Supporting Information: Exploring the Role of Hydroxy- and Phosphate-Terminated cis-1,4-Polyisoprene Chains in the Formation of Physical Junction Points in Natural Rubber: Insights from Molecular Dynamics Simulations

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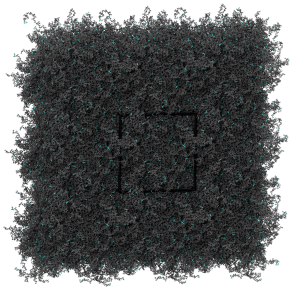
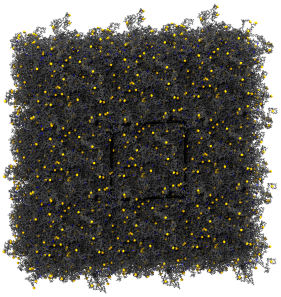
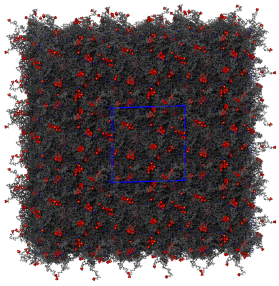


(a) PI_0 ($_HPI_H$)

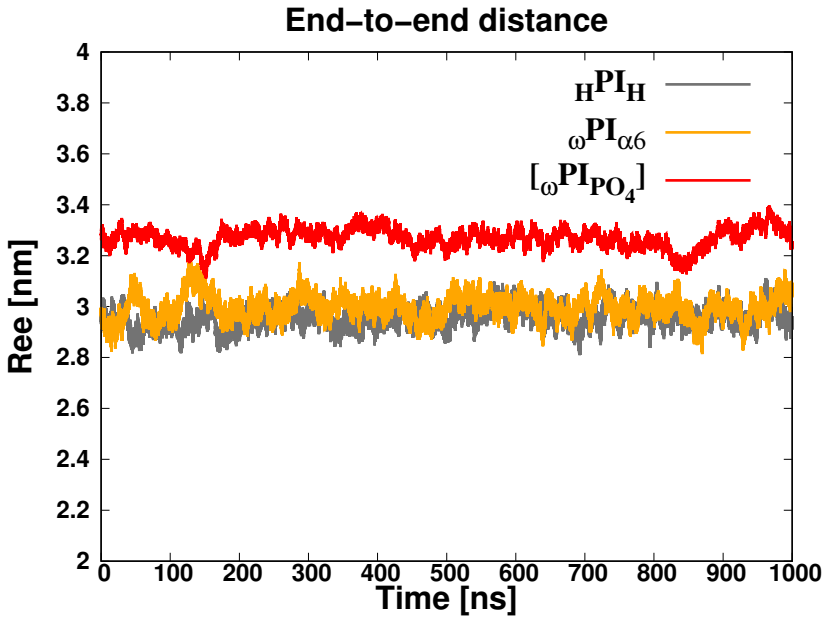


(b) PI_{VI} ($_\omega PI_{\alpha 6}$)

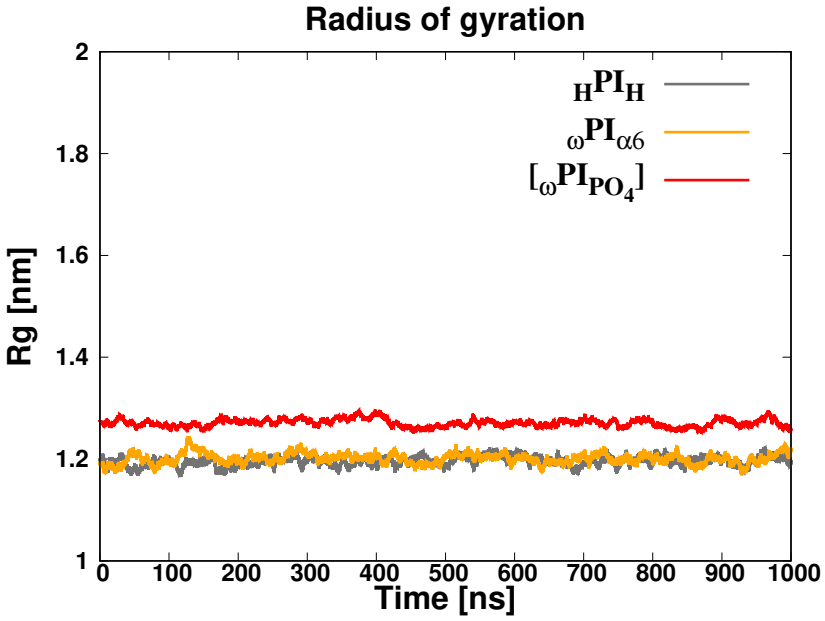


(c) PI_{ph} ($_\omega PI_{PO_4}$)

Figure S1: The initial structures of (a) PI_0, (b) PI_{VI} and (c) PI_{ph} melt systems. Dimethyl allyl group of ω terminals (Dimethyl allyl group and two trans-1,4-isoprene) are shown by blue and cis-1,4-isoprene, $\alpha 6$ and PO_4 terminals are shown by cyan, orange and red colors respectively. The backbone carbon and hydrogen atoms of each main PI chain are shown in gray color.



(a) The end-to-end distance vs time.



(b) The Radius of gyration vs time

Figure S2: The end-to-end distance vs time (a) and Radius of gyration vs time (b) for each melt system in NVT ensemble.

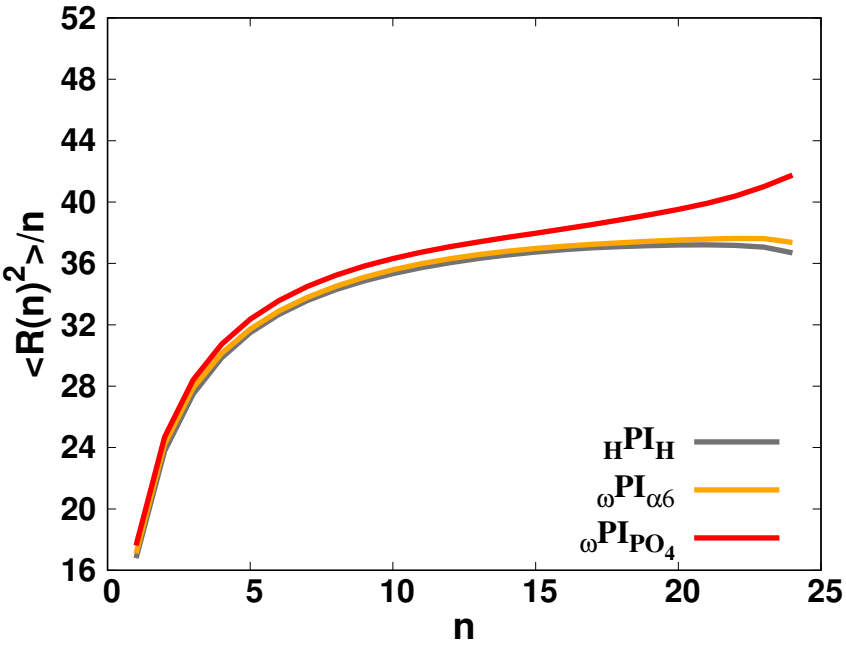


Figure S3: The mean square internal distances for the three different melt systems.

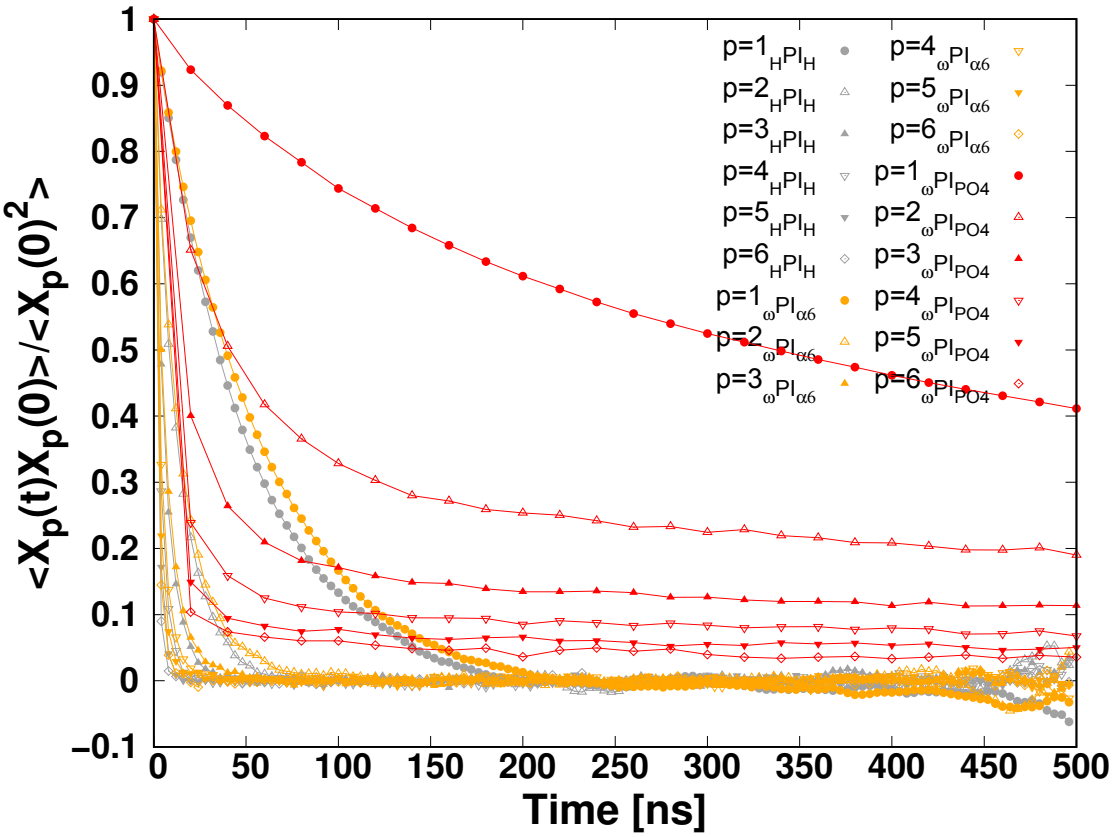


Figure S4: Time autocorrelation function of normal modes p =1, 2, 3, 4, 5 and 6 for each melt system, as obtained from the all-atom MD simulations.

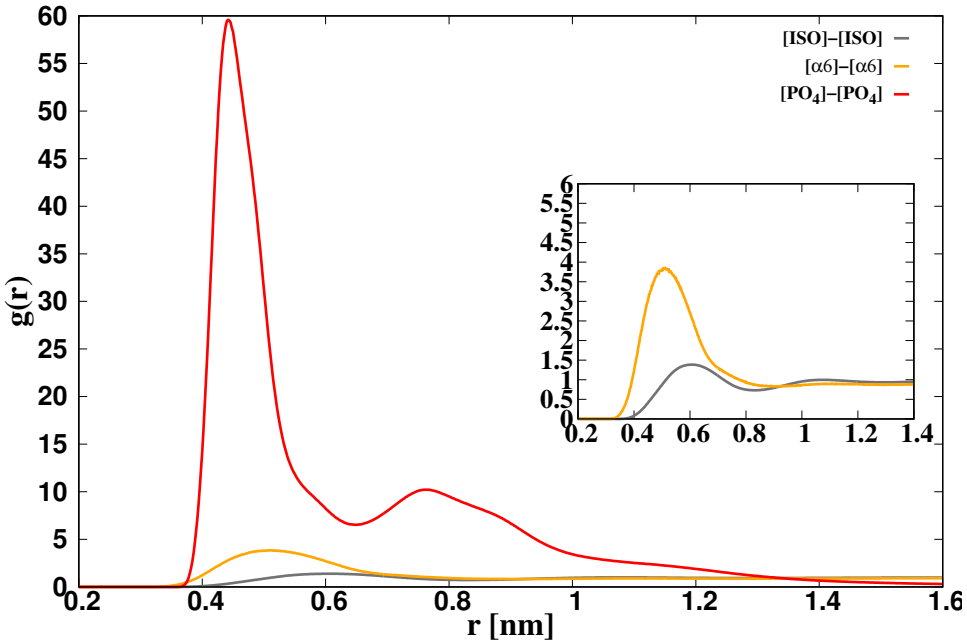


Figure S5: The radial distribution function between the terminals of cis polyisoprene. In the case of pure PI, the center of mass of isoprene residues of terminals and for PI_{VI} melt system, the center of mass of $\alpha 6$ terminal and for PI_{ph} melt system, the center of mass of PO_4 terminal group are chosen for RDFs calculations.

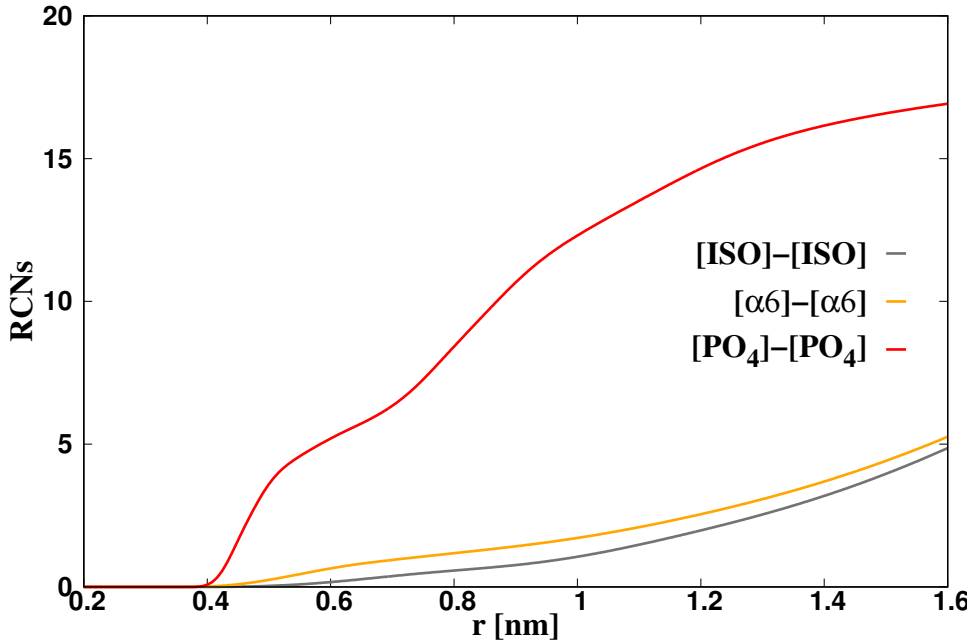


Figure S6: The running coordination numbers (RCNs) between the terminals of cis polyisoprene. In the case of pure PI, the center of mass of isoprene residues of terminals and for ${}_{\omega}\mathrm{PI}_{\alpha 6}$, the center of mass of $\alpha 6$ terminal is taken for RCN calculations. For ${}_{\omega}\mathrm{PI}_{\mathrm{PO}_4}$, we have calculated the RCN in between $[\mathrm{PO}_4] - [\mathrm{PO}_4]$ (red color).

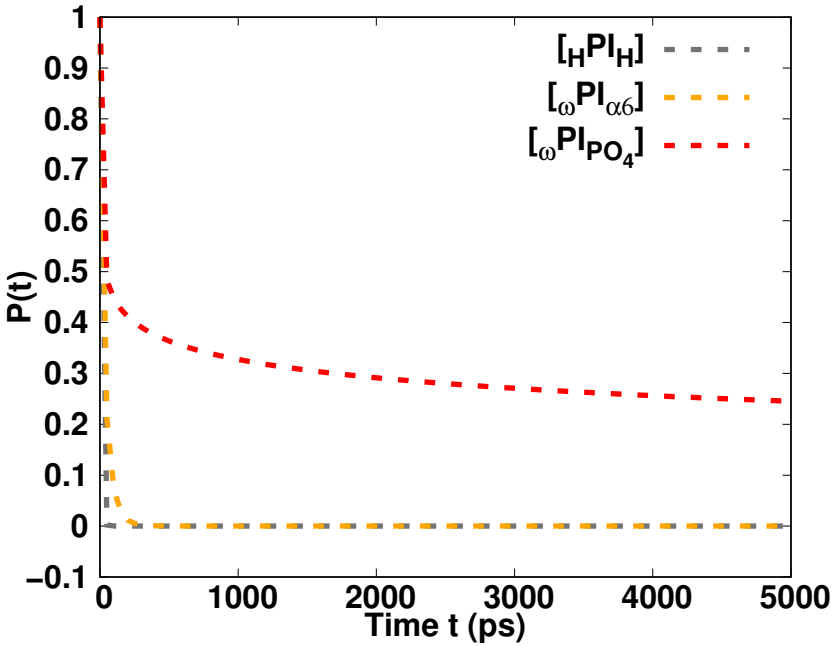


Figure S7: The fitted Survival probabilities $P(\mathrm{t})$ for terminal groups within the first coordination shell of the terminal group. The $P(\mathrm{t})$ is fitted by using Kohlrausch-Williams-Watts stretched exponential function. The last 50ns out of 1000ns for each independent MD simulation is used for Survival probabilities calculations. Each Survival probability was computed by averaging for each of the time windows available at the given interval (from 1 to 5000 ps).

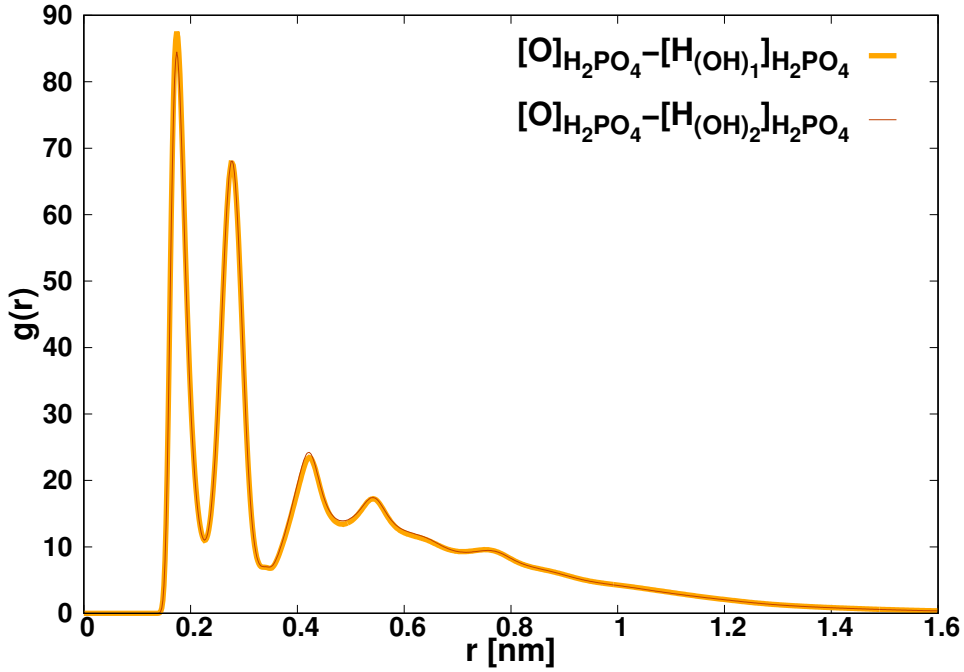


Figure S8: The radial distribution function between the $[\mathrm{O}]_{\mathrm{H_2PO_4}}$ and $[\mathrm{H_{OH1}}]_{\mathrm{H_2PO_4}}$ and$[\mathrm{H_{OH2}}]_{\mathrm{H_2PO_4}}$ groups. $-\mathrm{H_2PO_4}$ represents $-\mathrm{O}-\mathrm{P}(=\mathrm{O})(-\mathrm{OH})_1(-\mathrm{OH})_2$.