxidation of PP

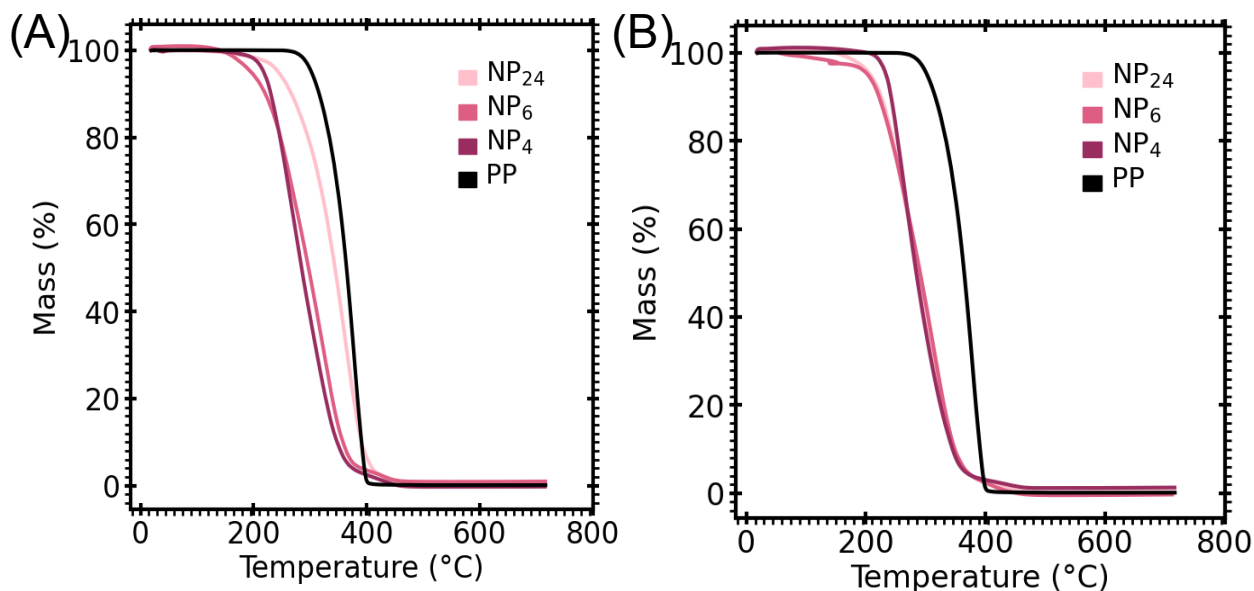


Figure S32: TGA curves of virgin PP with MNPL collected from the quiescent oxidation of PP for reaction times up to 24 h at (A) 200 °C and (B) 240 °C. The measurement is performed by ramping the temperature to 700 °C at the rate of 20 °C/min in a nitrogen environment with a flow rate of 25 mL/min.

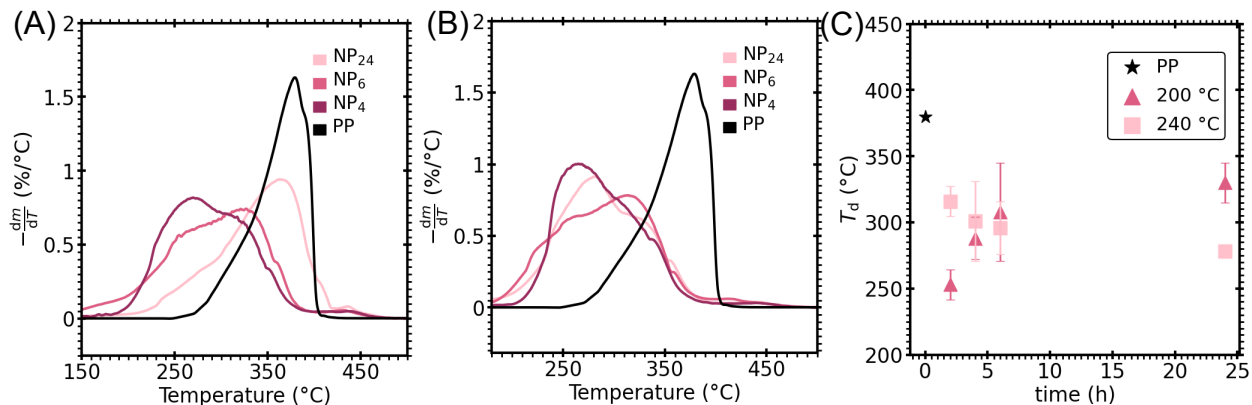


Figure S33: Derivative Thermogravimetric Analysis (DTA) curves of virgin PP along with MNPL collected from PP quiescent oxidation at (A) 200 °C and (B) 240 °C. (C) The degradation temperature (T_d) defined as the peak of the DTA curves for the MNPL collected at different temperatures up to 24 h in comparison to that of virgin PP. The error bar (some smaller than the symbols) are the standard deviations of three measurements.

Polystyrene

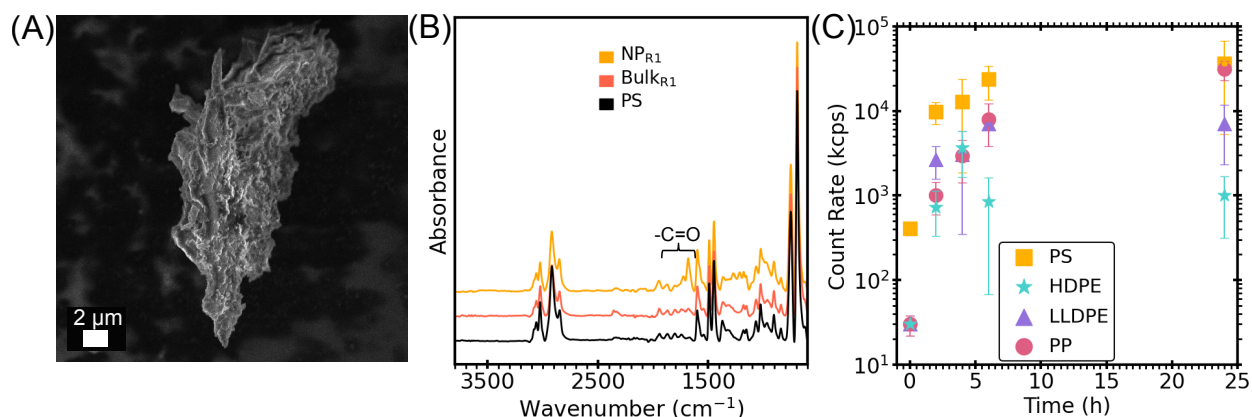


Figure S34: (A) SEM micrograph of polystyrene (PS) MNPL collected after the first extrusion. (B) The ATR-FTIR spectra of the virgin PS with bulk and MNPL collected after the first extrusion. (C) Light scattering on the supernatant water collected after quiescent oxidation of PS at 200 °C up to 24 h in comparison to that of semicrystalline polyolefins. The error bar (some smaller than the symbols) are the standard deviations of three measurements.

MNPL generation from polar polymers

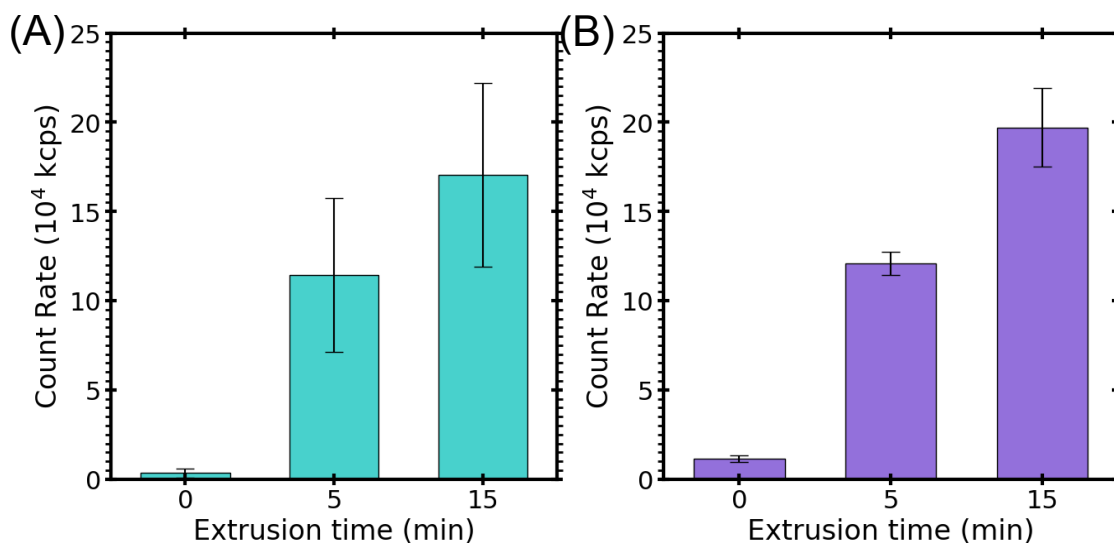


Figure S35: Light scattering count rates of water contacted with (A) Nylon-6 and (B) bisphenol-A-polycarbonate in the virgin state and after the 5 min and 15 min extrusion. These experiments were conducted on a Litesizer 500 DLS (Anton Paar) with a scattering angle of 15° . Note this experiment was performed on a different instrument and scattering angle than the rest of the work and hence the absolute count rates should not be compared. These results qualitatively demonstrate that just like the non-polar semicrystalline and amorphous polymers, extruded polar polymers also released MNPL. Error bars are based on the standard deviations of three independent measurements.

MD simulations schematic

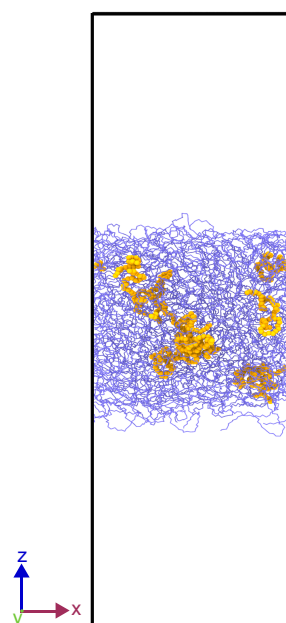


Figure S36: Schematic of the simulated systems. Periodic boundary conditions are applied in all three directions with the simulation box extended along the z-axis to create a polymer film surrounded by vacuum. This is an example simulation for PE/PE_o 100/25 chains with a mass fraction of 5 % PE_o at 500 K.

Mixtures of short and long unfunctionalized PE chains

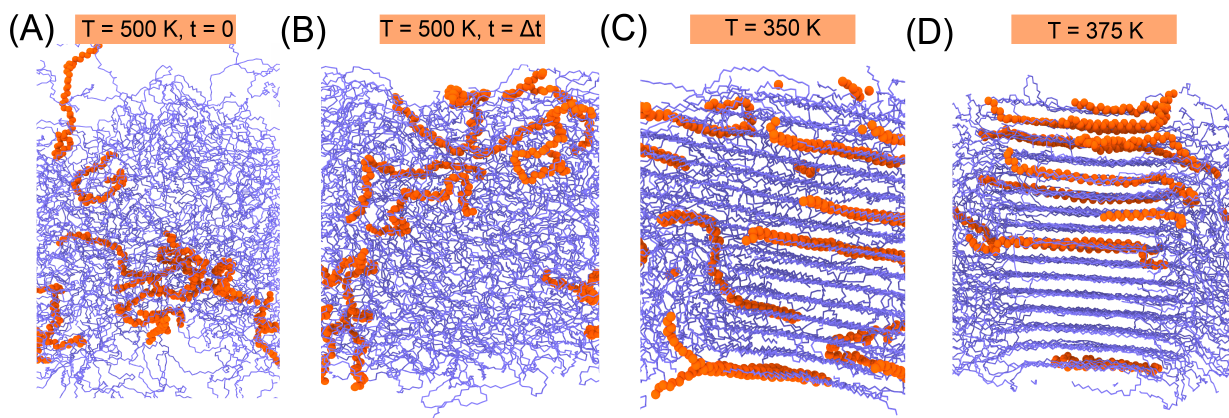


Figure S37: PE ($n = 100$) melt mixed with short PE chains ($n = 25$) at $w = 5\%$ (A) initial melt-mixed system at a temperature $T = 500\text{ K}$ (time, $t = 0$), (B) still at $T = 500\text{ K}$ but after equilibration and crystallized at (C) 350 K and (D) 375 K . Unlike oxidized chains of the same chain length, at 500 K , these migrate to the surface due to entropic effects. On crystallization, they co-crystallize with the bulk at both 350 K and 375 K .

Density profiles of blends with short and long unfunctionalized chains

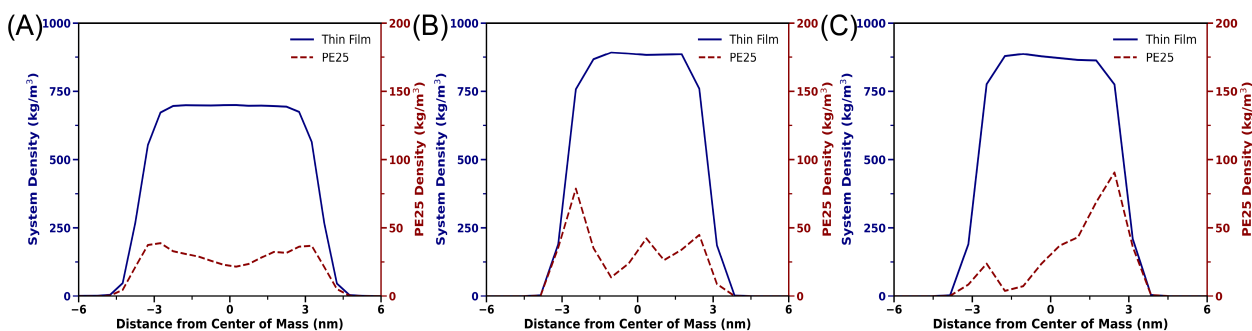


Figure S38: Mass density profiles of the thin film matrix and unfunctionalized short PE chains as a function of distance from the film center ($Z - Z_{\text{COM}}$). Data is shown for a PE ($n = 100$) melt mixed with short PE chains ($n = 25$) at $w = 5\%$ at (A) 500 K and then crystallized at (B) 350 K and (C) 375 K .

Short PE_o chains volatilize

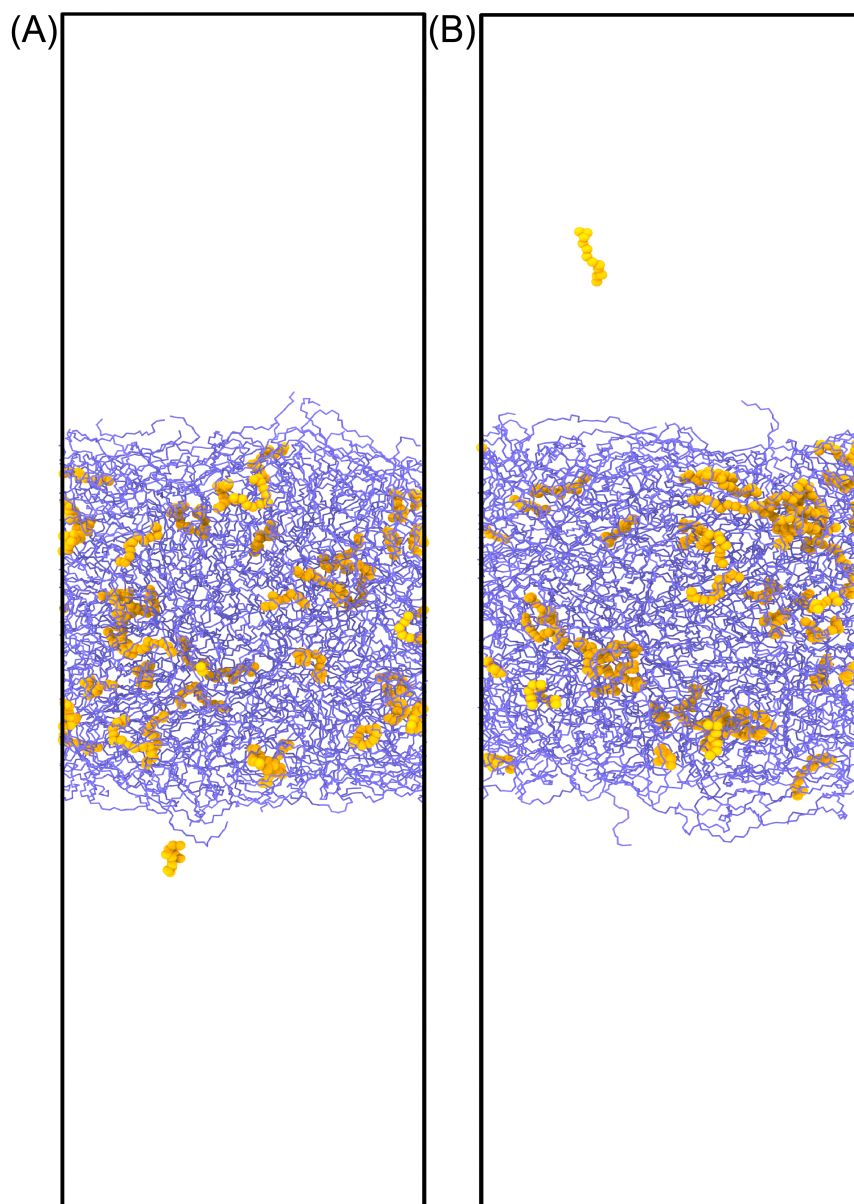


Figure S39: Simulation of PE/ PE_o 100/5 chains with a mass fraction of 5 % PE_o at 500 K. This demonstrates that chains of length $n = 5$ are miscible with the long, unfunctionalized chains but they are prone to leave the bulk and volatilize. (A) and (B) are snapshots of two simulation runs.

Trajectory analysis and structural characterization

To quantitatively evaluate the migration dynamics and the structural evolution of the polymer blends during the cooling phases, post-processing of the simulation trajectories was conducted. The coordinate trajectories generated via GROMACS were parsed and analyzed utilizing custom Python routines built upon the MD Analysis library.

To track the macroscopic phase separation and the selective migration of the oxidized fragments to the polymer-air interface, we calculated the absolute difference in the center of mass (COM) along the z-axis (the axis normal to the film interface). This spatial divergence over time, $\Delta Z(t)$, is defined as:

$$\Delta Z(t) = \left| Z_{\text{COM}}^{\text{PE}}(t) - Z_{\text{COM}}^{\text{PE}_o}(t) \right| \quad (\text{S12})$$

where $Z_{\text{COM}}^{\text{PE}}(t)$ and $Z_{\text{COM}}^{\text{PE}_o}(t)$ represent the instantaneous z-coordinates of the center of mass for the native polyethylene matrix and the oxygenated telechelic chains, respectively. A value of $\Delta Z \approx 0$ indicates a uniformly mixed state where the components share a spatial center, whereas a monotonically increasing magnitude confirms the dynamic segregation of the PE_o fragments away from the bulk center and toward the bounding surfaces.

Simultaneously, the kinetics of the liquid-to-solid phase transition were monitored by calculating the global orientational order parameter, $P_{2,\text{NN}}$, based on the second Legendre polynomial. This parameter quantifies the degree of chain alignment relative to a primary reference director (typically the global axis of maximal alignment or the z-axis). It is formulated as:

$$P_{2,\text{NN}} = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (\text{S13})$$

where θ is the angle between the local chord vector (connecting next-nearest neighbor carbon atoms, i and $i + 2$, along the polymer backbone) and the reference director, and the angular brackets $\langle \dots \rangle$ denote an ensemble average over all defined bonds in the system. The value of $P_{2,\text{NN}}$ ranges from 0, corresponding to an isotropic, randomly oriented amorphous melt, to 1, representing a perfectly aligned, highly crystalline domain. Tracking this parameter as a function of simulation time provides a robust metric for determining the onset, rate, and saturation of the crystallization process at various undercooling temperatures.

MD simulations of PE/PE_o 100/50 at other mass fractions

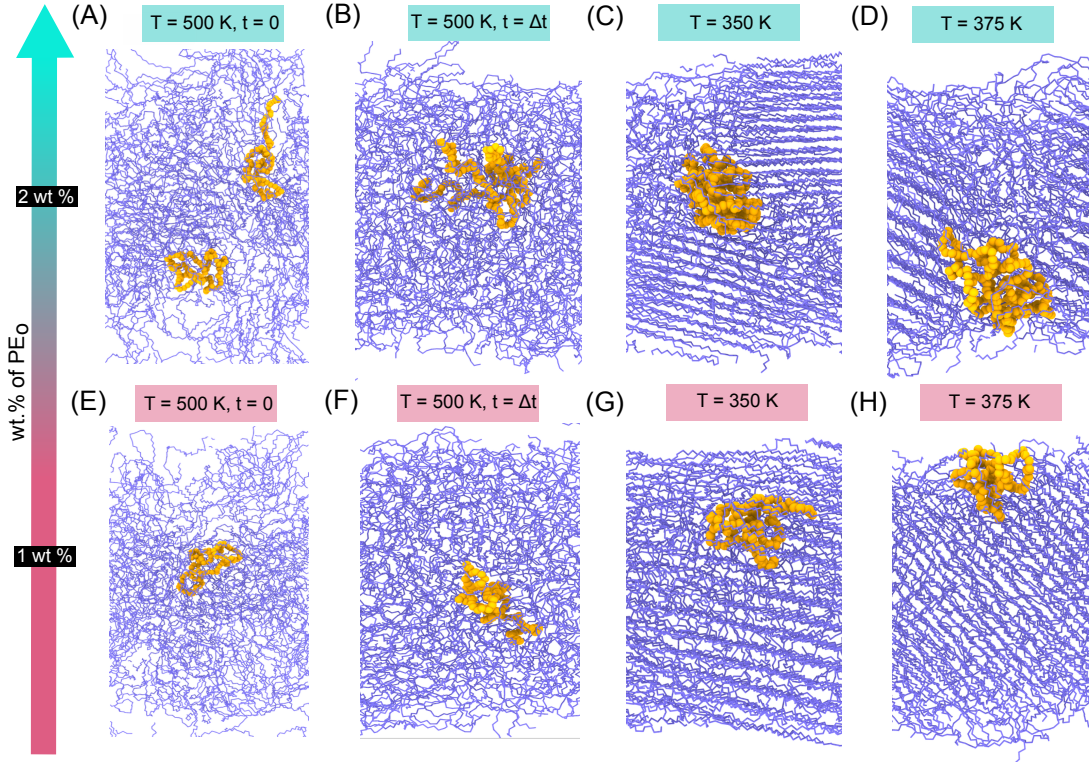


Figure S40: MD simulation snapshots of the PE/PE_o 100/50 systems. (A-D) are for PE/PE_o 100/50 systems with a PE_o mass fraction of 2 %: (A) initial setup, (B) at 500 K, (C) at 350 K, and (D) at 375 K. (E-H) are PE/PE_o 100/50 systems with a PE_o mass fraction of 1 %: (E) initial setup, (F) at 500 K, (G) at 350 K, and (H) at 375 K.

PE/PE_o 100/50 simulations

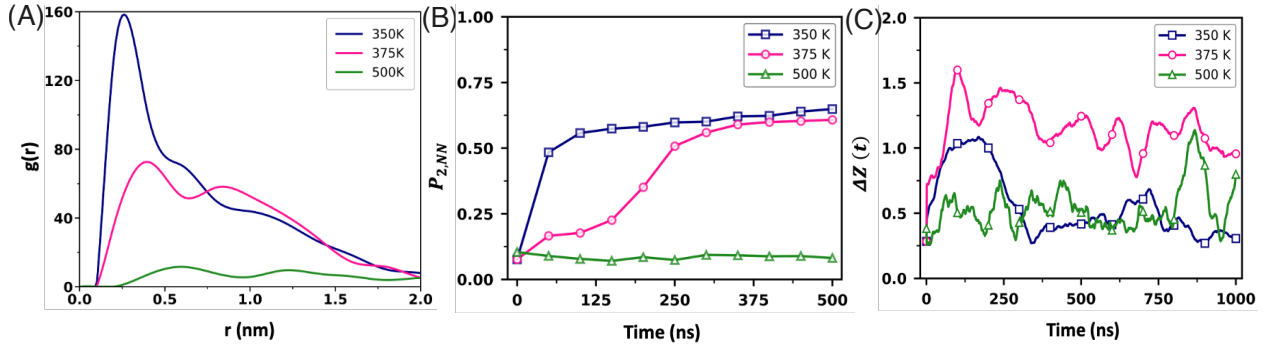


Figure S41: (A) Radial distribution function, $g(r)$, of the PE/PE_o 100/50 system with a PE_o mass fraction of 5 % at 350 K, 375 K, and 500 K. The curves demonstrate temperature-dependent structural ordering, with the emergence of distinct coordination peaks at lower temperatures indicating crystalline packing, in contrast to the amorphous melt at 500 K. (B) The $P_{2,NN}$ order parameter as a function of simulation time, illustrating the kinetics of crystal growth. (C) The absolute difference in the center of mass along the z-axis (ΔZ) between the polymer film and the functionalized chains as a function of simulation time, quantifying the extent of surface segregation of the functionalized chains.

Figure S52: ^1H NMR spectrum of PP_o.

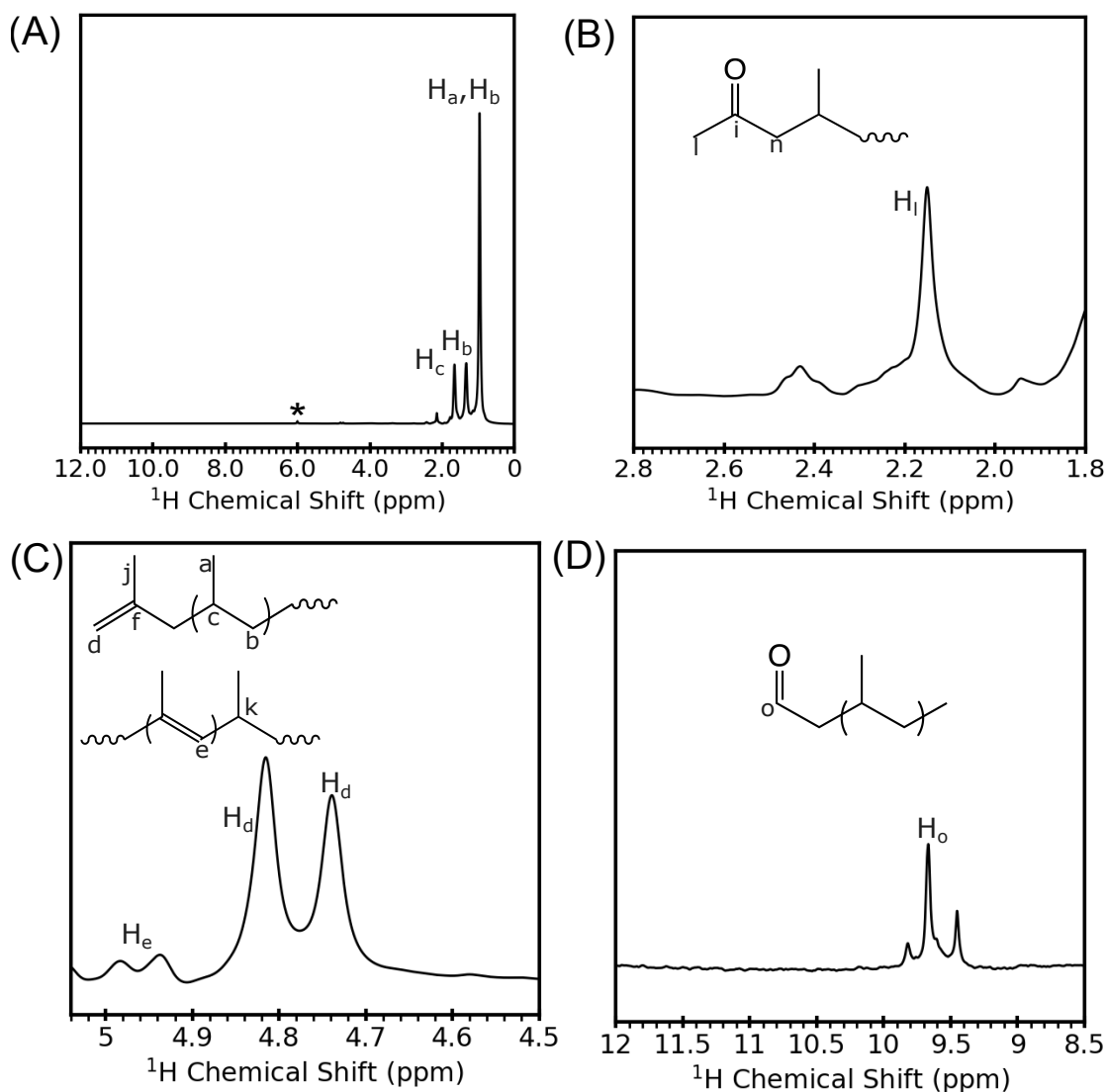


Figure S42: ^1H NMR spectrum of PP_o. (A) Complete spectrum. (B) Zoom-in of the spectrum from 1.8 ppm to 2.8 ppm with the peak assignment for methyl ketone. (C) Zoom-in of the spectrum from 4.5 ppm to 5.2 ppm with the peak assignment for the internal alkene and TVD groups. (D) Zoom-in of the spectrum from 8.5 ppm to 12.0 ppm with the peak assignment for the aldehyde. The peak at 6 ppm (*) is the reference solvent (TCE- d_2) peak. Assignments are based on our past work, and the work of several other authors (4, 9–11).

^{13}C NMR of PP_0

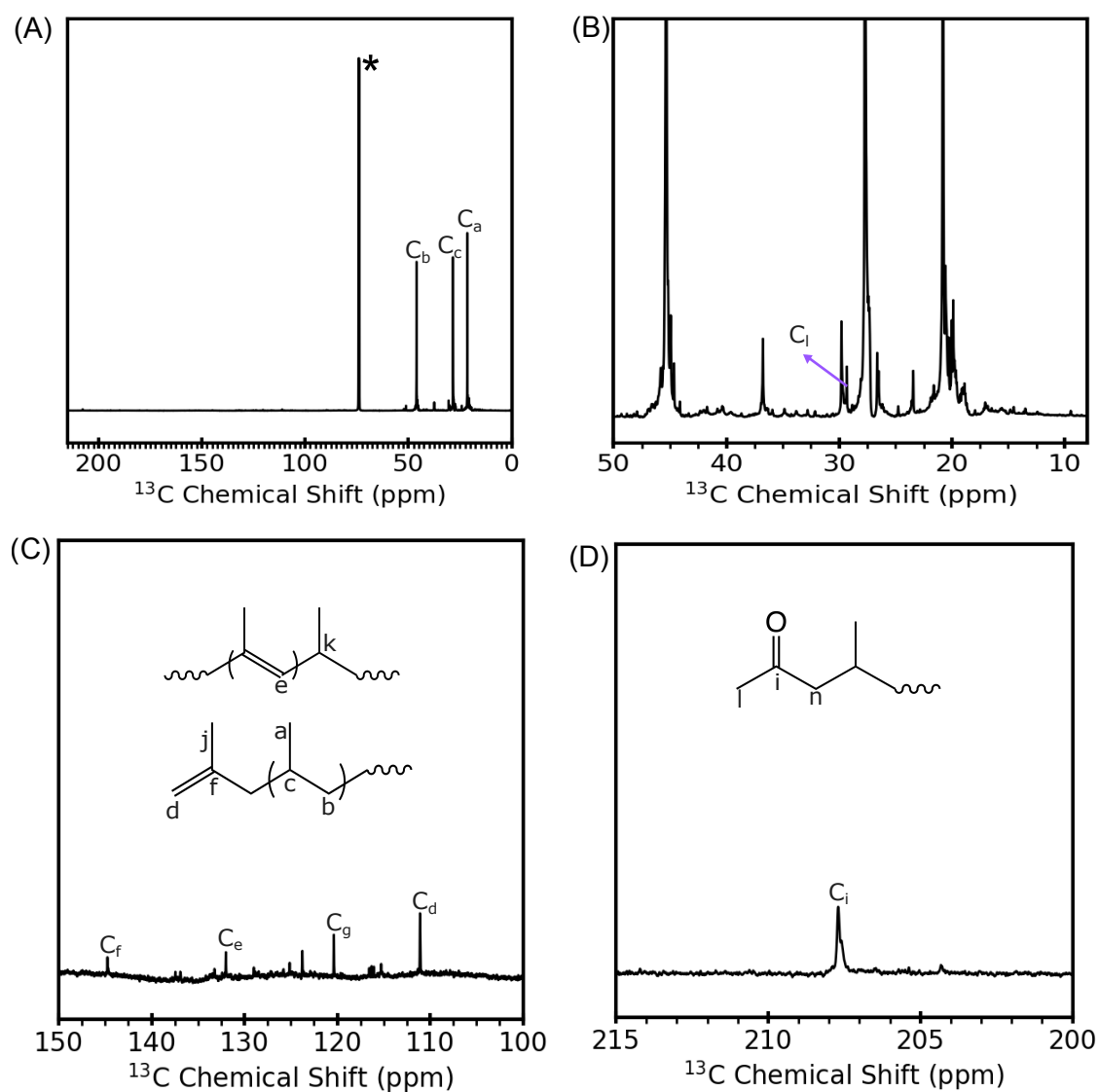


Figure S43: ^{13}C NMR spectrum of PP_0 . (A) Complete spectrum. (B) Zoom-in of the spectrum from 7 ppm to 43 ppm with the peak assignment for $\alpha\text{-CH}_3$ to the carbonyl carbon. (C) Zoom-in of the spectrum from 105 ppm to 150 ppm with the peak assignment for the internal alkene and TVD groups. C_g was assigned to an in-chain vinylene group (12). (D) Zoom-in of the spectrum from 200 ppm to 215 ppm with the peak assignment for the carbonyl carbon. The peak at 72.8 ppm (*) is the reference solvent (TCE-d_2) peak. Assignments are based on our past work, and the work of several other authors (4, 9–11).

DSC second heating scan of PP_o.

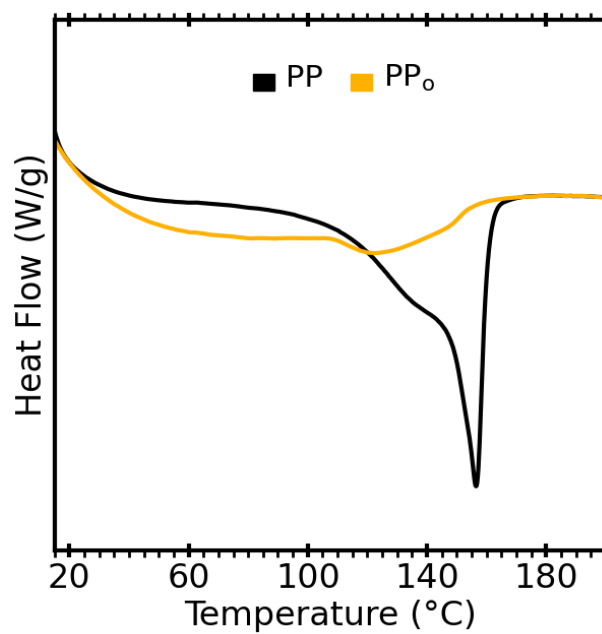


Figure S44: The DSC second heating scans conducted at a 20 °C/min ramp rate for PP and PP_o.

Sample	X _c (%)	T _m	f _o	M _n	Đ
PP _o	12 ± 5	139 ± 2	1.48 ± 0.08	3.9 ± 0.2	2.9 ± 0.1

Table S5: Characterization of PP_o.

PE/PE_o 100/25 recrystallized at 375 K

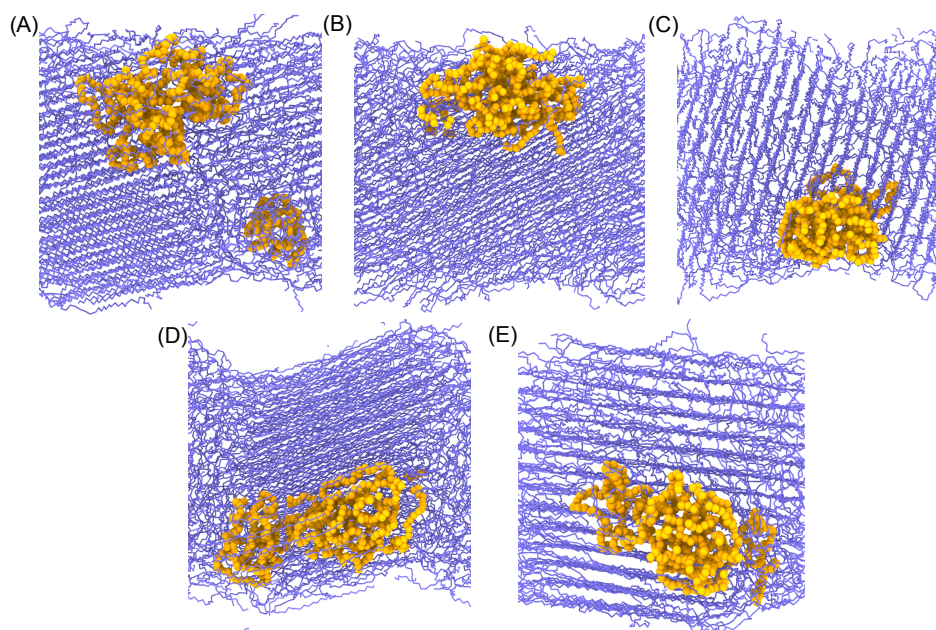


Figure S45: Five repeat runs of the recrystallization of the PE/PE_o 100/25 with a mass fraction of 5 % loading at 375 K for 1000 ns. Each run uses a different starting point taken from a 100 ns NVT simulation at 500 K.

PE/PE_o 100/25 recrystallized at 350 K

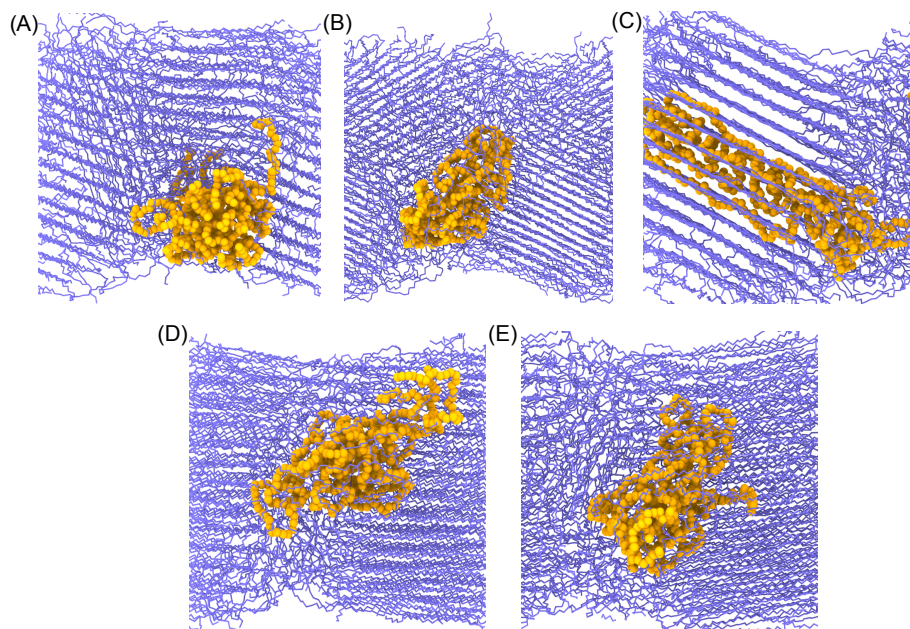


Figure S46: Five repeat runs of the recrystallization of the PE/PE_o 100/25 with a mass fraction of 5 % loading at 350 K for 1000 ns. Each run uses a different starting point taken from a 100 ns NVT simulation at 500 K.

Analysis of PE/PE_o 100/25

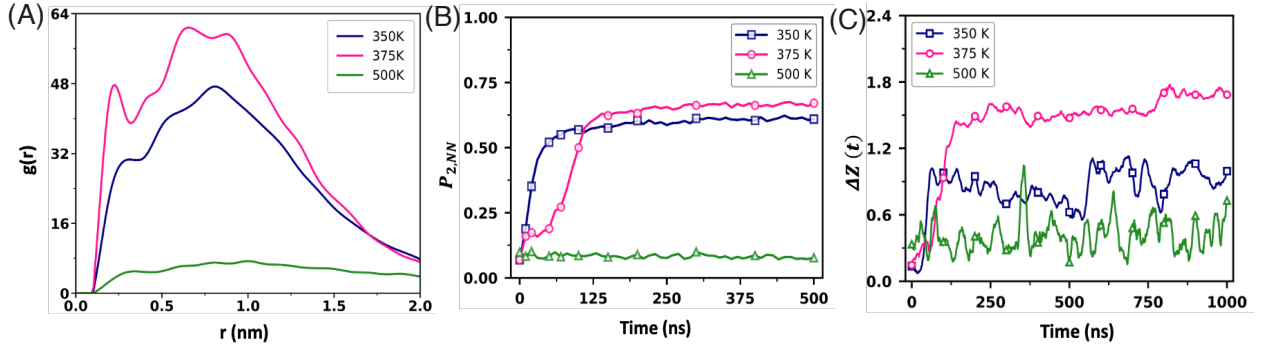


Figure S47: (A) Radial distribution function, $g(r)$, of the PE/PE_o 100/25 system with a PE_o mass fraction of 5 % at 350 K, 375 K, and 500 K. Similar to the 100/50 system, the curves demonstrate temperature-dependent crystalline packing. (B) The $P_{2,NN}$ order parameter as a function of simulation time, illustrating the kinetics of crystal growth. (C) The absolute difference in the center of mass along the z-axis (ΔZ) between the polymer film and the functionalized chains as a function of simulation time, quantifying the extent of surface segregation.

PE/PE_o 100/25 recrystallized at 350 K and 375 K

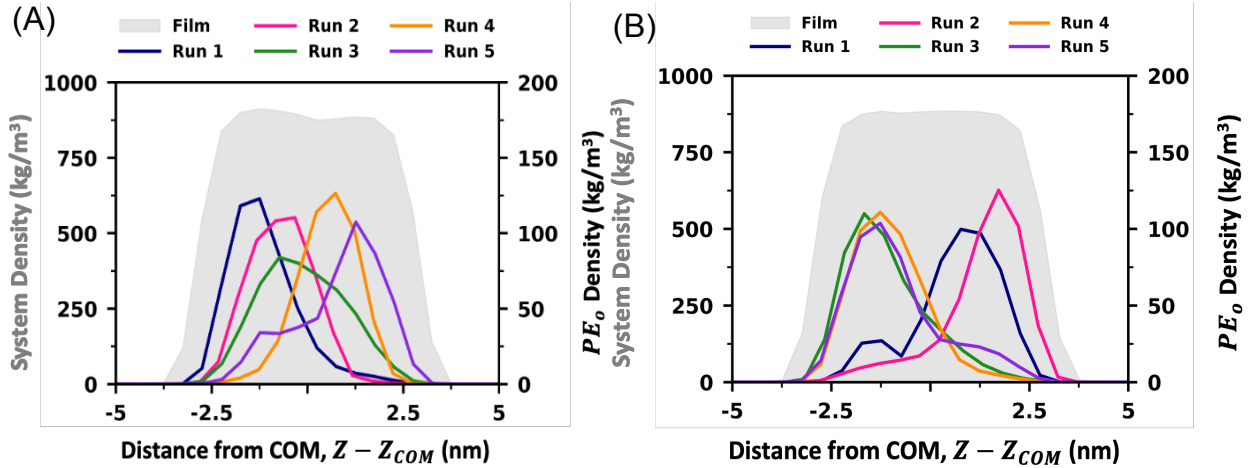


Figure S48: Mass density profiles of the thin film matrix and functionalized PE_o chains as a function of distance from the film center ($Z - Z_{COM}$). Data are shown for a PE/PE_o 100/25 blend (5 % loading) crystallized at (A) 350 K and (B) 375 K across five replicates. The distributions show that higher crystallization temperatures (375 K) promote PE_o migration to the bounding surfaces, whereas rapid solidification at 350 K kinetically traps the PE_o chains within the bulk.

Flory-Huggins theory

We now use Flory-Huggins theory to estimate the χ parameter between the aldehyde groups and the alkane groups in the simulations. Since the chain ends themselves are the only species that are different from all other chain monomers, we can derive that the effective χ_{eff} between the short chain of length N_{short} and the matrix chains of length N is $\equiv \chi_{em} \frac{2}{N_{short}}$ where χ_{em} is the interaction parameter between an end bead and a regular monomer.

We now use the fact that at 500 K, the chains of length 50 are immiscible with the matrix (macrophase separation), while chains of length 25 are miscible. To gain further insight we use the equation that defines the spinodal for the Flory-Huggins model:

$$\frac{1}{N_{short}\phi_{short}} + \frac{1}{N(1-\phi_{short})} - \chi_{em} \frac{2}{N_{short}} \equiv 0 \quad (\text{S14})$$

at the spinodal. For systems inside the spinodal the derivative is less than 0 while outside it is greater than 0. By assuming that the former case is inside the spinodal and the latter case is outside, we derive that $\chi_{em} \approx 5$ at 500 K. This number should be compared to the work of Venetsanos et al. (13), who have used the Kirkwood-Buff theory to estimate the χ parameter between poly(ethyleneoxide) and polyethylene. They found numbers of order 0.3 for this interaction parameter which is an order of magnitude smaller. The literature suggests that the aldehyde groups can hydrogen bond to each other with an interaction energy in the (10-15) kJ/range. Using these numbers allows us to estimate that $\chi_{em} \approx 3-5$, which is in good agreement with these numbers.

We now ask why the telechelic chains do not undergo microphase separation as expected for a symmetric triblock copolymer. For the $N_{short}=25$ system we find that $\chi_{em}N_{short}= 62.5$ while the $\phi_{end}=0.08$, while for the $N_{short}=50$ system we find that $\chi_{em}N_{short}= 125$ but the $\phi_{end}=0.08$. These data fall at the end of the block copolymer morphology diagram, where the mean field phase diagram is not valid. Rather, comparing it to the experimental phase diagrams we conclude that these systems are not in the regime where microphase separation into cylinders should occur. This is consistent with our simulations where no such self assembly effects are found.

Mechanical properties of extruded PP (before and after MNPL extraction)

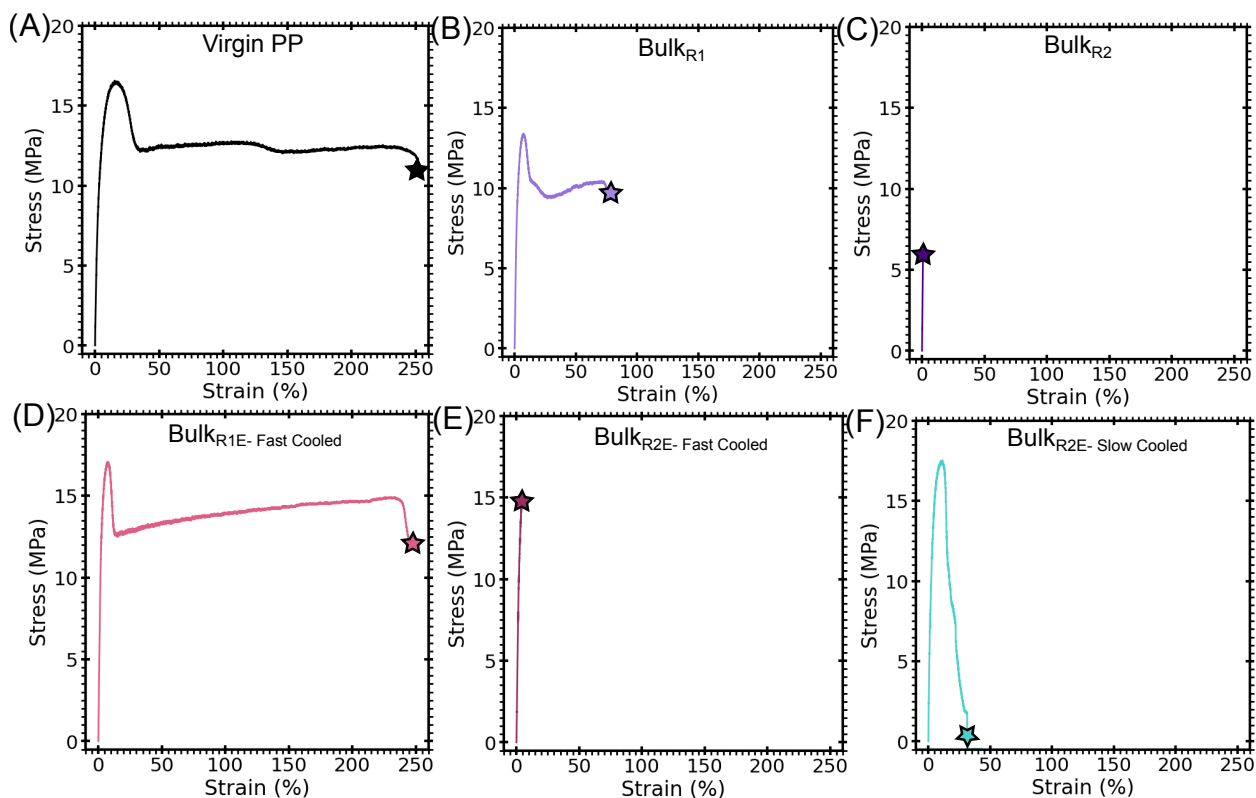


Figure S49: Uniaxial tensile stress-strain curves of (A) virgin PP, (B) bulk polymer processed once ($Bulk_{R1}$) and (C) twice ($Bulk_{R2}$). The stress-strain curves of these controls are compared to that of the bulk polymer post MNPL extraction. Stress-strain curves of the bulk after (D) fast cool MNPL extraction after the first extrusion ($Bulk_{R1E-Fast\ Cool}$) and (E) after the second extrusion ($Bulk_{R2E-Fast\ Cool}$). (F) Alternatively, stress-strains curves of the bulk after slow cool MNPL extraction after the second processing cycle is also reported ($Bulk_{R2E-Slow\ Cool}$). Note: The star in each stress-strain curve indicates the fracture point.

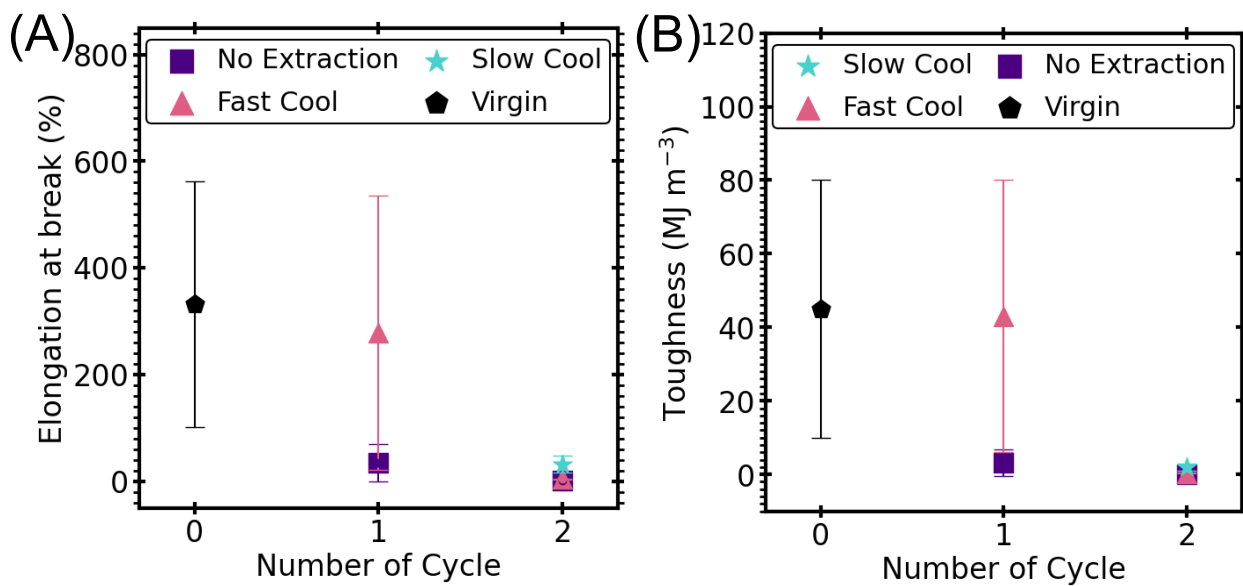


Figure S50: Mechanical properties measured via uniaxial tensile tests of virgin PP, extruded PP, and extruded PP after the removal of MNPL. (A) Elongation at break and (B) Toughness. Error bars (some smaller than the data points) are the standard deviation of at least 5 measurements.

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