Electronic Supplementary Material (ESI) for Chemical Science.

Conformations of polyolefins on platinum catalysts control product distribution in plastics recycling

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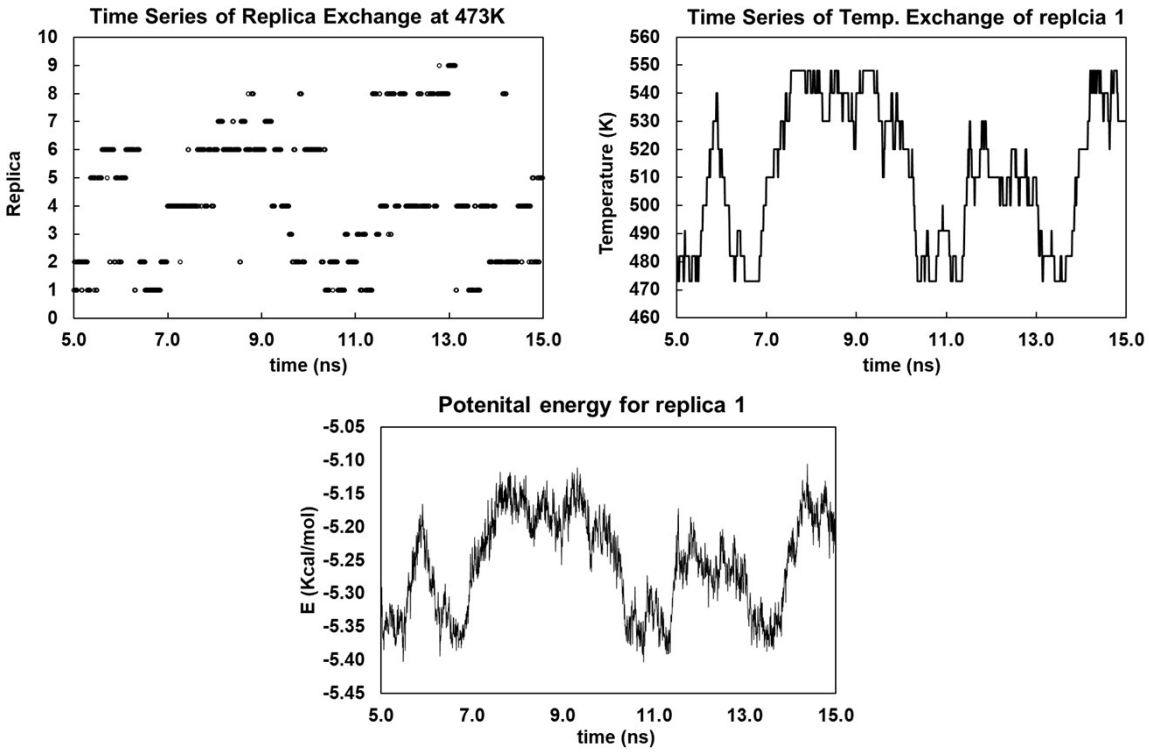

Figure S1. Times series obtained from replica exchange MD simulation of C_{26} PE melt over the Pt(111) catalyst surface. Plots prove a free random walk in both replica and temperature space. We note that the potential energies are normalized per number of atoms in the system.

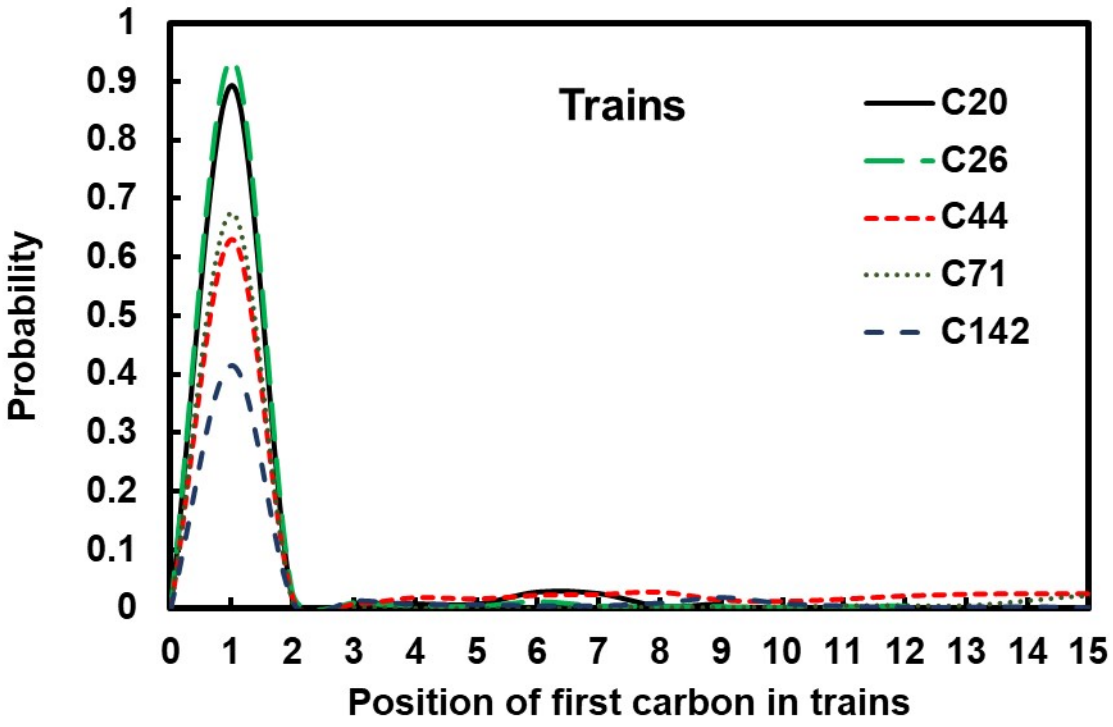

Figure S2. Probability of a chain atom being at the beginning of a train polymer chains of varying length. The distributions show that the preponderance of polymer chains preferably adsorb with their ends.

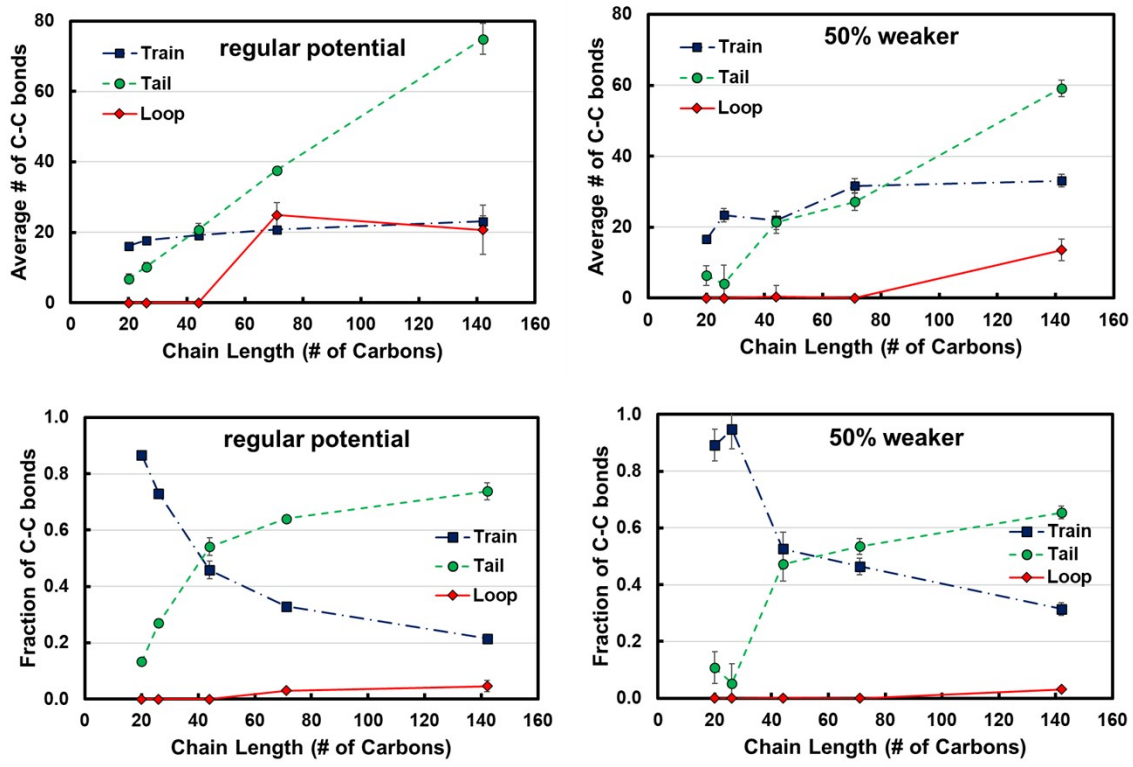

Figure S3. Effects of the Pt potential strength on λ_{train}, λ_{tail}, λ_{loop}, f_{train}, f_{tail}, and f_{loop}.

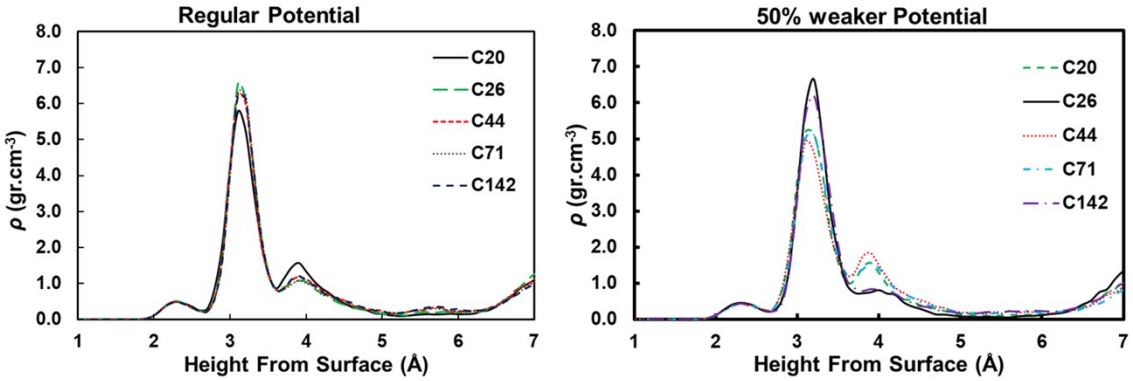

Figure S4. Effects of the Pt potential strength on density distributions as a function of height from the Pt(111) catalyst surface (along the surface normal) for the pure PE melts investigated in this work.

Table S1. Number of chains and simulation boxes used in this work to study the dynamics of PE melts over the Pt(111) catalyst surface at 473 K.

System	Simulation Box	Number of Chains
Pure PE melts		
C_{20}	33.24 Å × 33.59 Å × 60.00 Å	83
C_{26}	33.24 Å × 33.59 Å × 60.00 Å	64
C_{44}	41.55 Å × 40.79 Å × 75.00 Å	38
C_{71}	41.55 Å × 40.79 Å × 75.00 Å	43
C_{142}	41.55 Å × 40.79 Å × 75.00 Å	22
Mixtures of PE melts		
C_{142}:C_{20} (73%:27%)	41.55 Å × 40.79 Å × 75.00 Å	16 C_{142} : 43 C_{20}
C_{142}:C_{20} mixture (50%:50%)	41.55 Å × 40.79 Å × 75.00 Å	11 C_{142} : 78 C_{20}
C_{142}:C_{20} mixture (27%:73%)	41.55 Å × 40.79 Å × 75.00 Å	6 C_{142} : 114 C_{20}
Branched PE melts		
C_{71} with 7 methyl branches	41.55 Å × 40.79 Å × 75.00 Å	39
C_{71} with 13 methyl branches	41.55 Å × 40.79 Å × 75.00 Å	36
C_{71} with 7 ethyl branches	41.55 Å × 40.79 Å × 75.00 Å	36
C_{71} with 7 propyl branches	41.55 Å × 40.79 Å × 75.00 Å	33

Table S2. Radius of gyration (R_g) for the investigated PE melts in the bulk at 473 K.

PE melt	Radius of Gyration (Å)
C_{20}	5.63
C_{26}	6.87
C_{44}	9.84
C_{71}	13.56
C_{142}	20.51

Table S3. Temperatures (replicas) selected for replica exchange MD simulations and the acceptance probability of swap moves (P_{acc}) between adjacent replicas for a) pure PE melts, b) mixtures of PE melts, and c) branched PE melts systems over the Pt(111) surface.

a)

C_{20} PE melt		C_{26} PE melt		C_{44} PE melt		C_{71} PE melt		C_{142} PE melt	
T (K)	P_{acc}	T (K)	P_{acc}	T (K)	P_{acc}	T (K)	P_{acc}	T (K)	P_{acc}
473	0.21	473	0.19	473	0.23	473	0.22	473	0.18
482	0.23	482	0.23	482	0.24	480	0.22	480	0.19
491	0.24	491	0.20	491	0.23	487	0.21	487	0.21
500	0.22	500	0.18	500	0.22	494	0.17	494	0.18
510	0.21	510	0.23	509	0.22	501	0.22	501	0.18
520	0.23	520	0.23	518	0.22	508	0.21	508	0.19
530	0.19	530	0.22	527	0.23	515	0.20	515	0.19
540	0.22	540	0.21	536	0.19	522	0.20	522	0.17
548	0.22	548	0.24	545	0.25	529	0.20	529	0.19

b)

C_{142}:C_{20} (73%:27%)		C_{142}:C_{20} (50%:50%)		C_{142}:C_{20} (27%:73%)	
T (K)	P_{acc}	T (K)	P_{acc}	T (K)	P_{acc}
473	0.17	473	0.18	473	0.18
480	0.19	480	0.22	480	0.21
487	0.22	487	0.17	487	0.21
494	0.17	494	0.21	494	0.20
501	0.21	501	0.21	501	0.20
508	0.16	508	0.18	508	0.18
515	0.18	515	0.22	515	0.20
522	0.20	522	0.17	522	0.18
529	0.20	529	0.19	529	0.14

c)

C_{71} with 7 methyl branches		C_{71} with 13 methyl branches		C_{71} with 7 ethyl branches		C_{71} with 7 propyl branches	
T (K)	P_{acc}	T (K)	P_{acc}	T (K)	P_{acc}	T (K)	P_{acc}
473	0.20	473	0.21	473	0.18	473	0.19
480	0.21	480	0.22	480	0.21	480	0.22
487	0.18	487	0.18	487	0.21	487	0.20
494	0.22	494	0.21	494	0.19	494	0.19
501	0.20	501	0.18	501	0.19	501	0.23
508	0.16	508	0.22	508	0.20	508	0.20
515	0.20	515	0.19	515	0.20	515	0.21
522	0.18	522	0.24	522	0.20	522	0.17
529	0.17	529	0.23	529	0.20	529	0.22

Table S4. Effects of the Pt potential strength on τ_{tr} and Carbon populations of the pure PE chains studied in this work up to 6 Å height from the Pt(111) surface.

	Regular Potential		50% Weaker Potential	
Chain	τ_{tr}	0-6 Å Carbon population (#C/Å^2)	τ_{tr}	0-6 Å Carbon population (#C/Å^2)
C20	16±0.3	0.1726	17±1.2	0.1674
C26	18±0.5	0.1741	23±1.9	0.1633
C44	19±1.3	0.1781	22±2.6	0.1752
C71	21±0.3	0.1772	32±2.0	0.1752
C142	23±1.5	0.1806	33±1.8	0.1735