Supporting Information for: Investigating PVC Polymer-Plasticizer Interactions with Atomistic MD Simulations and Potential of Mean Force Calculations

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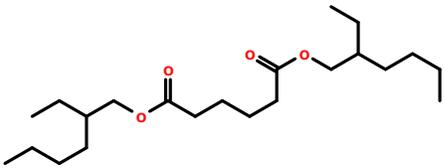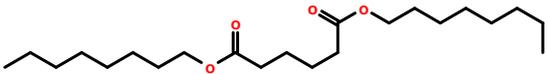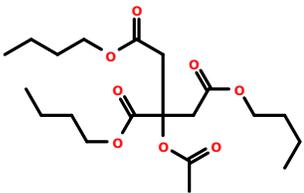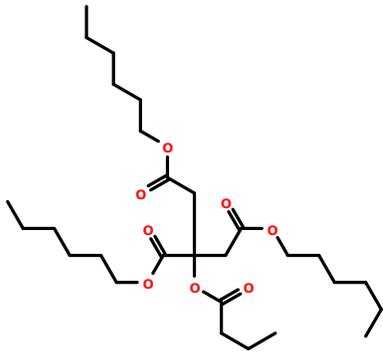†Department of Chemistry, Sri Sathya Sai Institute of Higher Learning, Puttaparthi, Andhra Pradesh - 515134, India
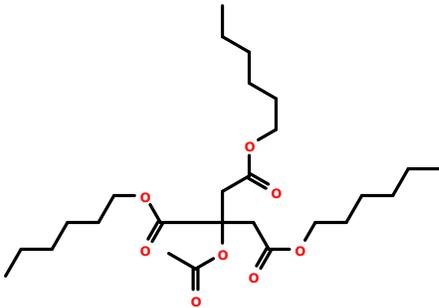
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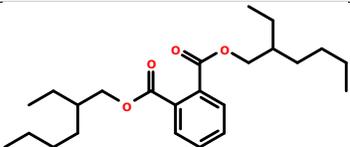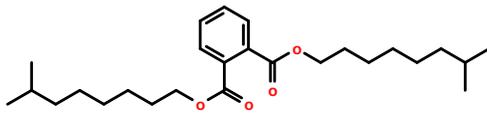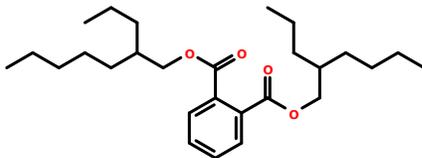¶Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

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Table S1: List of all plasticizers used in this study along with their acronyms.

Plasticizer	Structure	Molar Mass (g/mol)	Category
DEHA Bis(2-ethylhexyl) Adipate		370.6	Aliphatic dicarboxylate (Adipate)
DOA Dioctyl Adipate		370.6	Aliphatic dicarboxylate (Adipate)
ATBC Acetyl Tributyl Citrate Citroflex A-4 (CA-4)		402.5	Citrate
BTHC Butyryl Trihexyl Citrate Citroflex B-6		514.7	Citrate
ATHC Acetyl Trihexyl Citrate Citroflex A-6 (CA-6)		486.6	Citrate

DEHP Bis(2-ethylhexyl) Phthalate		390.6	Orthophthalate
DINP Diisononyl Phthalate		418.6	Orthophthalate
DPHP Di(2-propylheptyl) Phthalate		446.7	Orthophthalate
DIDP Diisodecyl Phthalate		446.7	Orthophthalate
DIBP Diisobutyl Phthalate		278.3	Orthophthalate
DIOP Diisooctyl Phthalate		390.6	Orthophthalate
DITP Diisotridecyl Phthalate		530.8	Orthophthalate
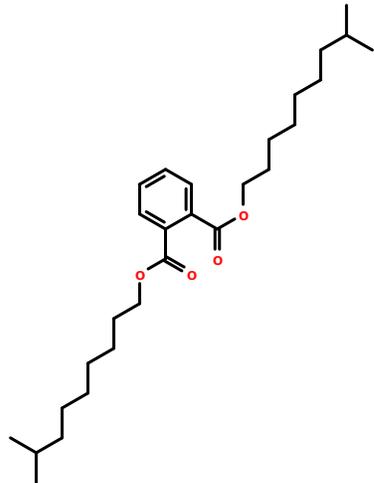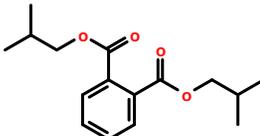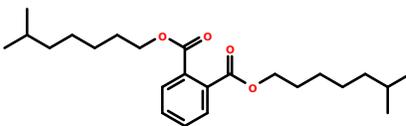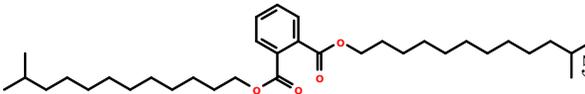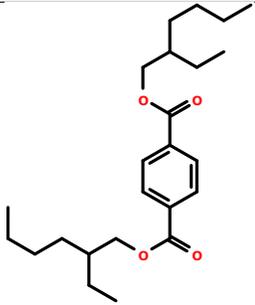
DEHT Bis(2-ethylhexyl) Terephthalate (DOTP/DEHT)		390.6	Terephthalate
TOTM Tris(2-ethylhexyl) Trimellitate (TEHTM)		546.8	Trimellitate
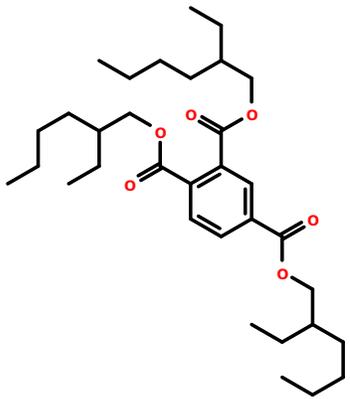
Table S2: Statistical analysis of the variation in slope and y-intercept values of pairs of plasticizers for investigation of the structure-property relationships of plasticizers interacting with PVC polymers of varying chain lengths (6-20 repeating units) derived from linear fits of N-PMF vs. molar mass of PVC polymer for different plasticizers

		Slope		y-Intercept	
Plasticizer 1	Plasticizer 2	t-Test value	Significance $(P < 0.05)$	t-Test value	Significance $(P < 0.05)$
DEHT	DIOP	5.582	Yes	-9.665	Yes
DEHP	DIOP	2.2043	Yes	-1.241	No
DEHP	DEHT	-3.153	Yes	9.0337	Yes
DEHT	TOTM	-2.527	Yes	-8.249	Yes
DEHP	TOTM	-4.579	Yes	1.4978	No
DEHA	DOA	-0.852	No	3.2033	Yes
DIDP	DPHP	-0.419	No	-2.266	Yes

System Preparation
- PVC and Plasticizer molecule
- GAFF2 force field (Ambertools)

Build Simulation Box
- Packmol
- 128x128x128 Å^3 (pbc)

MD Simulation Parameters
- LAMMPS
- 12-6 Lennard-Jones potential (10.0 Å cut-off)
- PPPM Electrostatics
- Lorentz-Berthelot mixing rules
- Stoermer-Verlet: 1 fs timestep

Equilibration
- NVE with Langevin thermostat for 5 ps @ 300K
- NVT @ 300K for 0.5 ns

Umbrella Sampling
- 0.1Å for 300 steps (30 Å)
- Spring force with a constant of 20 (kcal/mol)/Å^2 between PVC and plasticizer
- Nose-Hoover thermostat
- 50 ps for each step (Equilibration)
- 0.1 ns for each step (Production Step)

PMF Calculation
- WHAM algorithm

Analysis
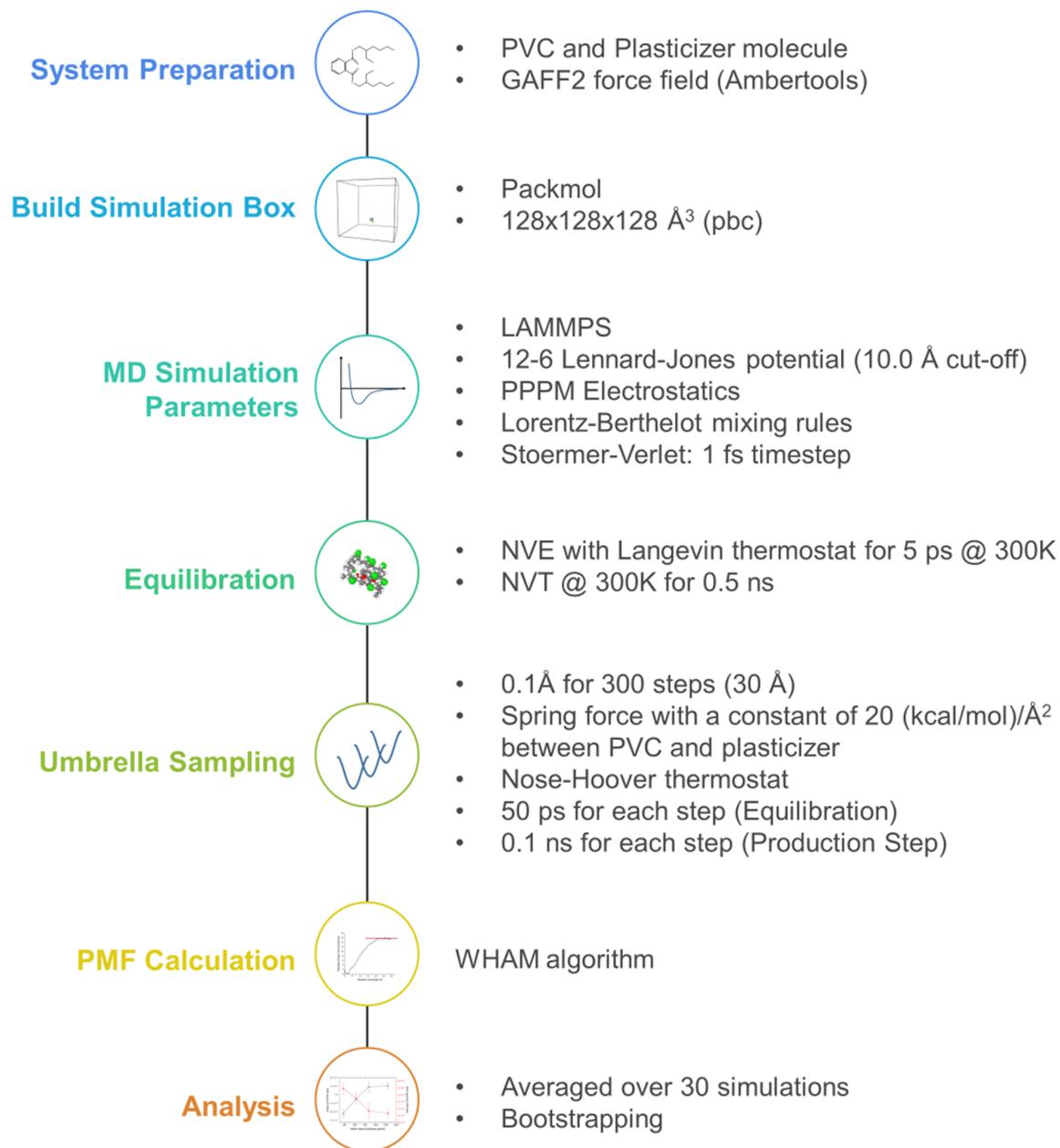- Averaged over 30 simulations
- Bootstrapping

Figure S1: Flowchart illustrating the methodology and parameters used in all simulations.
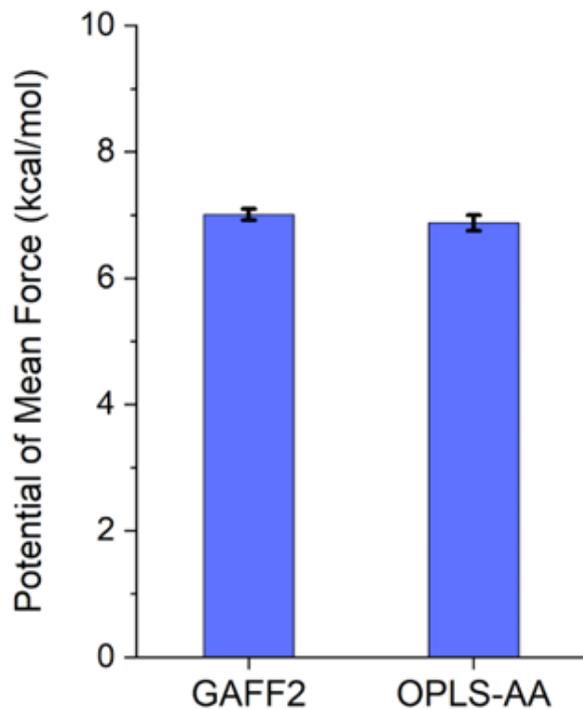
Figure S2: Correlation of PMF values for a system consisting of PVC20 and DEHP with GAFF2 and OPLS-AA force fields. For the PMF calculations using OPLS-AA force field, the parameter files were generated using libpargen[1–3] and polypargen[4] online web servers. The simulation settings for the OPLS-AA included a non-bonded cutoff set to 12 Å, and all remaining settings were identical to those used for the GAFF2 force field.
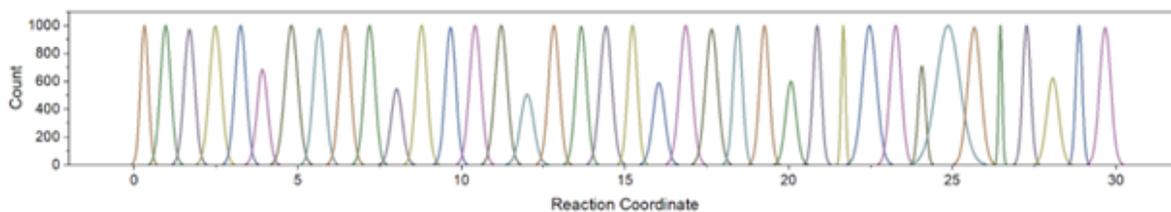

Figure S3: Histogram of configurations obtained from uniformly spaced windows generated by pulling the polymer along the reaction coordinate.
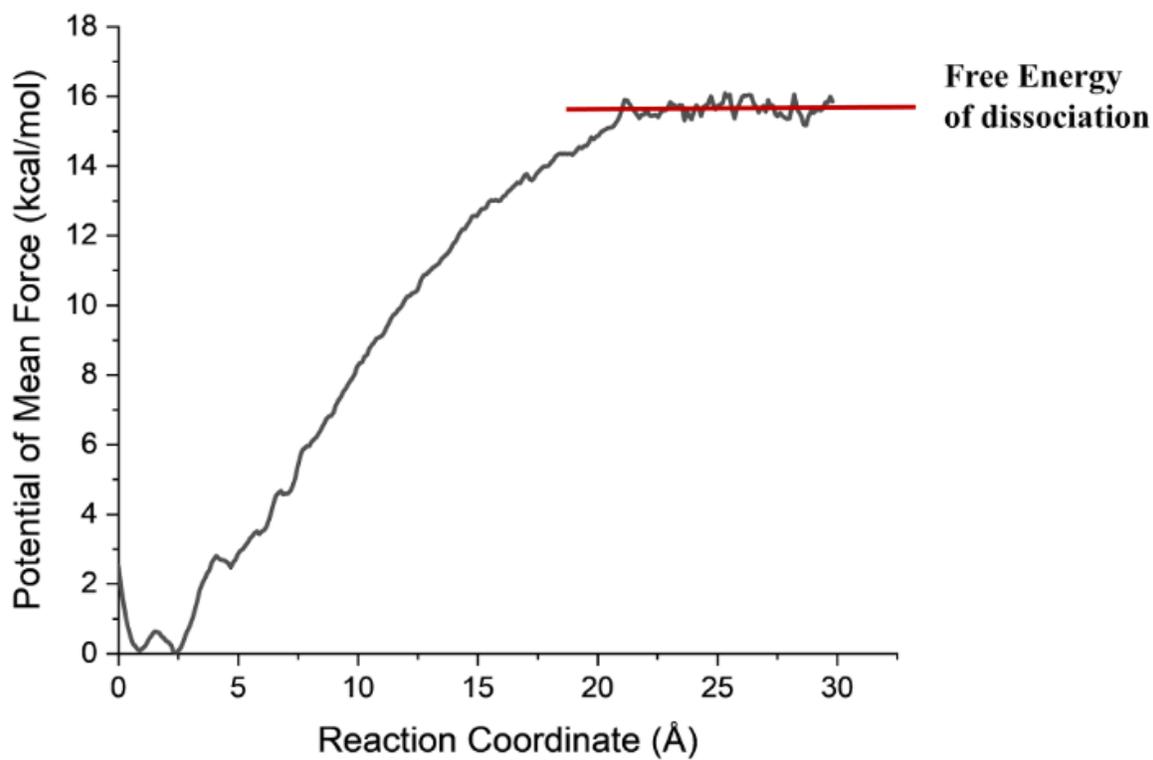
Figure S4: A typical PMF plot showing the interaction between polymer PVC20 and TOTM.
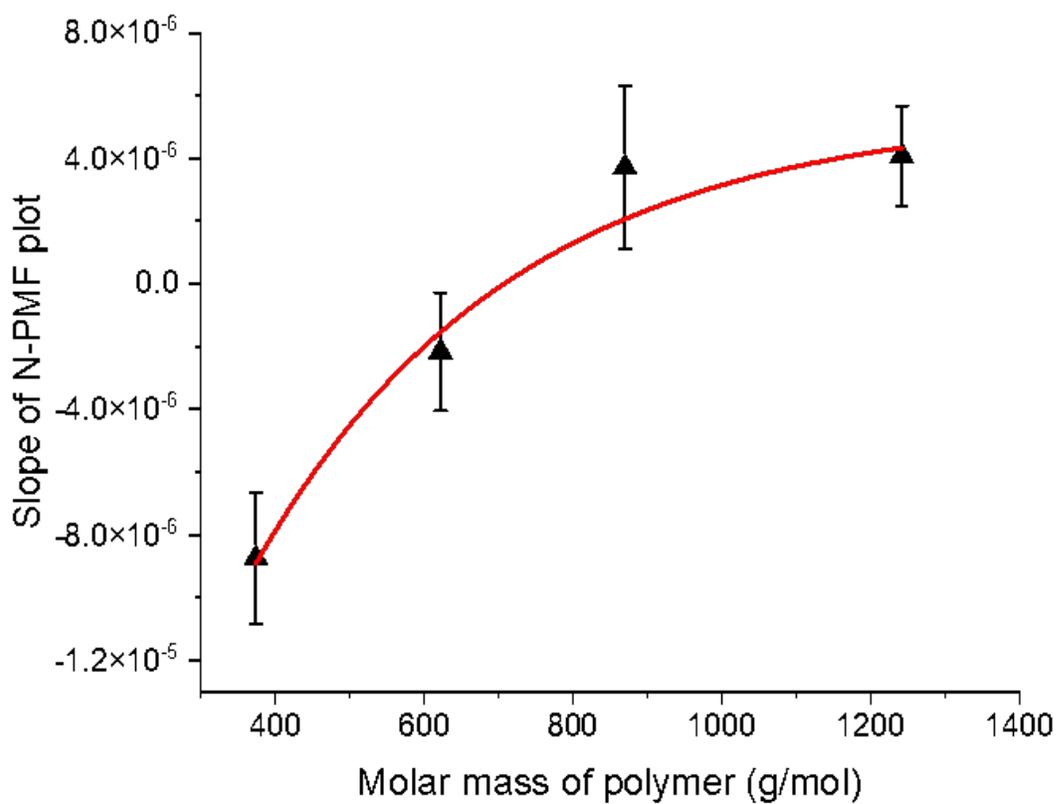
Figure S5: Plot of slope values from the N-PMF plots of orthophthalates plotted against the molar mass of PVC polymer with 6-20 monomer units. The red line is a visual guide and is drawn to show the trend.
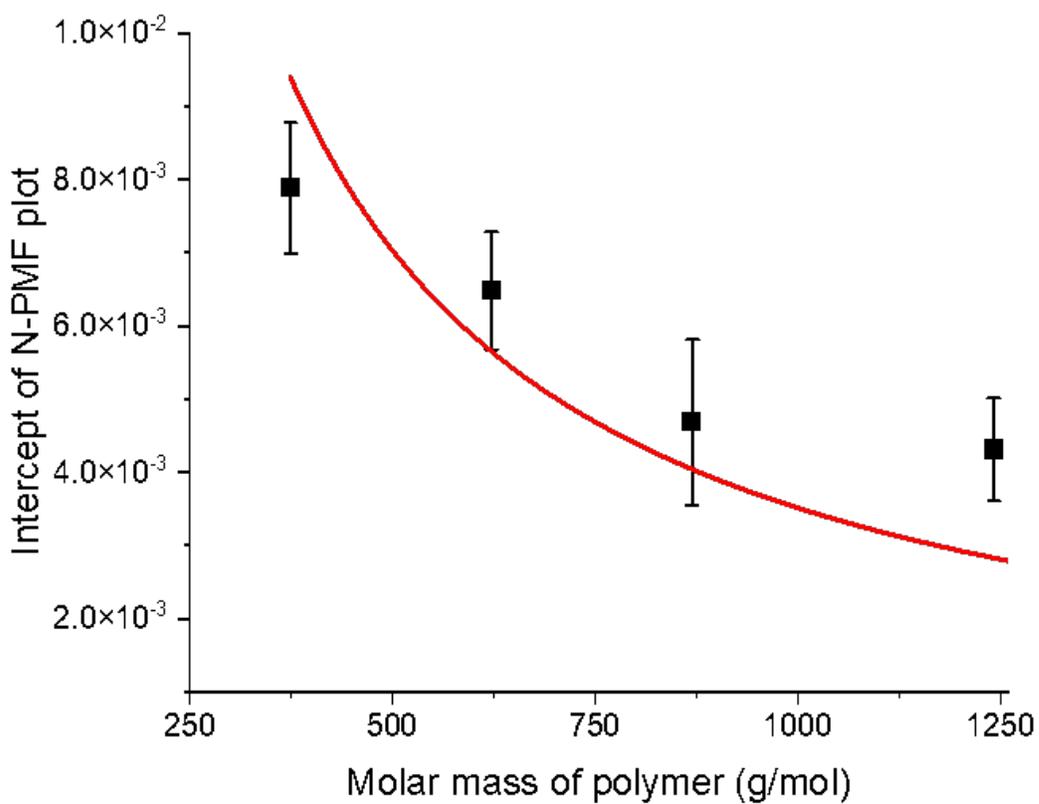
Figure S6: Plot of y-intercept values from the N-PMF plots of orthophthalates plotted against the molar mass of PVC polymer with 6-20 monomer units and a $1/r$ fit using the equation $y = c/x$, where $c = 3.51 \pm 0.33$, with a regression coefficient of 0.85.
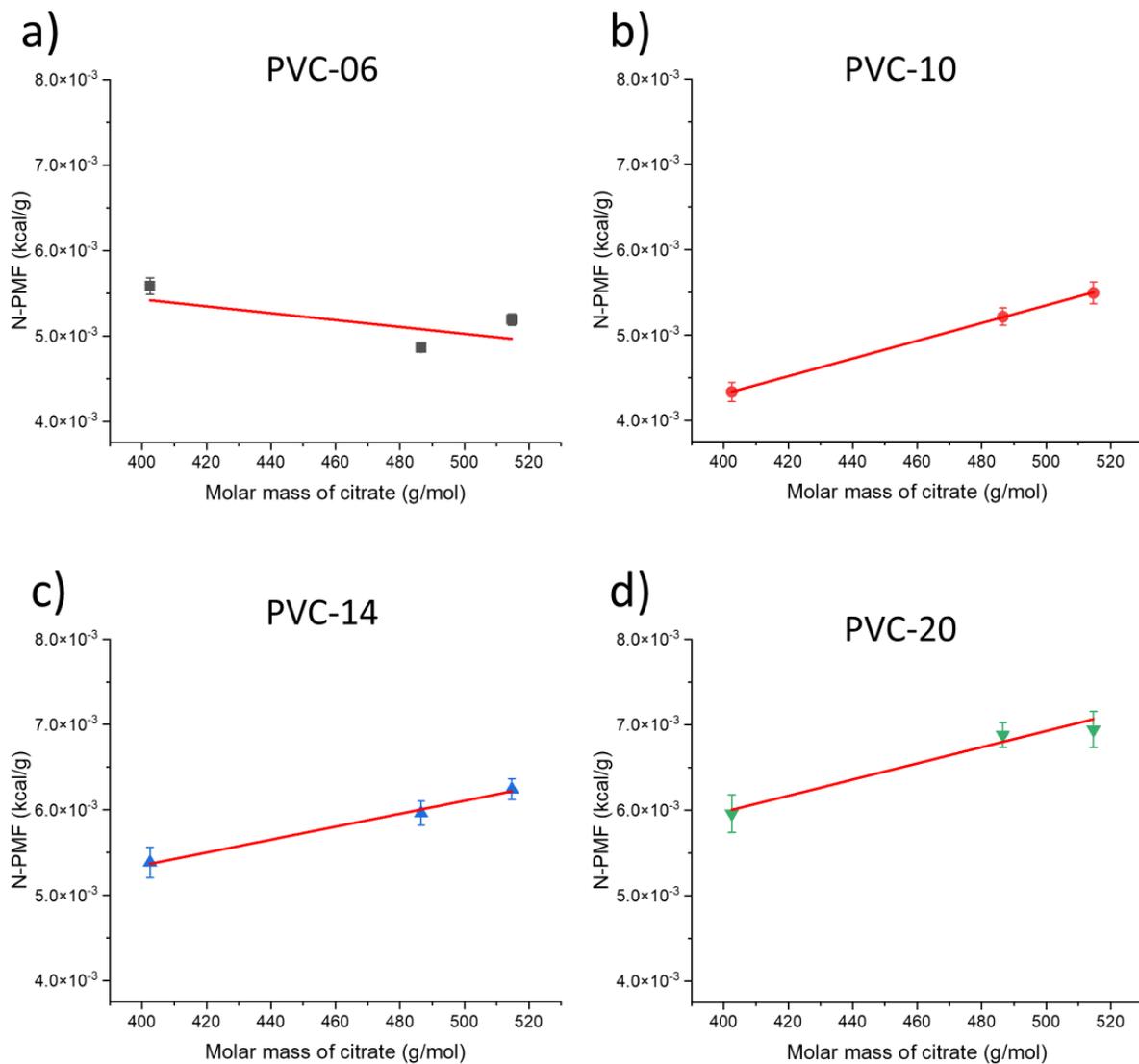
Figure S7: N-PMF versus molar mass of citrate plasticizer along with the linear fit for PVC polymers of different lengths.
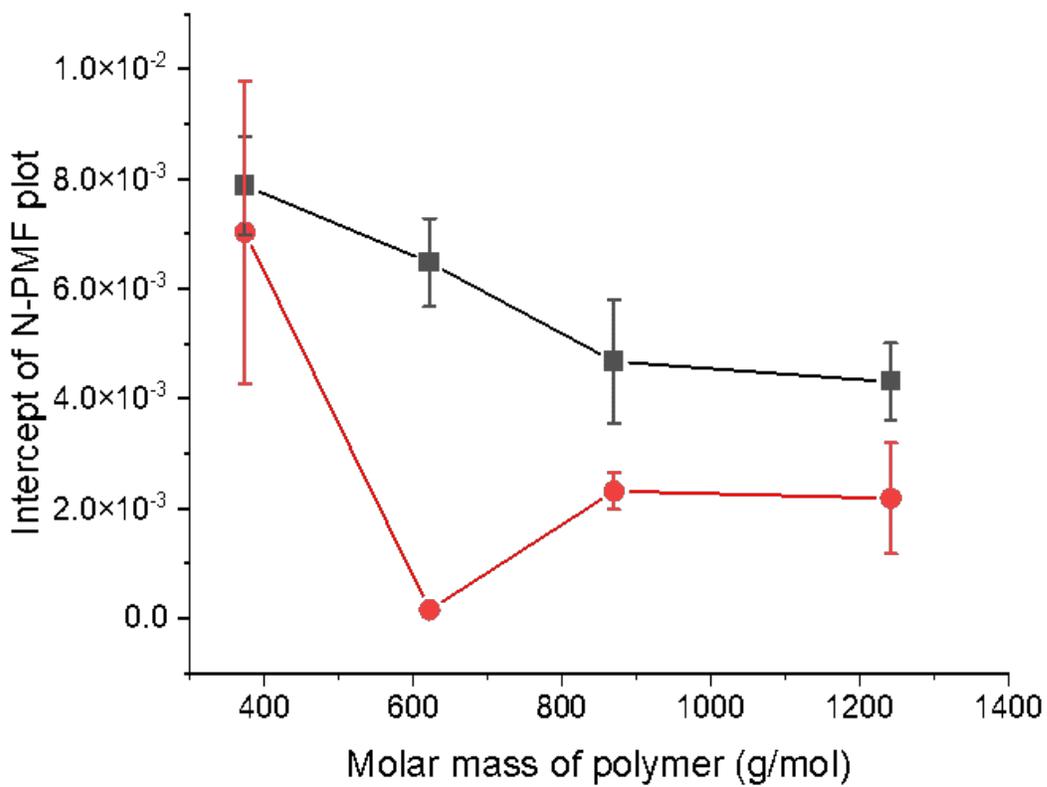
Figure S8: Plot of y-intercept values derived from N-PMF plot of citrates (red circles) and orthophthalates (black squares) plotted against the molar mass of PVC polymer.
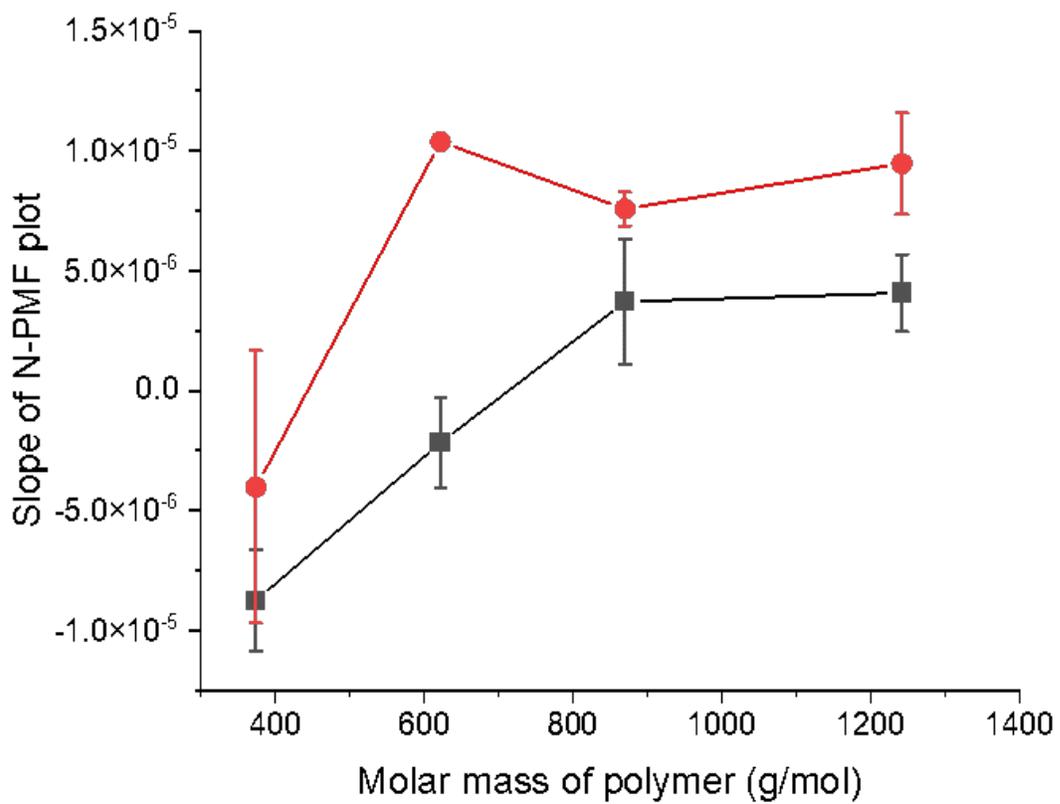
Figure S9: Plot of slope values derived from N-PMF plot of citrates (red circles) and orthophthalates (black squares) plotted against the molar mass of PVC polymer.
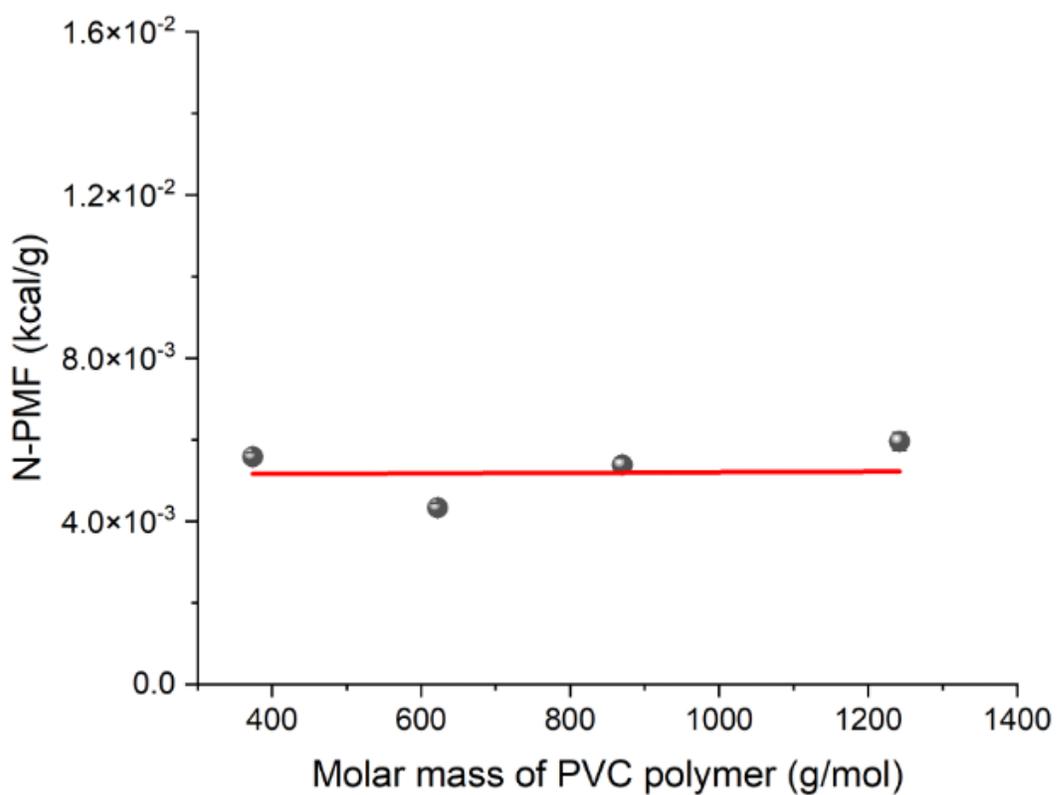
Figure S10: N-PMF plot of plasticizer ATBC with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 7.09×10^{-8} and a y-intercept of 5.13×10^{-3}

Figure S11: N-PMF plot of plasticizer ATHC with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 2.25×10^{-6} and a y-intercept of 3.99×10^{-3}.
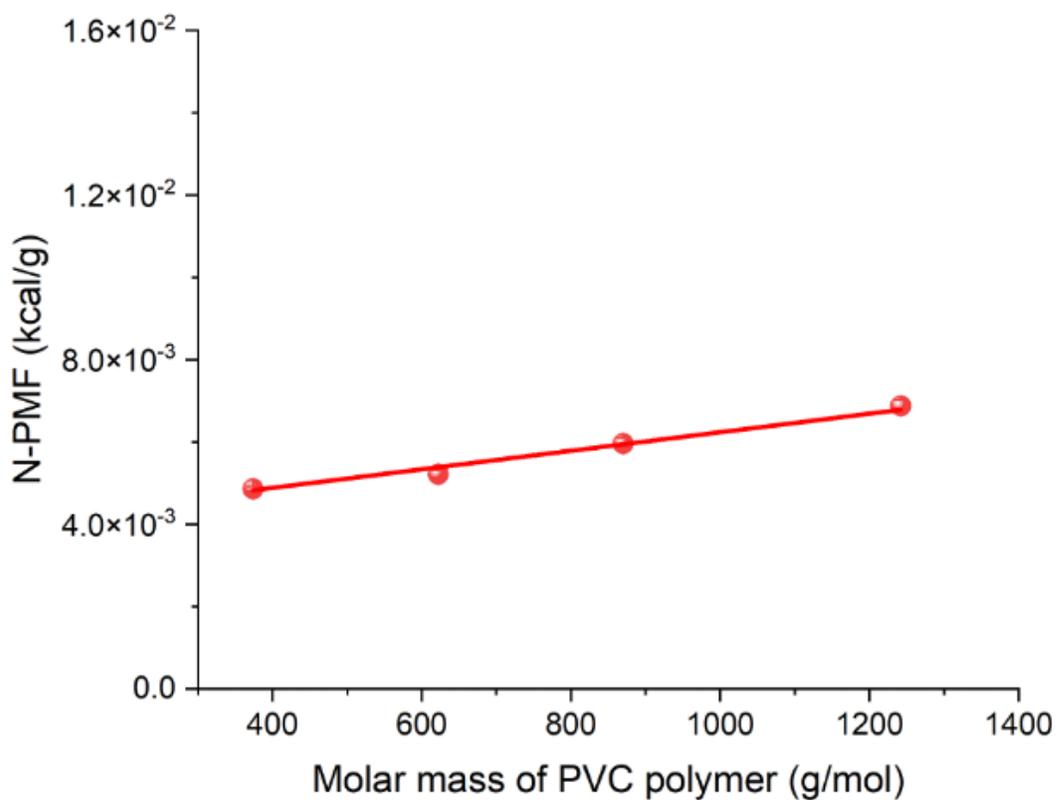
Figure S12: N-PMF plot of plasticizer BTHC with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 2.02×10^{-6} and a y-intercept of 4.41×10^{-3}.
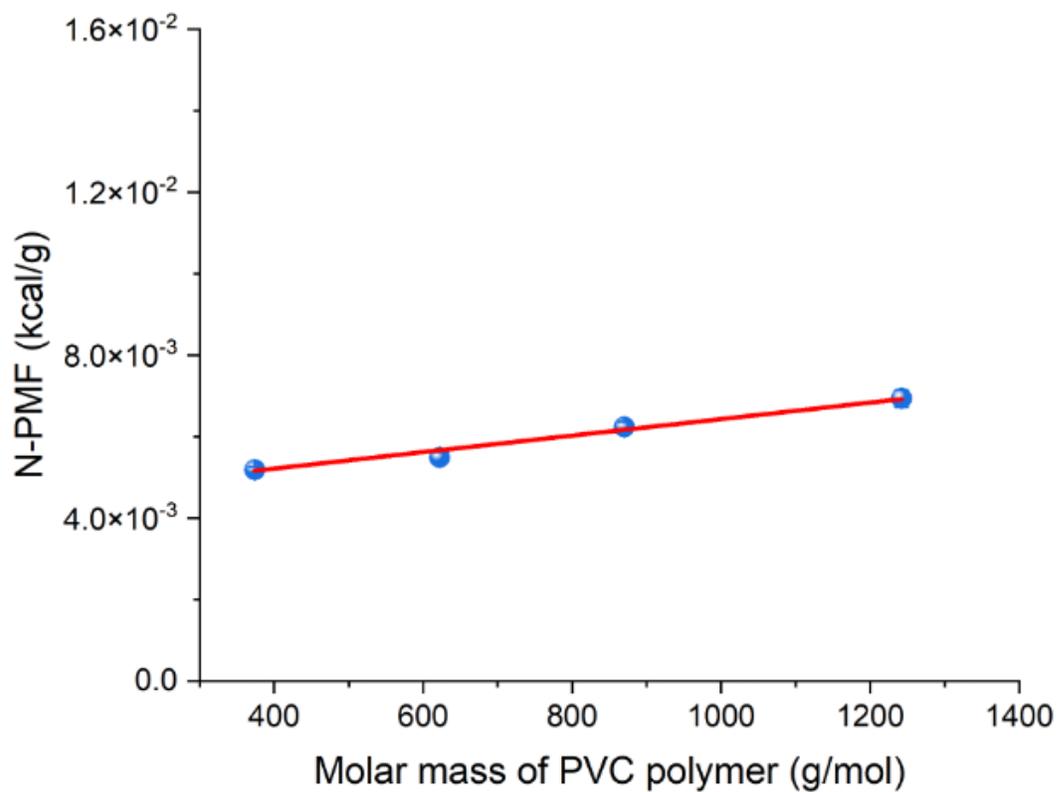
Figure S13: N-PMF plot of plasticizer DEHA with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 2.33×10^{-6} and a y-intercept of 1.77×10^{-3}.
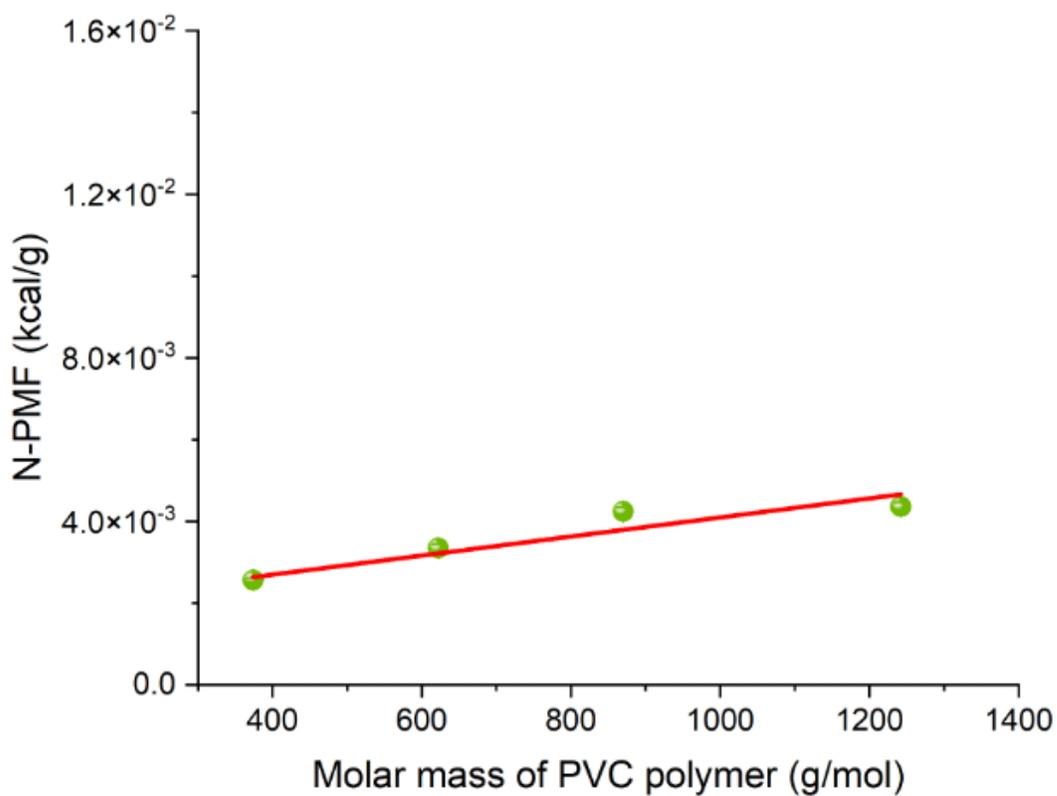
Figure S14: N-PMF plot of plasticizer DEHP with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 3.54×10^{-6} and a y-intercept of 3.23×10^{-3}.
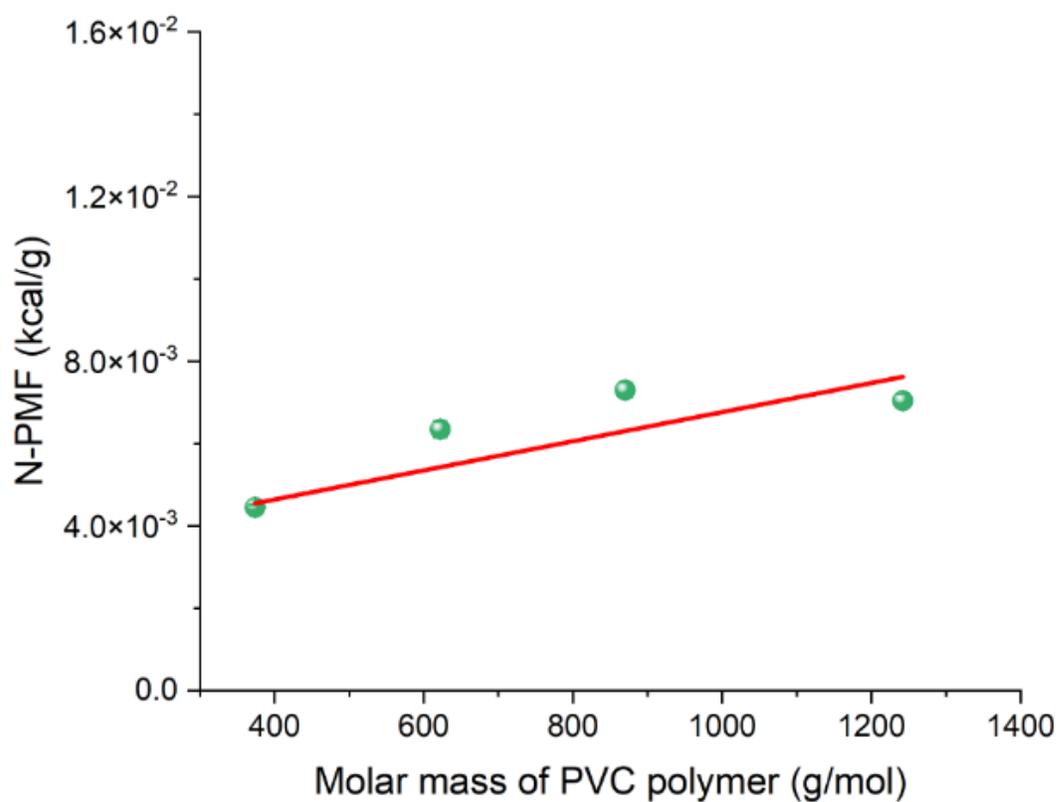
Figure S15: N-PMF plot of plasticizer DEHT with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 4.20×10^{-6} and a y-intercept of 2.10×10^{-3}.
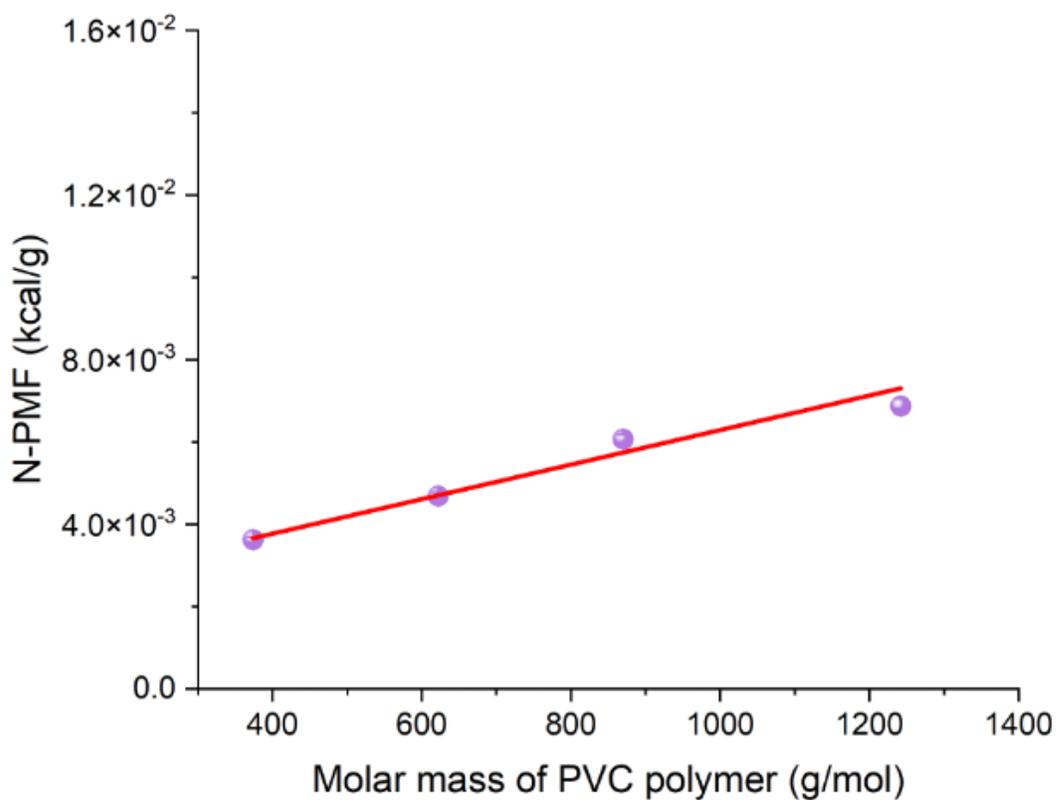
Figure S16: N-PMF plot of plasticizer DIBP with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of -7.83×10^{-7} and a y-intercept of 6.10×10^{-3}.
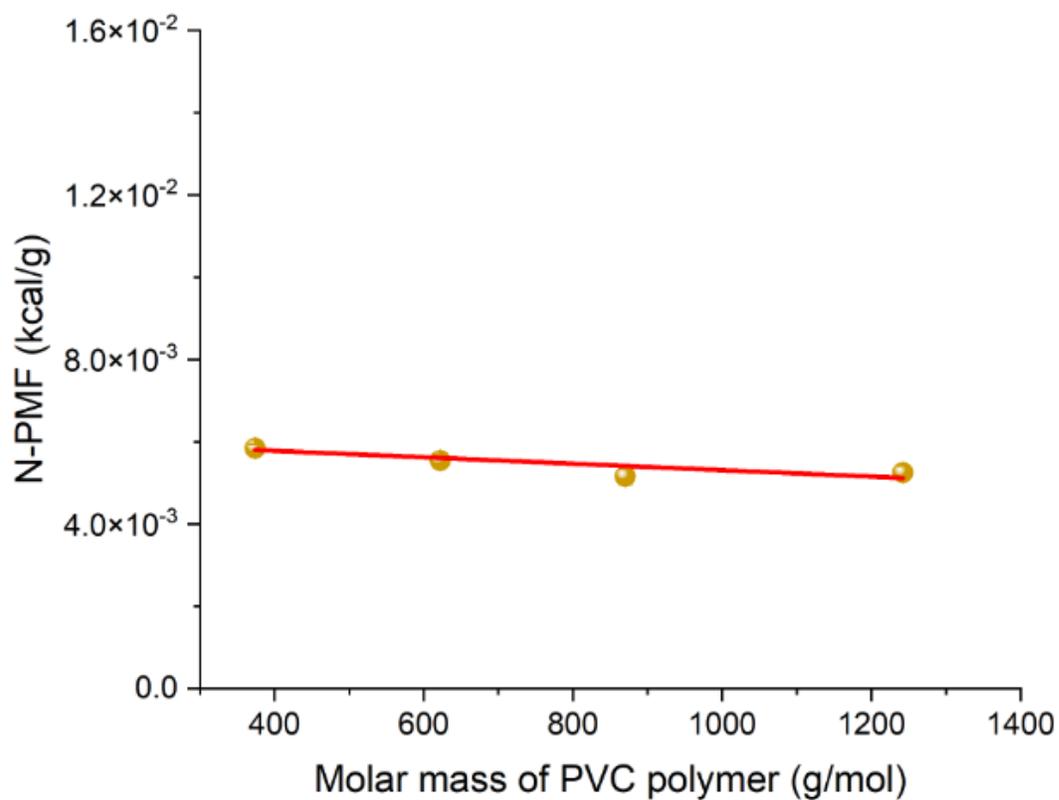
Figure S17: N-PMF plot of plasticizer DIDP with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 3.02×10^{-6} and a y-intercept of 2.98×10^{-3}.
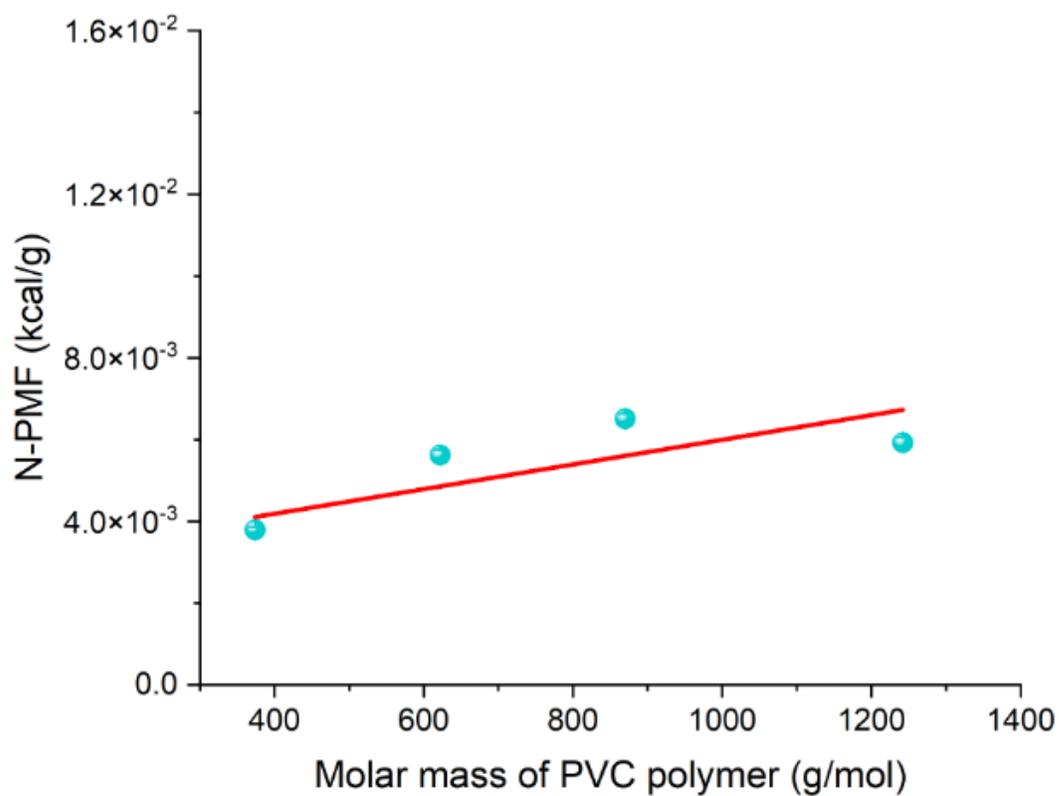
Figure S18: N-PMF plot of plasticizer DINP with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 3.22×10^{-6} and a y-intercept of 2.91×10^{-3}.

Figure S19: N-PMF plot of plasticizer DIOP with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 2.91×10^{-6} and a y-intercept of 3.44×10^{-3}.
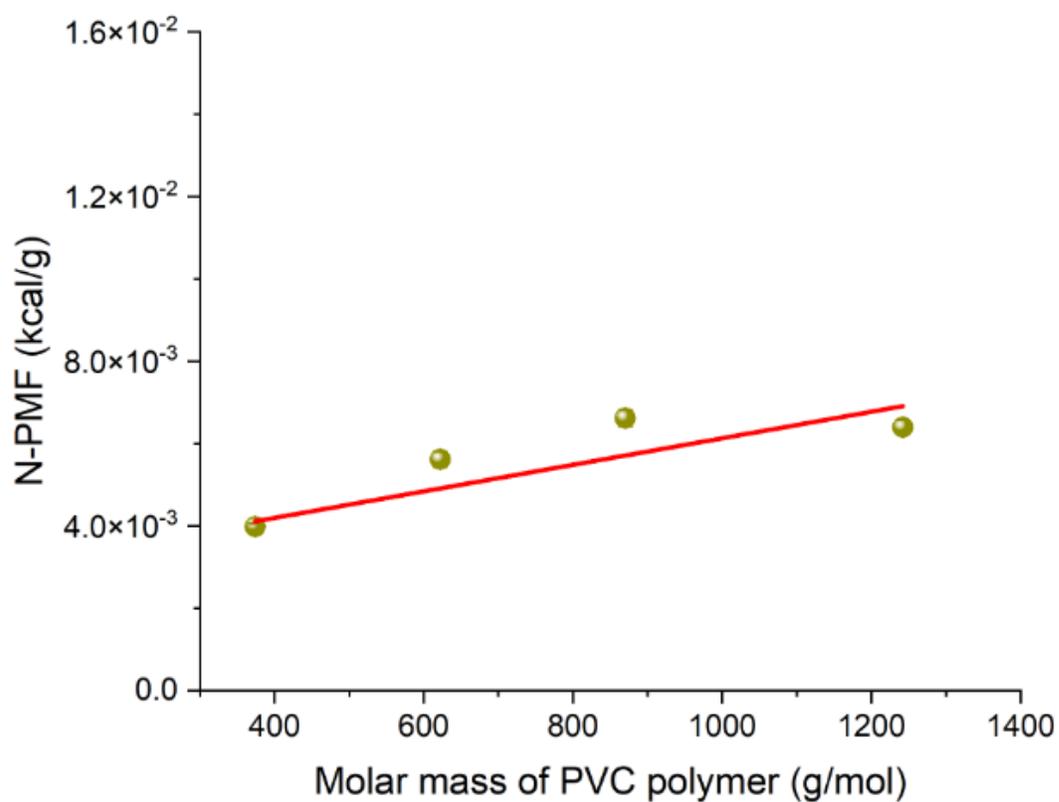
Figure S20: N-PMF plot of plasticizer DITP with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 3.48×10^{-6} and a y-intercept of 2.52×10^{-3}.
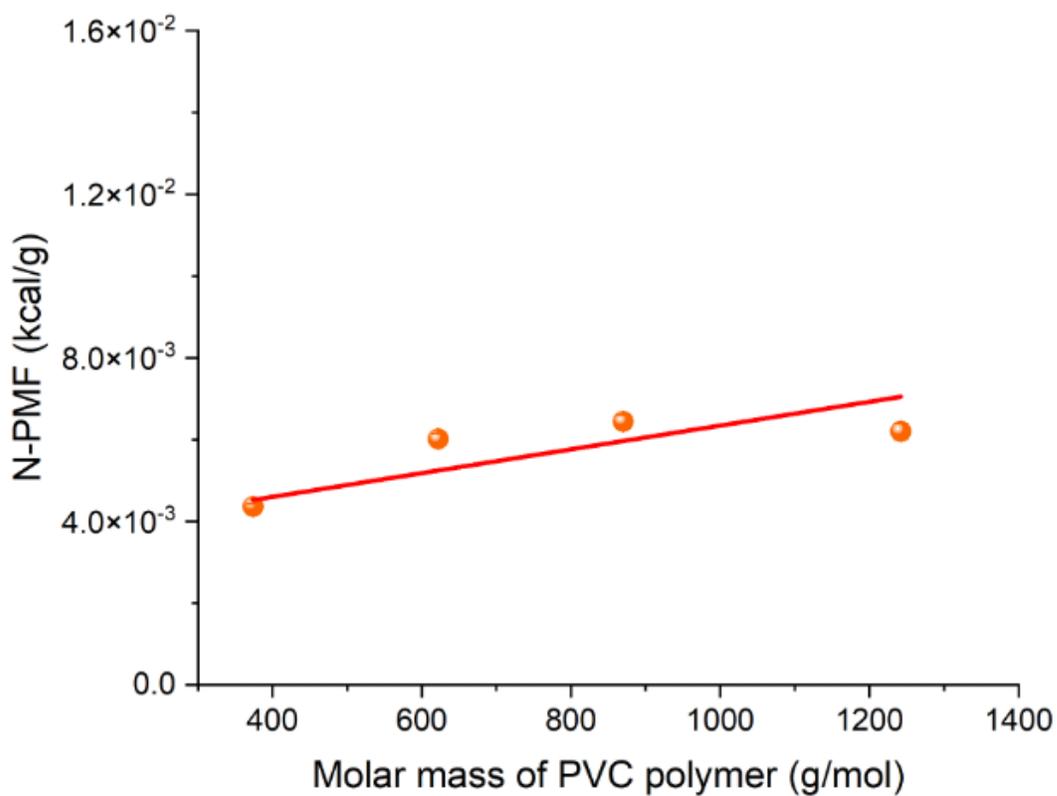
Figure S21: N-PMF plot of plasticizer DOA with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 2.43×10^{-6} and a y-intercept of 1.51×10^{-3}.
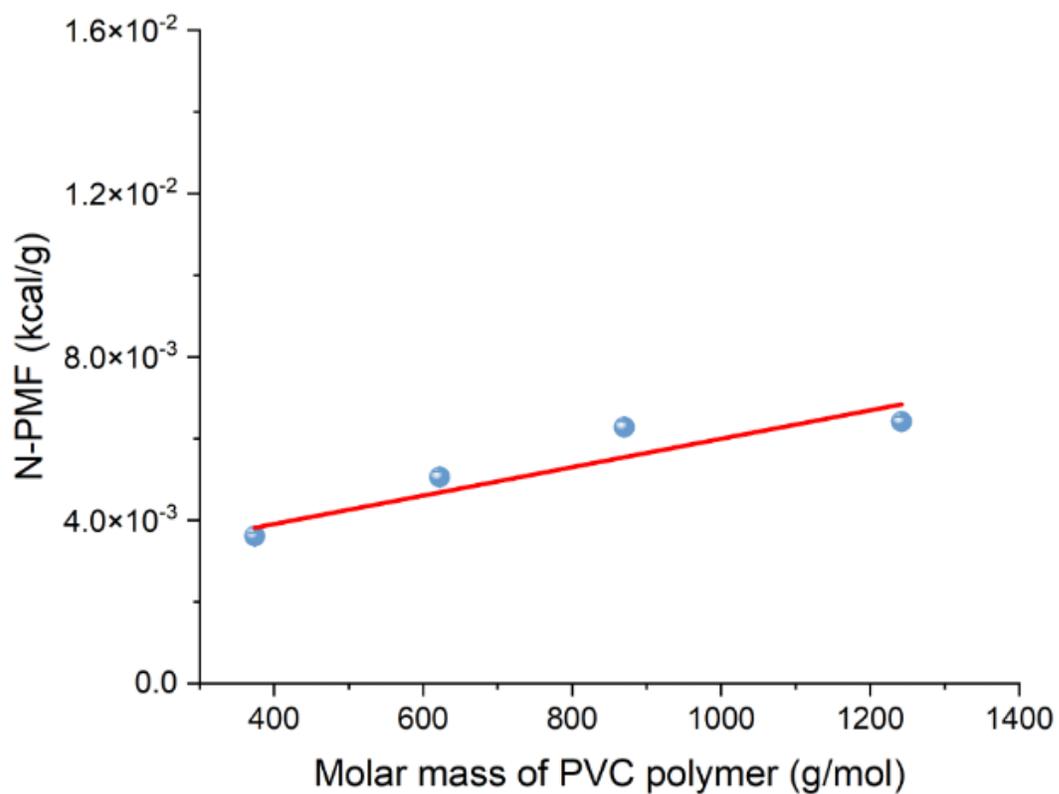
Figure S22: N-PMF plot of plasticizer DPHP with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 3.18×10^{-6} and a y-intercept of 3.55×10^{-3}.
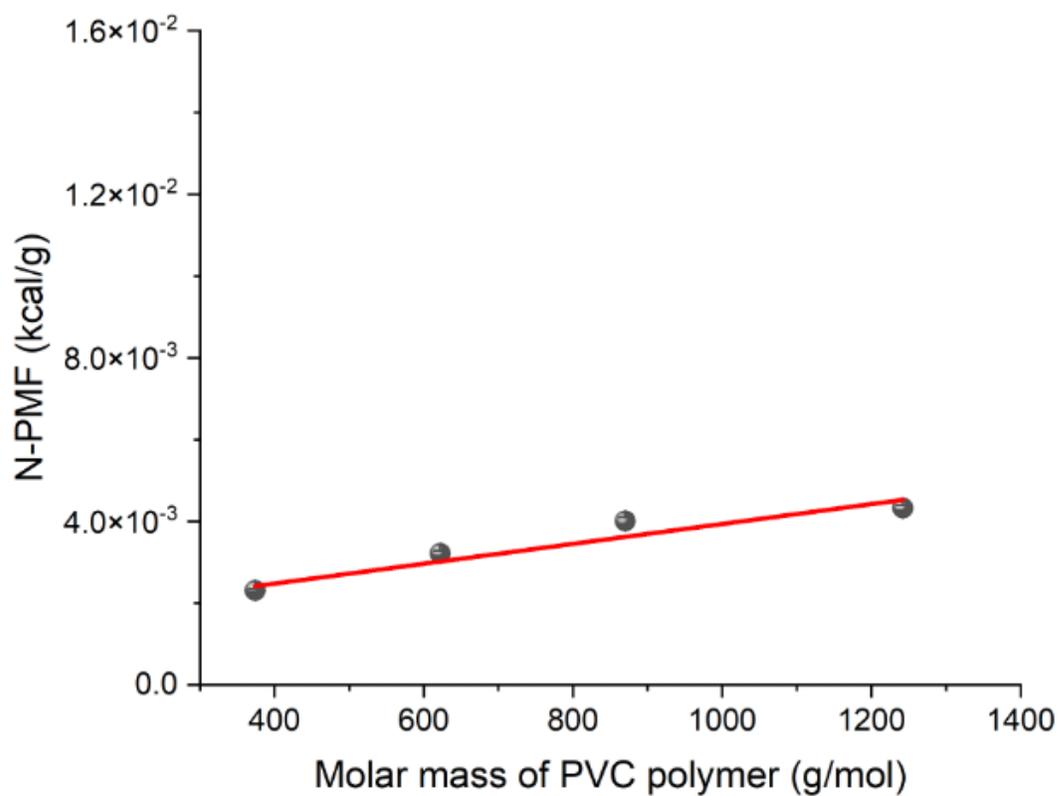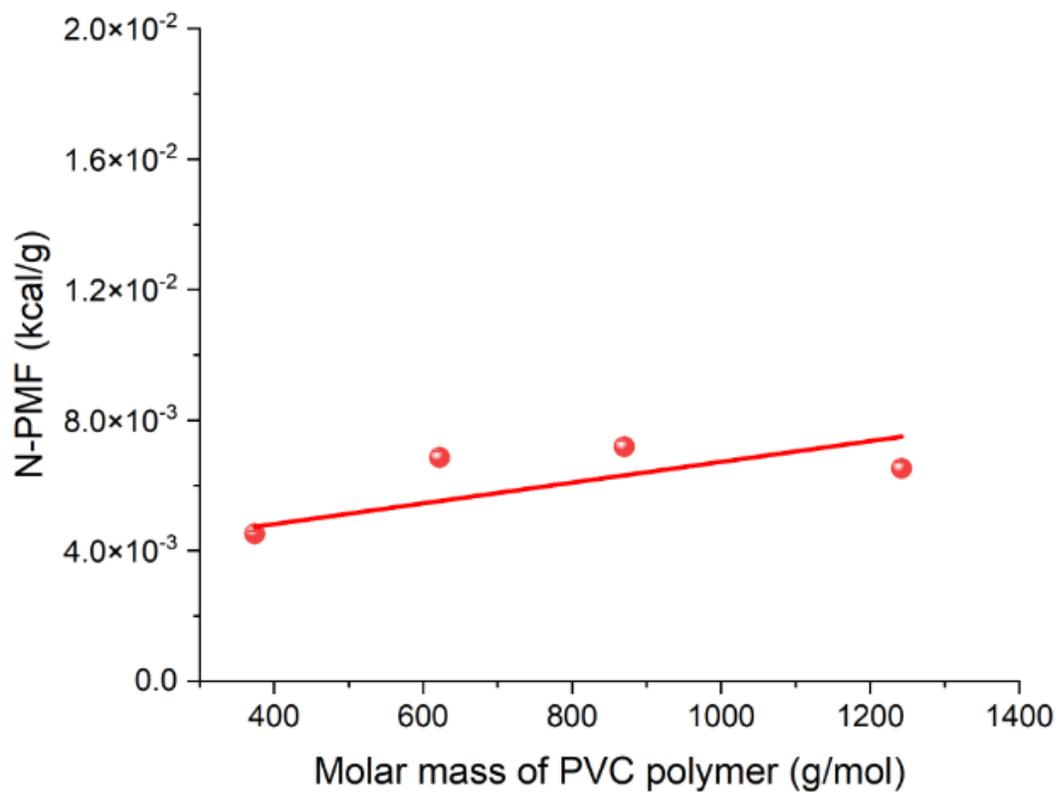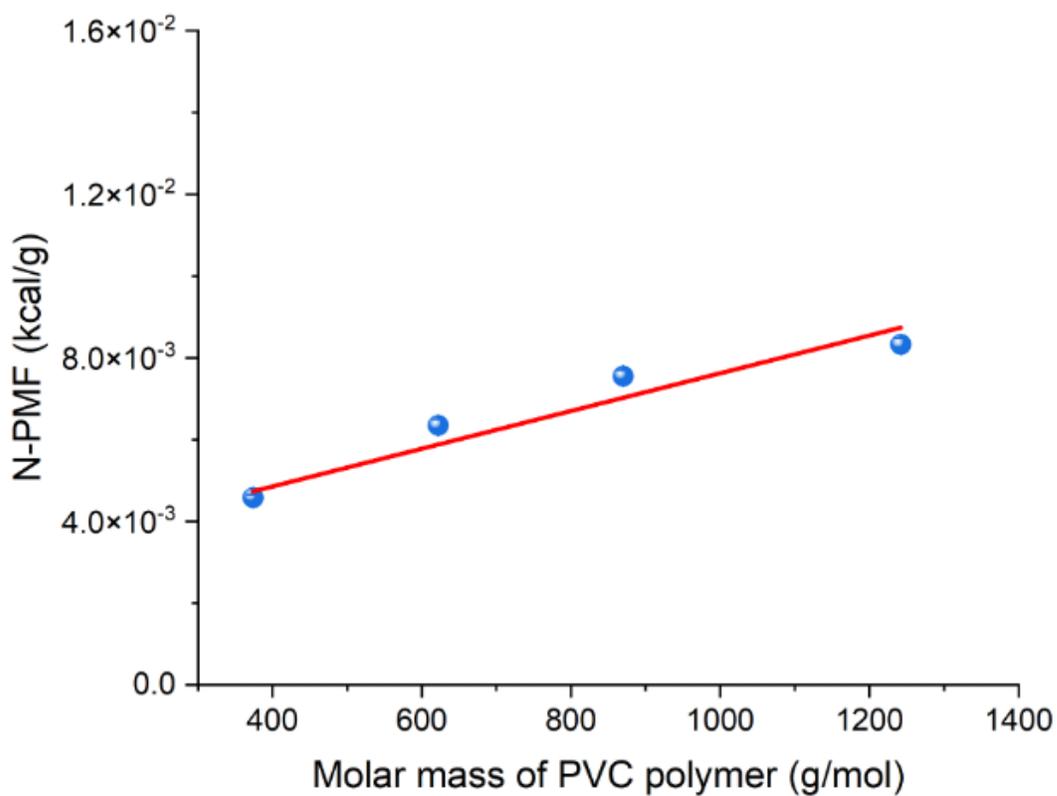
Figure S23: N-PMF plot of plasticizer TOTM with molar mass of PVC polymer of different lengths (6-20 repeating units). The linear fit of the data is also shown in the figure. Linear regression analysis of the data gave a slope of 4.61×10^{-6} and a y-intercept of 3.01×10^{-3}.
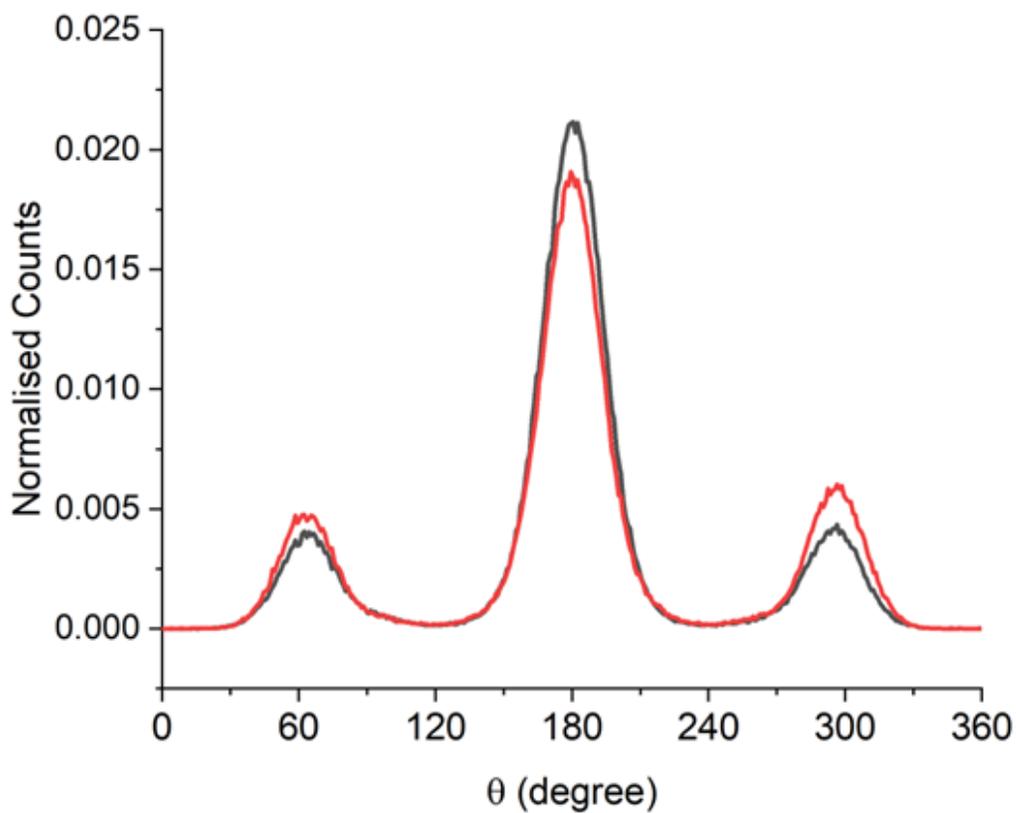
Figure S24: Histogram plot of all the backbone dihedral angles of PVC10 polymer in DITP - PVC10 system. Dihedral angles from total interaction studies are shown in Black (both LJ and Coulombic interactions included) and angles from only LJ studies, i.e., electrostatic interactions being turned off, are shown in red.

Figure S25: Radius of gyration (R_g) values of DIBP plasticizer and PVC polymer of 20 repeating units from DIBP-PVC20 potential of mean force (PMF) calculations along the reaction coordinate. The R_g values are plotted for both cases, one with only van der Waals interactions (Blue triangles-PVC; Green triangles-DIBP) and the other considering all interactions *i.e.*, both van der Waals and electrostatic interactions (Black squares-PVC20; Red circles-DIBP) between PVC polymer and plasticizer.
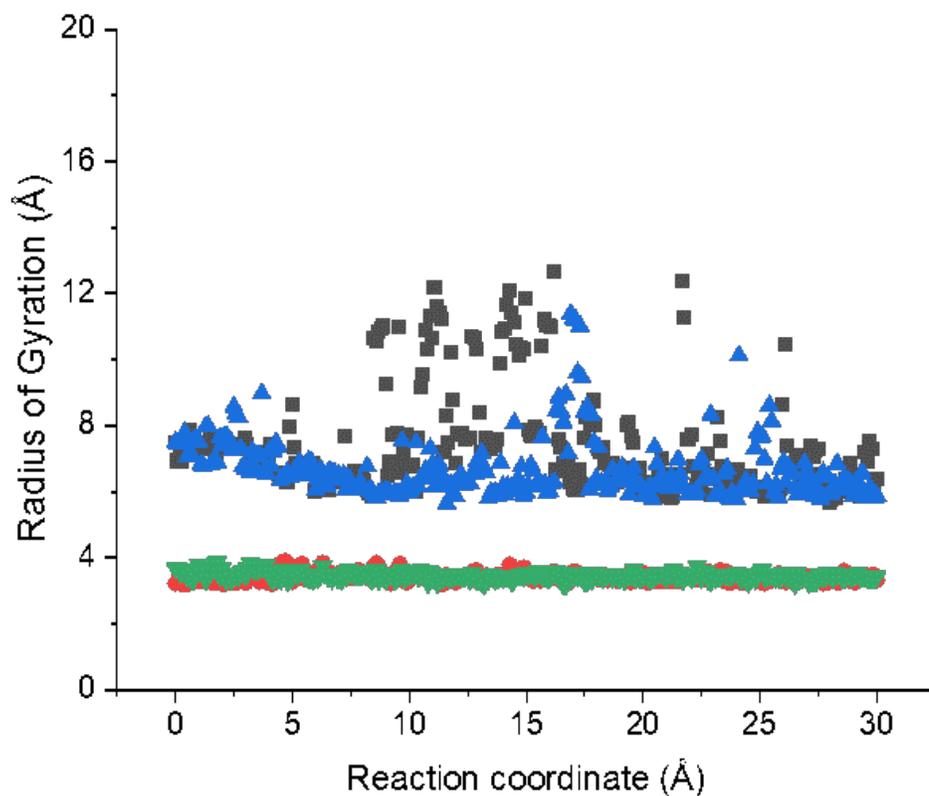
Figure S26: Radius of gyration (R_g) values of DITP plasticizer and PVC polymer of 20 repeating units from DITP-PVC20 potential of mean force (PMF) calculations along the reaction coordinate. The R_g values are plotted for both cases, one with only van der Waals interactions (Blue triangles-PVC; Green triangles-DITP) and the other considering all interactions *i.e.*, both van der Waals and electrostatic interactions (Black squares-PVC20; Red circles-DITP) between PVC polymer and plasticizer.
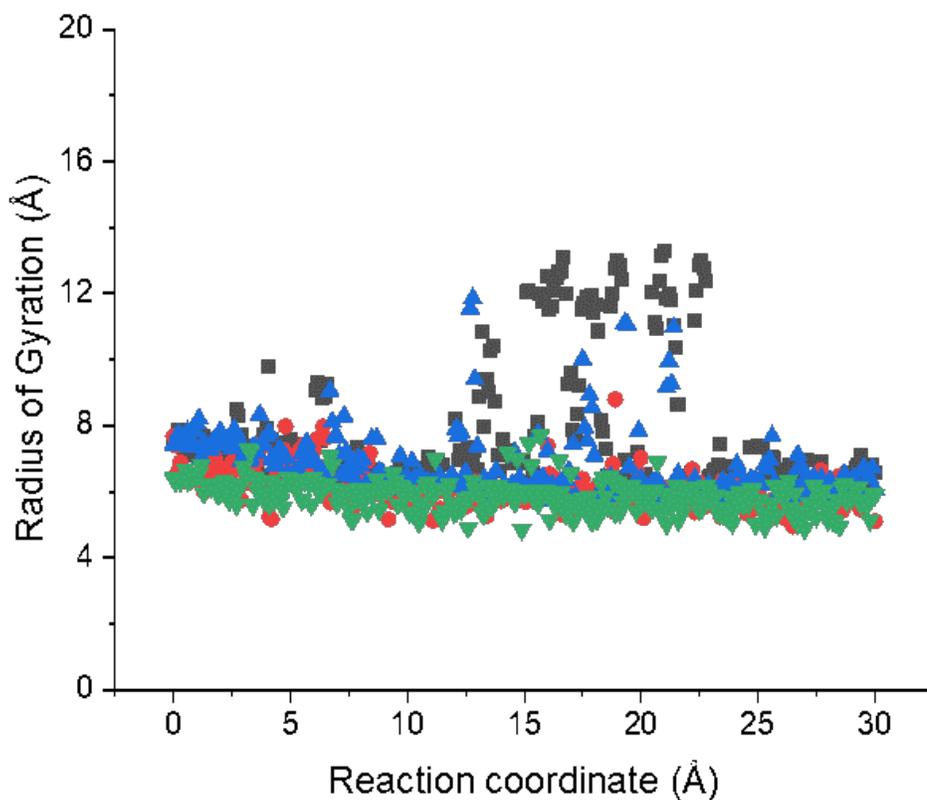
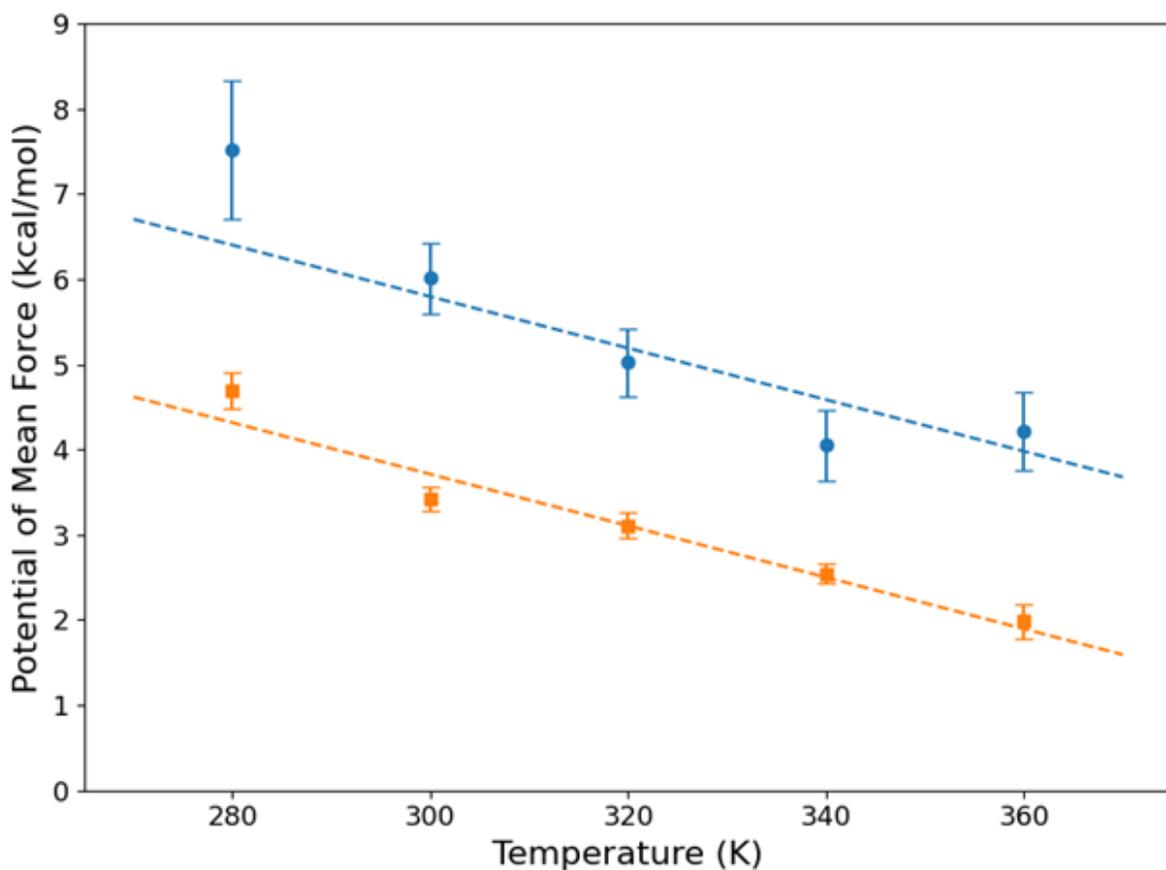Figure S27: Plot of PMF vs temperature of DITP - PVC10 system. PMF data points arising from total interactions (both LJ and Coulombic) are shown in Blue and the PMF data from LJ only studies are shown in orange. The linear fits of the data shown by dashed lines resulted in a slope (m) of -0.030 $\pm$ 0.003; intercept (b1) of 14.87 $\pm$ 0.90; intercept (b2) = 12.79 $\pm$ 0.88; and Global weighted R^2 = 0.95.
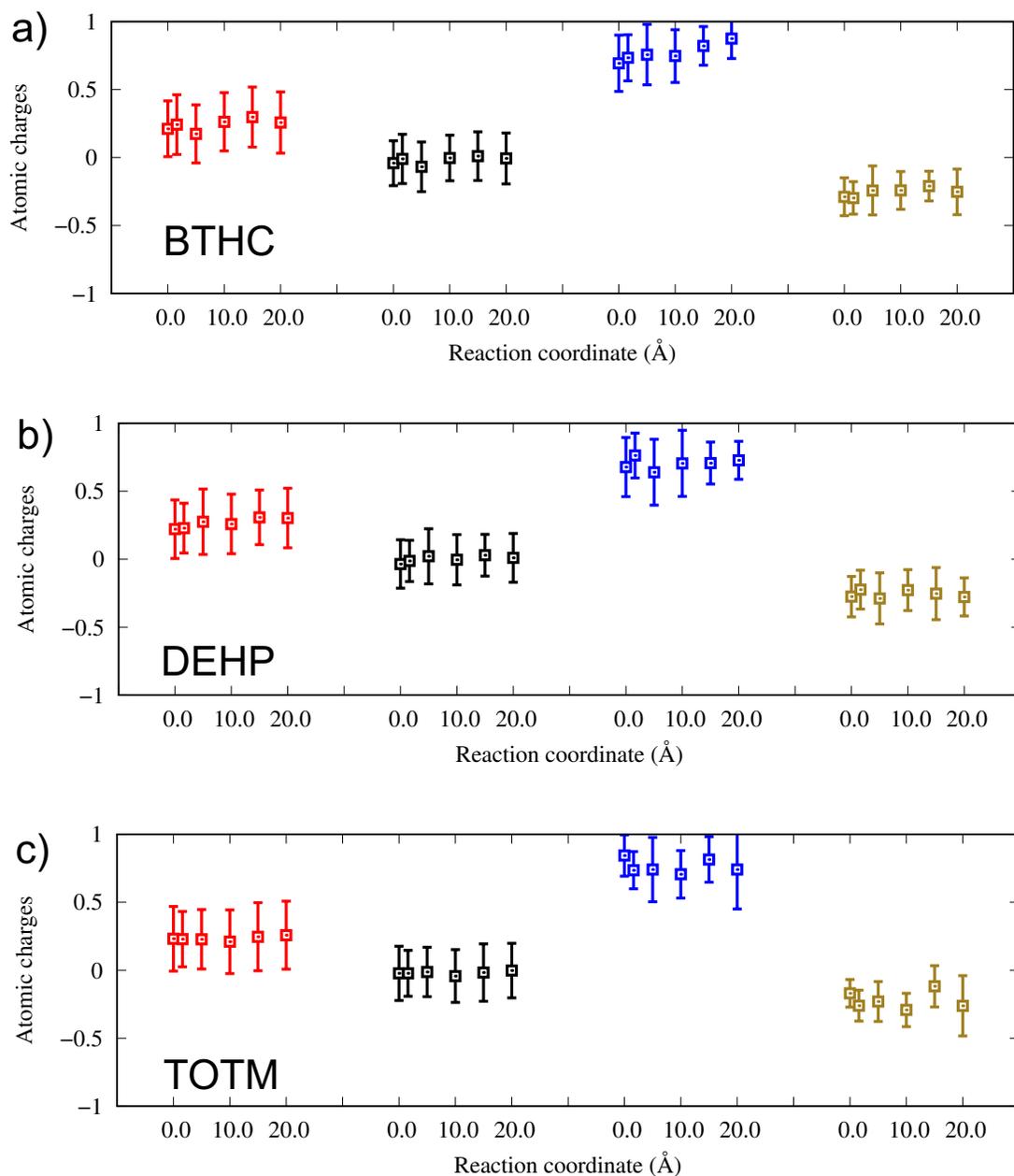
Figure S28: Average CHELPG atomic charges (squares) and corresponding RMS fluctuations (error bars) are shown as a function of the reaction coordinate (RC) from ωB97X-D3 single-point DFT calculations for PVC-20 in contact with (a) BTHC, (b) DEHP, and (c) TOTM. For each RC value (0.0–20.0 Å), the reported charges are averaged over an ensemble of 11 MD snapshots. Four charge descriptors are reported(from left to right) for each system: (i) the charge on the PVC carbon atom adjacent to Cl (C_{adj}, red), (ii) the total charge of the –CCl group (C_{adj}+Cl, black), (iii) the charge on the plasticizer ester carbon atom (C_{ester}, blue), and (iv) the total charge of the ester group (sum of CHELPG charges over atoms in the ester group, green).
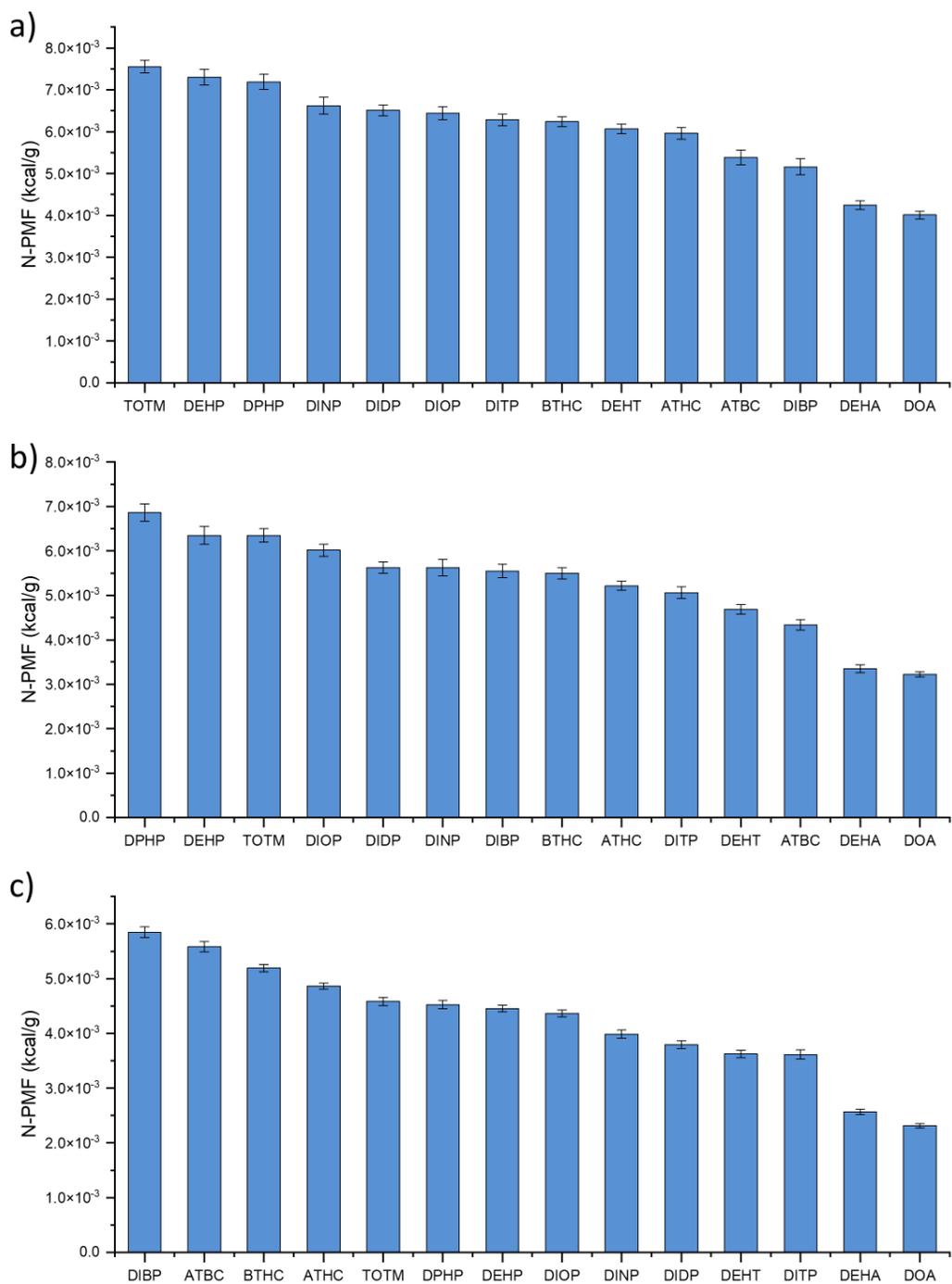
Figure S29: N-PMF values obtained from interaction studies between a PVC polymer with 14, 10, and 6 repeating units, respectively, and various plasticizers
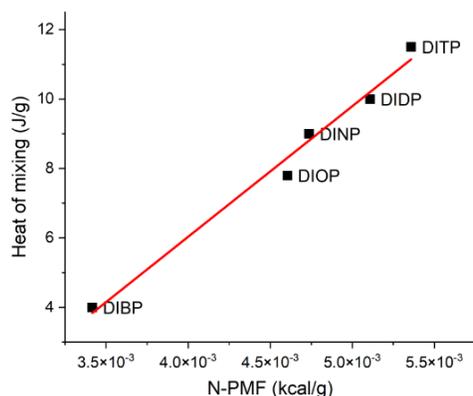
Figure S30: Correlation between the N-PMF valves obtained for interaction between PVC20 and five orthophthalates and the heat of mixing calculated in ref.[5]

References

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