

# **Molecular dynamics calculations for the temperature response of poly(alkylated tri(ethylene oxide)isocyanate) aqueous solution**

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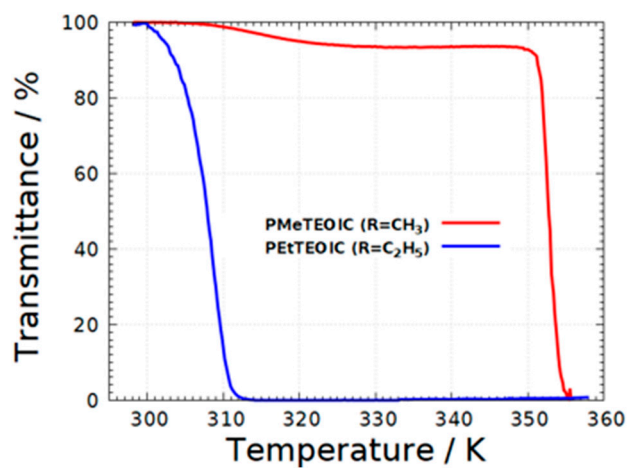
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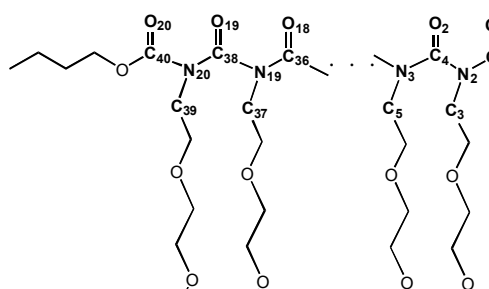


**Figure S1.** Transmittance versus temperature plots of 40 g L<sup>-1</sup> aqueous PMeTEOIC and PEtTEOIC solutions. The data were recorded at 400 nm at the heating rate of 1 K, reproduced from Reference [30] in the main text.

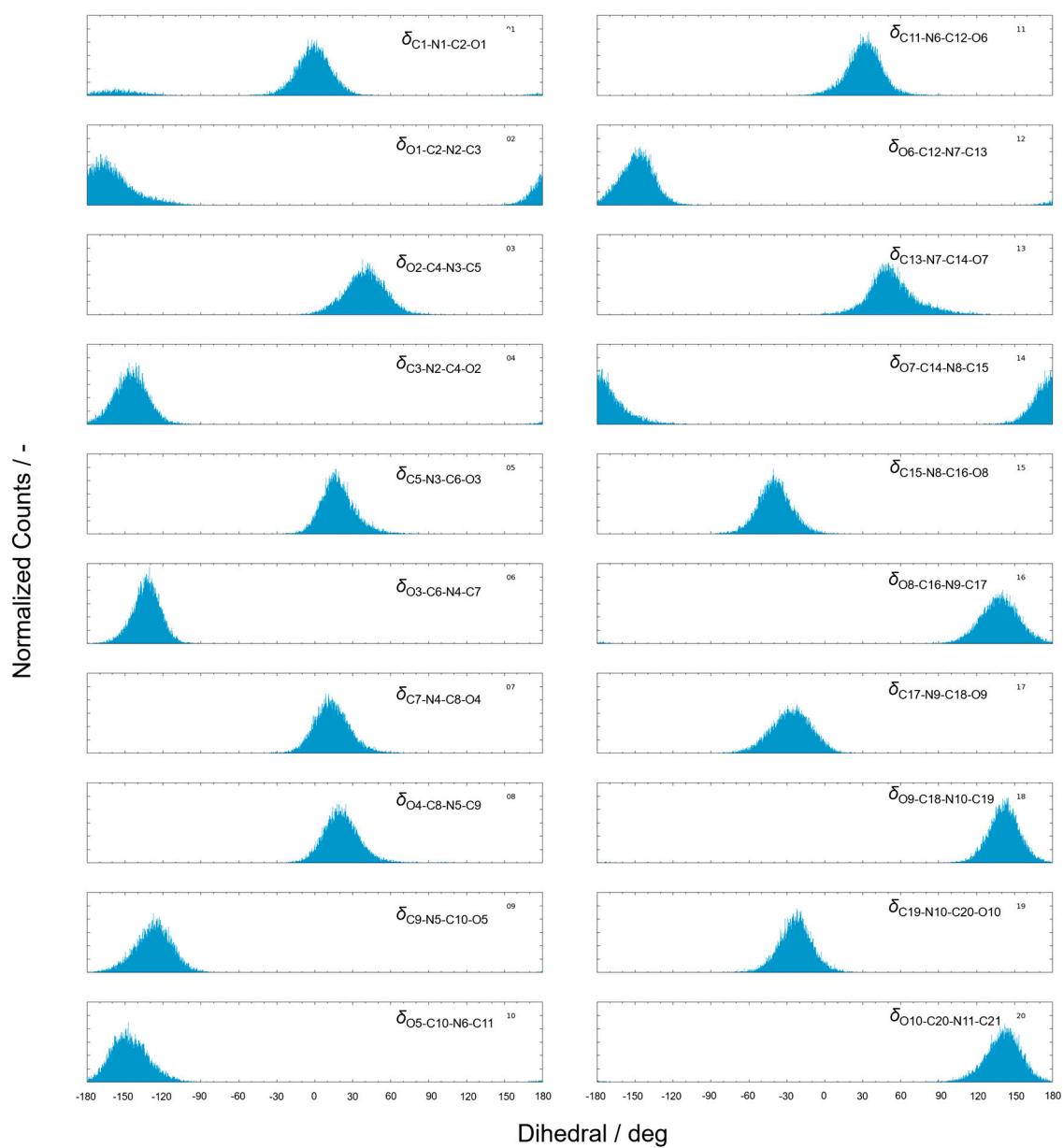
**Table S1.** Water numbers, molecular weight of polymers, and the concentrations of polymers.

polymer	$N_w$ <sup>1</sup>	$M_w$ <sup>2</sup>	g/L
(PMeTEOIC) <sub>2</sub>	6791	3854	63.1
(PEtTEOIC) <sub>2</sub>	7739	4134	59.3

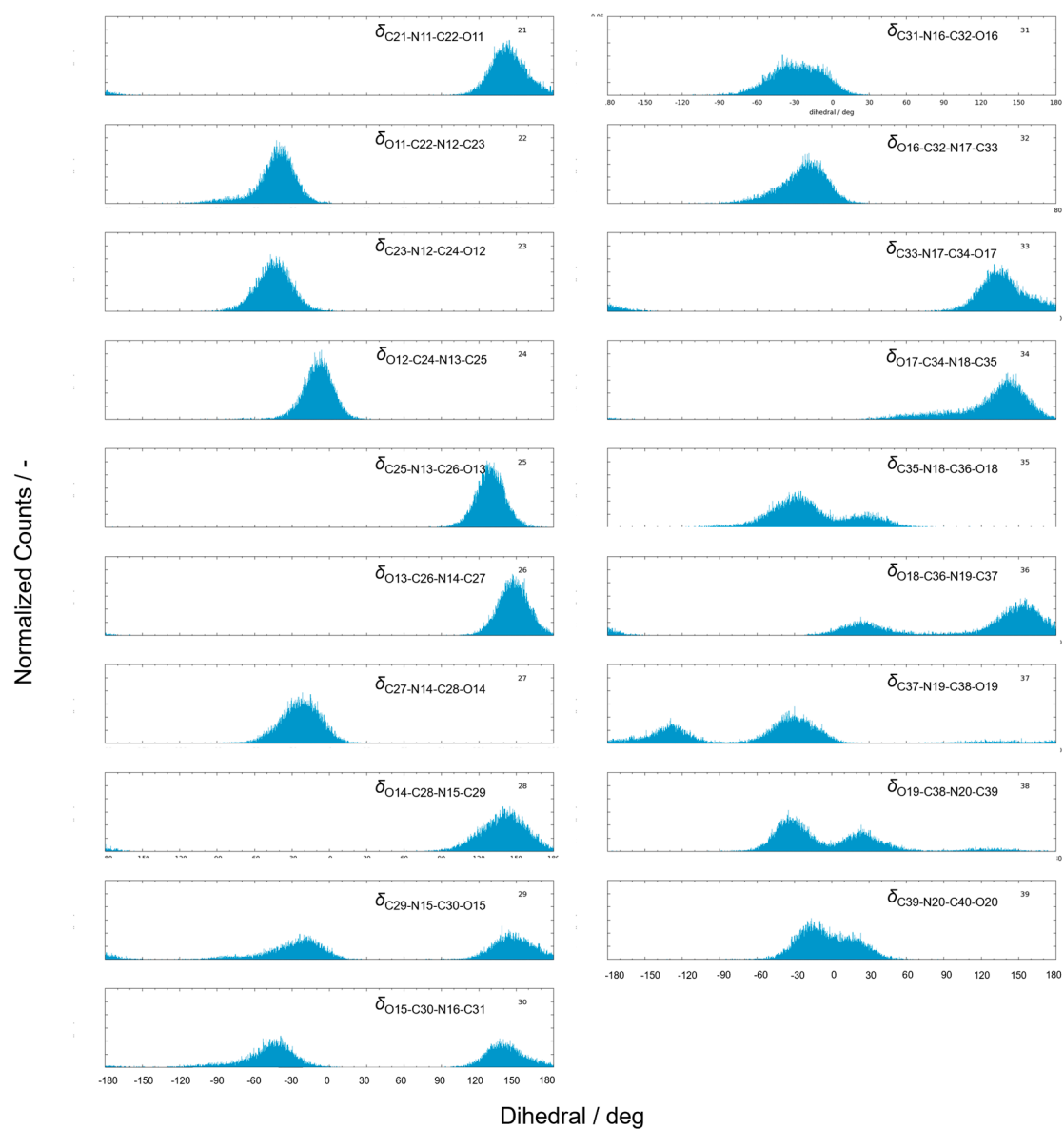
<sup>1</sup> The number of water molecules. <sup>2</sup> The molecular weight of polymers.



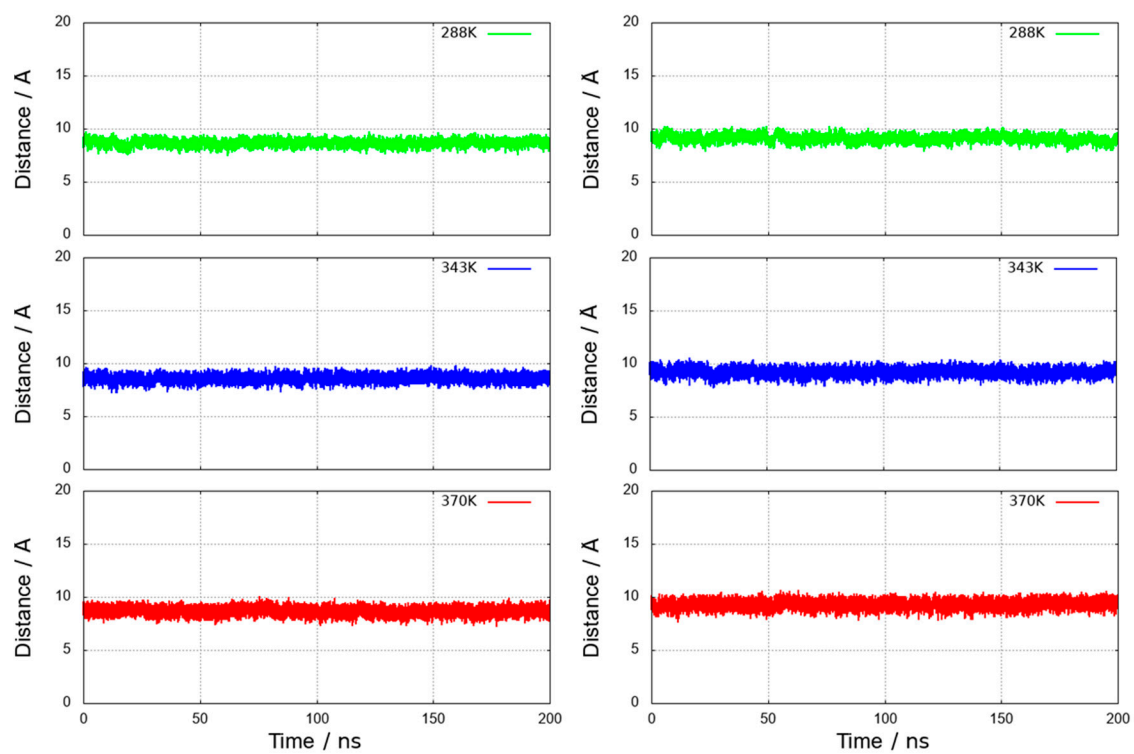
**Figure S2.** The chemical structure of PRTEOIC with the numbering of atoms which compose the dihedral angles in the polymer main chain.



**Figure S3.** Distributions of dihedral angles ( $\delta_{C1-N1-C2-O1}$ – $\delta_{O10-C20-N11-C21}$ ) in the main chain of PMeTEOIC at 363 K.

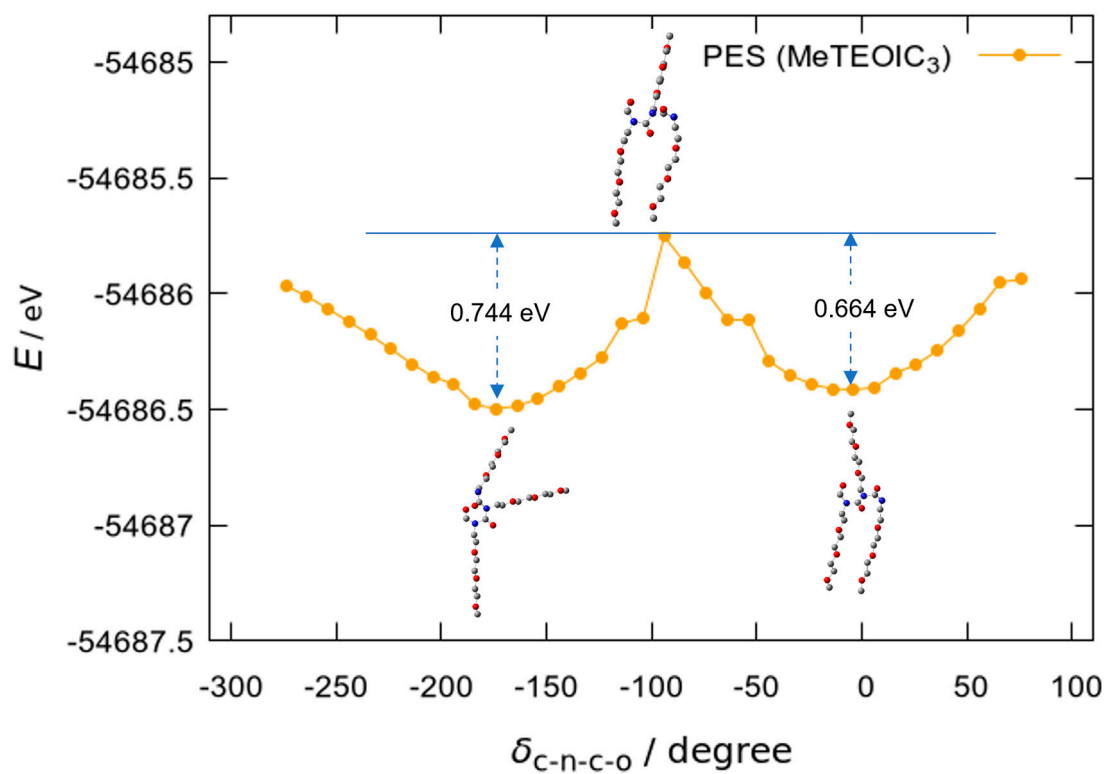


**Figure S4.** Distributions of dihedral angles ( $\delta_{C21-N11-C22-O11}$ – $\delta_{C39-N20-C40-O20}$ ) in the main chain of PMeTEOIC at 363 K.

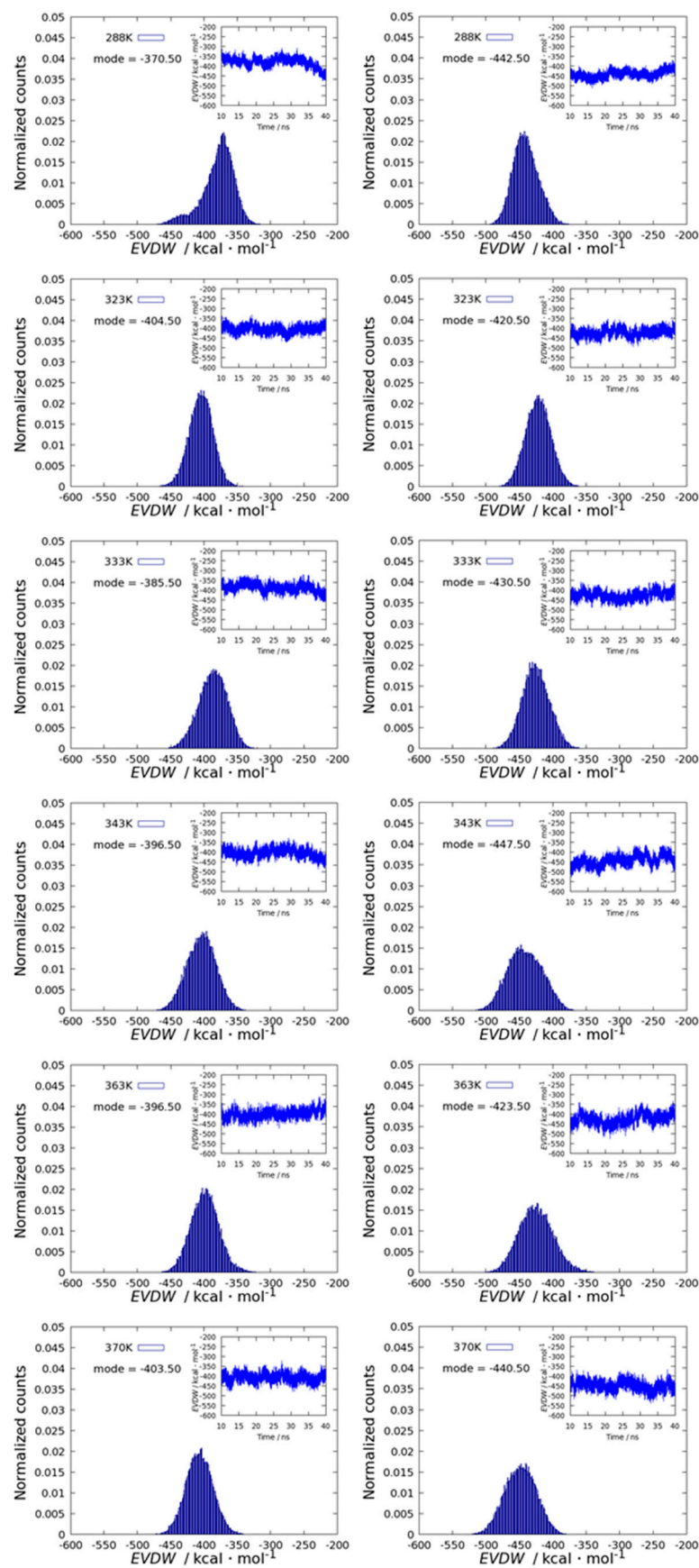


**Figure S5.** The side chain end-to-end distances for PMeTEOIC (left) and PEtTEOIC (right) at 288 K, 343 K and 370 K for 200 ns.

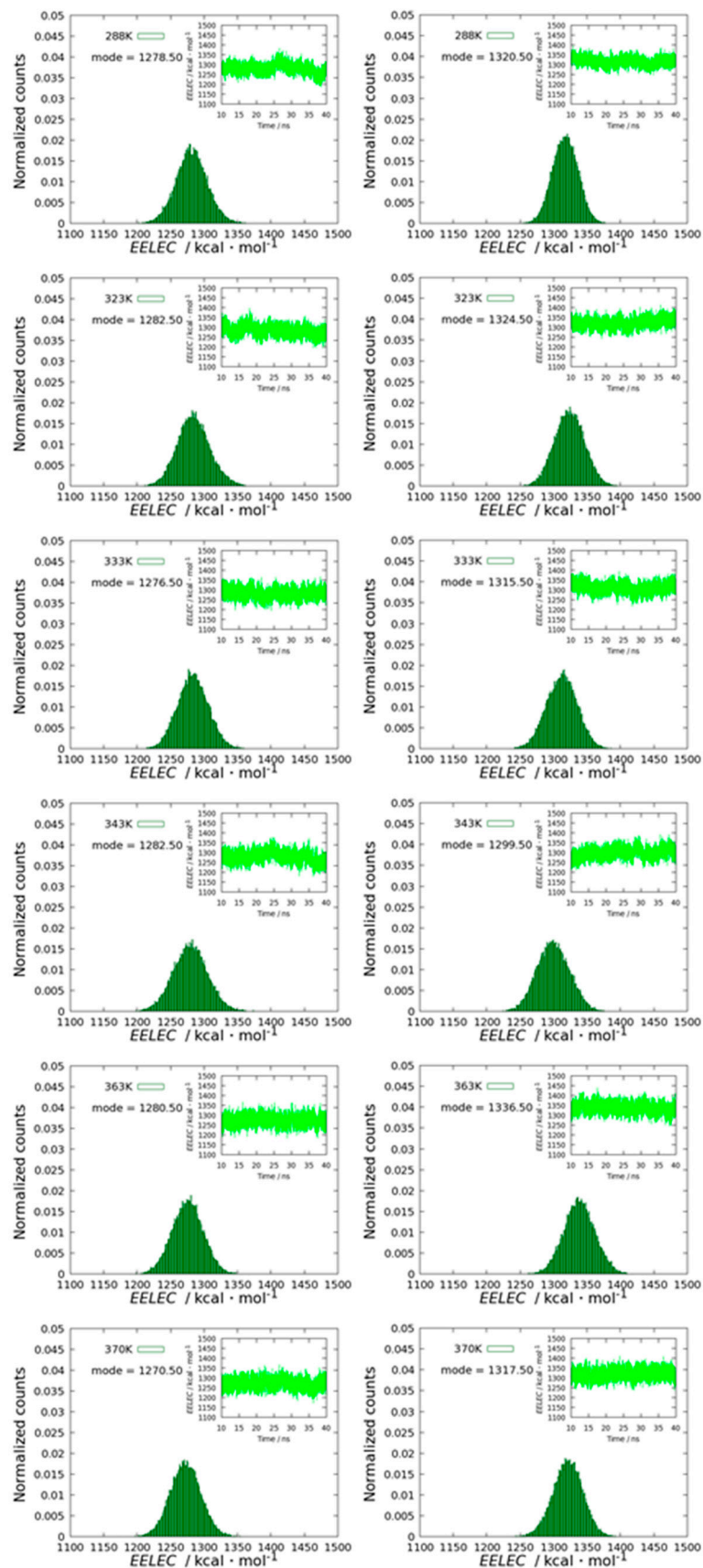
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**Figure S6.** Potential Energy Surface (PES) along with the rotation of MeTEOIC<sub>3</sub> main chain was shown. Horizontal axis is the dihedral angle ( $\delta_{C-N-C-O}$ ) which consists of four atoms in trimer backbone. The calculations were conducted at B3LYP/6-31G(d) level.

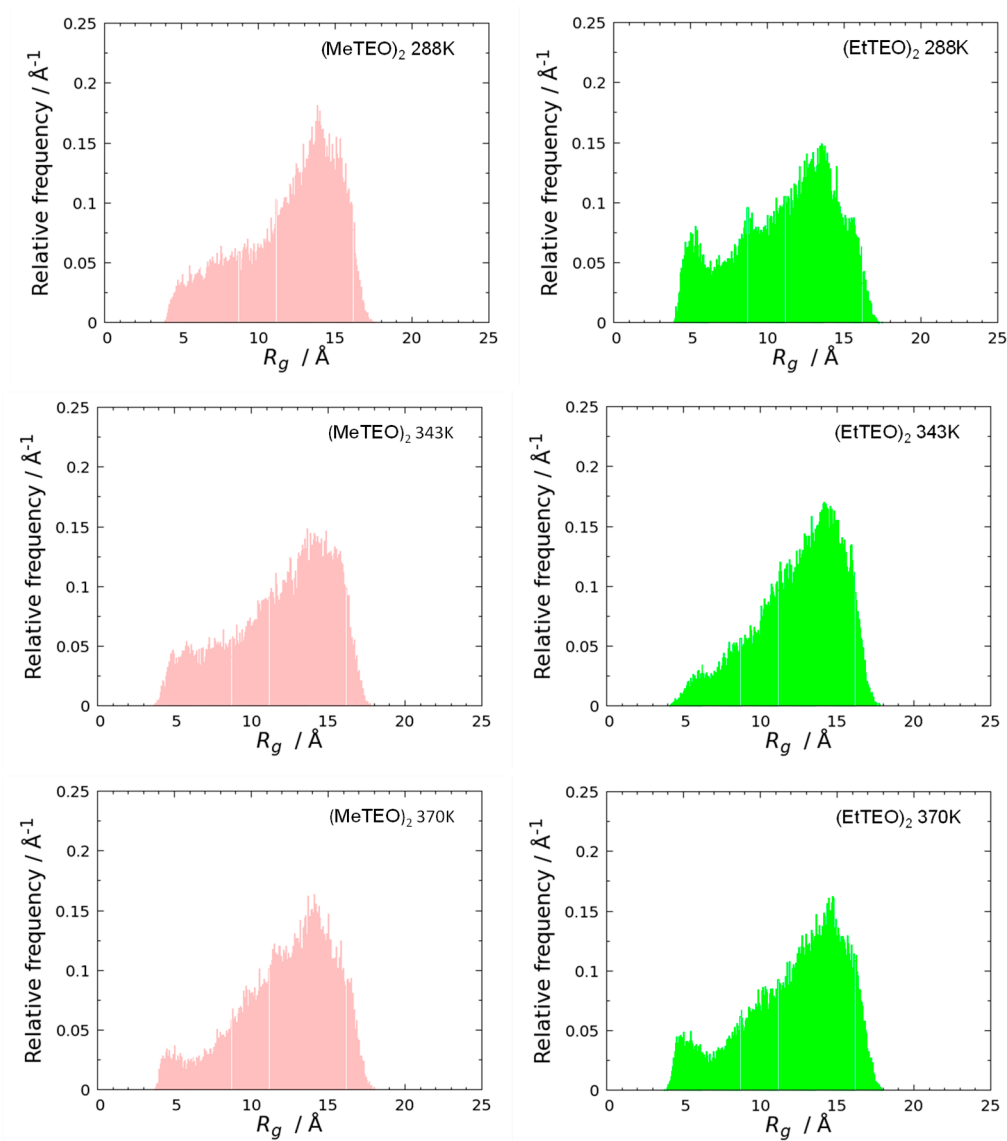


**Figure S7.** Distributions of Van der Waals energy (EVDW) for (PMeTEOIC)<sub>2</sub> (left) and (PEtTEOIC)<sub>2</sub> (Right) at six temperatures from 288 K to 370 K.



**Figure S8.** Distributions of electrostatic energy ( $EELEC$ ) for  $(PMeTEOIC)_2$  (left) and  $(PEtTEOIC)_2$  (Right) at six temperatures from 288 K to 370 K.





**Figure S9.**  $R_g$  distributions of  $(\text{MeTEO})_2$  (left) and  $(\text{EtTEO})_2$  (right) in water at 288, 343, and 370K.

**Table S2.** Electrostatic energy for (PRTEOIC)<sub>2</sub> at six temperatures.

polymer chains	$E_{elec}$ [kcal/mol]						$\mu^1$	$\sigma^2$
	283 K	323 K	333 K	343 K	363 K	370 K		
(PMeTEOIC) <sub>2</sub>	1280	1280	1280	1280	1280	1270	1280	4
(PEtTEOIC) <sub>2</sub>	1320	1320	1320	1300	1340	1320	1320	12

<sup>1</sup> Value of  $E_{elec}$  averaged over six temperatures. <sup>2</sup> Standard deviation of  $E_{elec}$  at six temperatures.

**Table S3.** Van der Waals energy for (PRTEOIC)<sub>2</sub> at six temperatures.

polymer chains	$E_{vdW}$ [kcal/mol]						$\mu^1$	$\sigma^2$
	283 K	323 K	333 K	343 K	363 K	370 K		
(PMeTEOIC) <sub>2</sub>	−370	−400	−390	−400	−400	−400	−390	12
(PEtTEOIC) <sub>2</sub>	−440	−420	−430	−450	−420	−440	−430	10

<sup>1</sup> Value of  $E_{elec}$  averaged over six temperatures. <sup>2</sup> Standard deviation of  $E_{elec}$  at six temperatures.