Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Molecular Dynamics Study of Natural Rubber-Fullerene Composites: Connecting Microscopic Properties to Macroscopic Behavior

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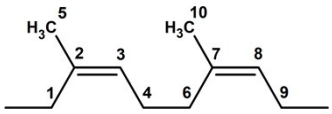
1. Structure and interaction parameter

The united atom force filed of cis-1,4-polyisoprene was taken from the existing literatures [1-4]. The details of structure, bonded- and non-bonded-interactions are provided in Table S1.

Table S1: United atom force field of *cis*-PI



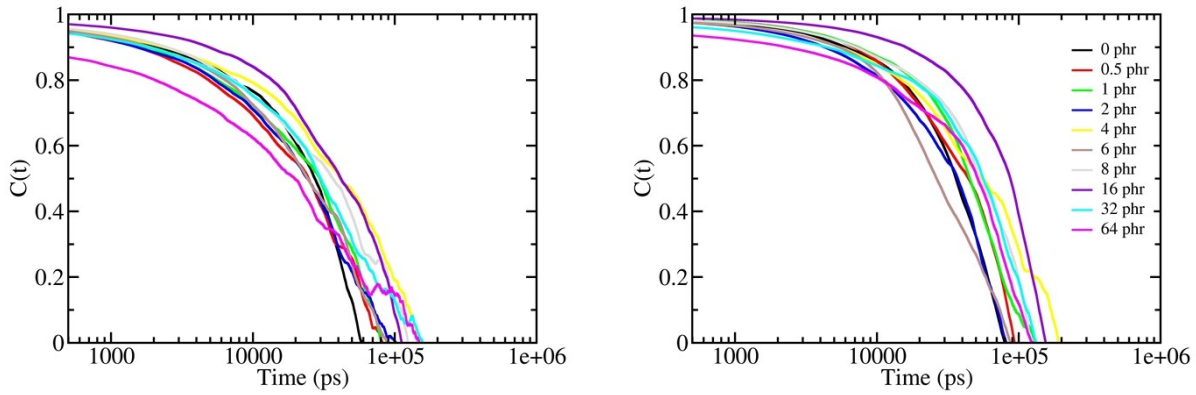
cis-1,4-polyisoprene

Atom type							
1		CH2					
2		CH0					
3		CH1					
4		CH2					
5		CH3					
Bonded interaction							
Rigid bond		k_b (kJmol^{-1}nm^{-4})	b_0 (nm)				
1-2		5.43×10^{6}	0.151				
2-3		1.08×10^{7}	0.134				
2-5		5.43×10^{6}	0.151				
3-4		5.43×10^{6}	0.151				
4-6		5.43×10^{6}	0.153				
Angle bending		k_θ (kJmol^{-1}rad^{-2})	θ_0 (deg)				
1-2-3		374.0	125.9				
2-3-4		374.0	125.9				
3-4-6		481.16	111.65				
5-2-3		374.0	125.9				
4-6-7		481.16	111.65				
Torsions		k_n(n=1,…,6) (kJmol^{-1})					
4-6-7-8		3.598	-0.167	4.853	0.669	1.590	-0.502
2-3-4-6		3.598	-0.167	4.853	0.669	1.590	-0.502
3-4-6-7		-4.142	-2.594	-16.903	-0.293	-1.046	-0.795
Improper dihedral		k_ϕ (kJmol^{-1}rad^{-2})	ϕ_0 (deg)				
1-2-3-4		160	0				
5-2-3-4		160	180				
Non-bonded interaction: Lennard-Jones potential							
		C6	C12				
CH0	CH0	0.00252	3.79310×10^{-6}				
CH0	CH1	0.00252	3.79310×10^{-6}				
CH0	CH2	0.00505	1.50419×10^{-5}				
CH0	CH3	0.00750	2.23034×10^{-5}				
CH1	CH1	0.00252	3.79310×10^{-6}				
CH1	CH2	0.00505	1.50419×10^{-5}				
CH1	CH3	0.00750	2.23034×10^{-5}				
CH2	CH2	0.00650	2.70034×10^{-5}				
CH2	CH3	0.01012	4.20052×10^{-5}				
CH3	CH3	0.01573	6.53158×10^{-5}				

2. System setup and stability

Table S2: Number of molecules and the simulation time

[C60]	Number of C60 molecule	Number of *cis*-PI chain	Simulation time (μs)
0	0	200	7.0
0.5	3	200	5.0
1	5	200	5.0
2	11	200	5.0
4	21	200	5.0
6	32	200	5.0
8	43	200	5.0
16	85	200	5.0
32	171	200	8.3
64	341	200	6.6



(a) **(b)**

Figure S1: Autocorrelations of rubber chains (a) R_0 and (b) R_g are determined by $C(t) = \langle R(\xi)R(\xi+t) \rangle_{\xi}$, where ξ is the time origin and $\langle\ \rangle$ is the average over ξ [5, 6].

Table S3: Autocorrelation relaxation time of R_0 and Rg

[C60]	Autocorrelation relaxation time (ns)	
	R_0	R_g
0	58	79
0.5	81	93
1	80	132
2	101	81
4	144	191
6	87	87
8	123	121
16	111	154
32	157	133
64	149	125

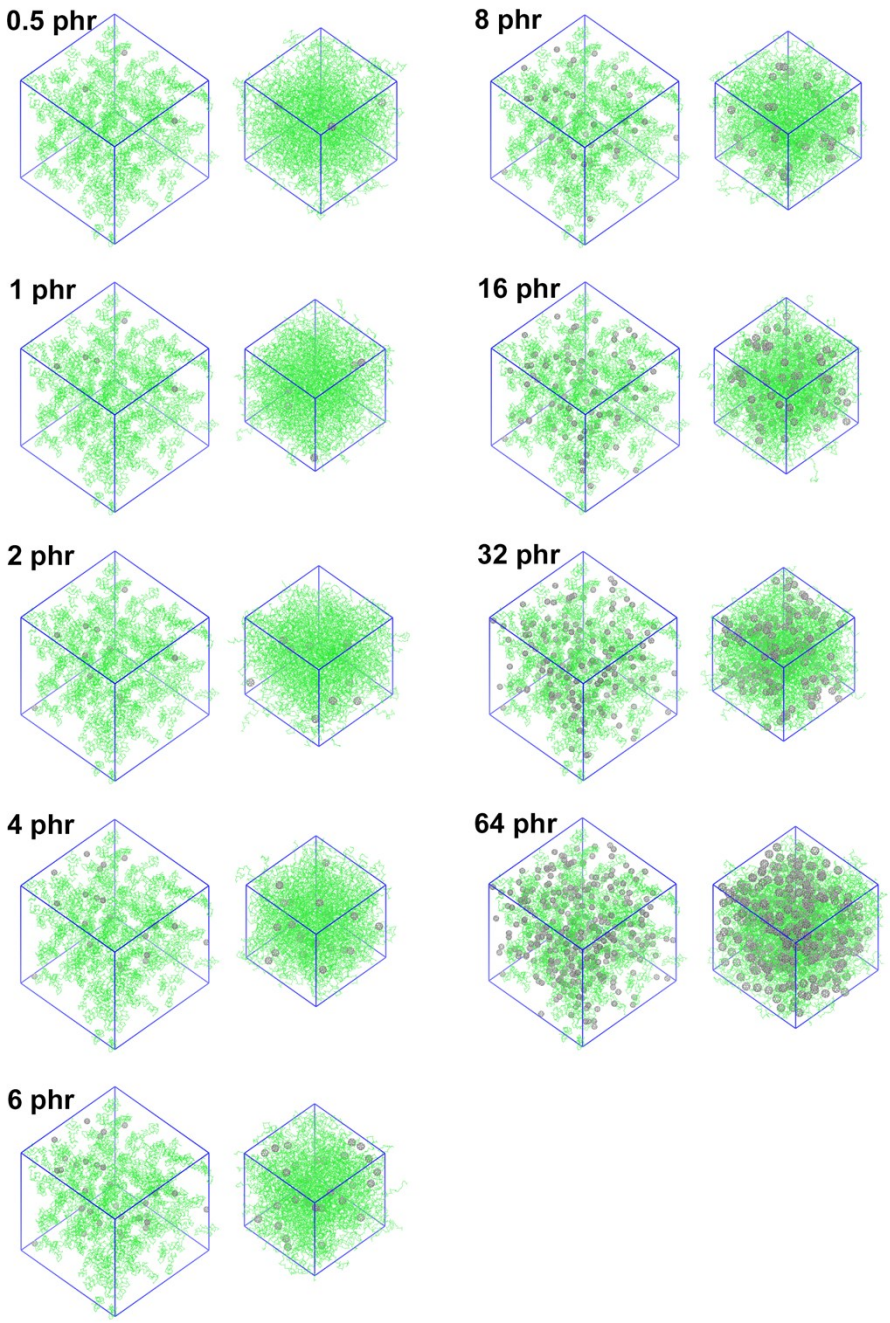


Figure S2: The initial structure of each simulation system; the C_{60} molecules and *cis*-PI chains are initially random added in the simulation box (left) comparing to their final structure (right).

3. Force field testing

Table S4: Comparison of the structural and bulk properties of *cis*-PI in melts at 300 K to the previous studies.

Properties	Simulation*	Refs.	Simulation details
***cis*-PI in melts** (200 chains PI, *DP* of PI=32)			
density (kg/m^3)	853.9±1.6	910[a7]	
		825[b2, 3]	*DP* of PI=20, united-atoms at 413 K
		840[b8]	*DP* of PI=24, all-atoms at 413 K
		885.1±0.2[b6]	*DP* of PI=32, united-atom at 298 K and 1 bar
$<R_0^2>$ (nm^2)	12.85±0.41	14.10 ± 0.20 [b6]	*DP* of PI=32, united-atom at 298 K and 1 bar
$<R_g^2>$ (nm^2)	2.07±0.04	2.28 ± 0.5 [b6]	*DP* of PI=32, united-atom at 298 K and 1 bar
$<R_0^2>/<R_g^2>$	6.20	6.18 [b6]	*DP* of PI=32, united-atom at 298 K and 1 bar
Bulk modulus (GPa)	1.37±0.02	2.020[a6, 9],	
		1.95 [b6],	*DP* of PI=32, united-atom at 298 K and 1 bar
Thermal expansion (10^{-4}·K^{-1})	7.80±0.15	6.1[a 6, 10, 11],	
		6.6[b 6]	*DP* of PI=32, united-atom at 298 K and 1 bar

* average from the last 1000 ns of current simulations

[a]experiment, [b] simulations

4. Mean Square Displacement (MSD)

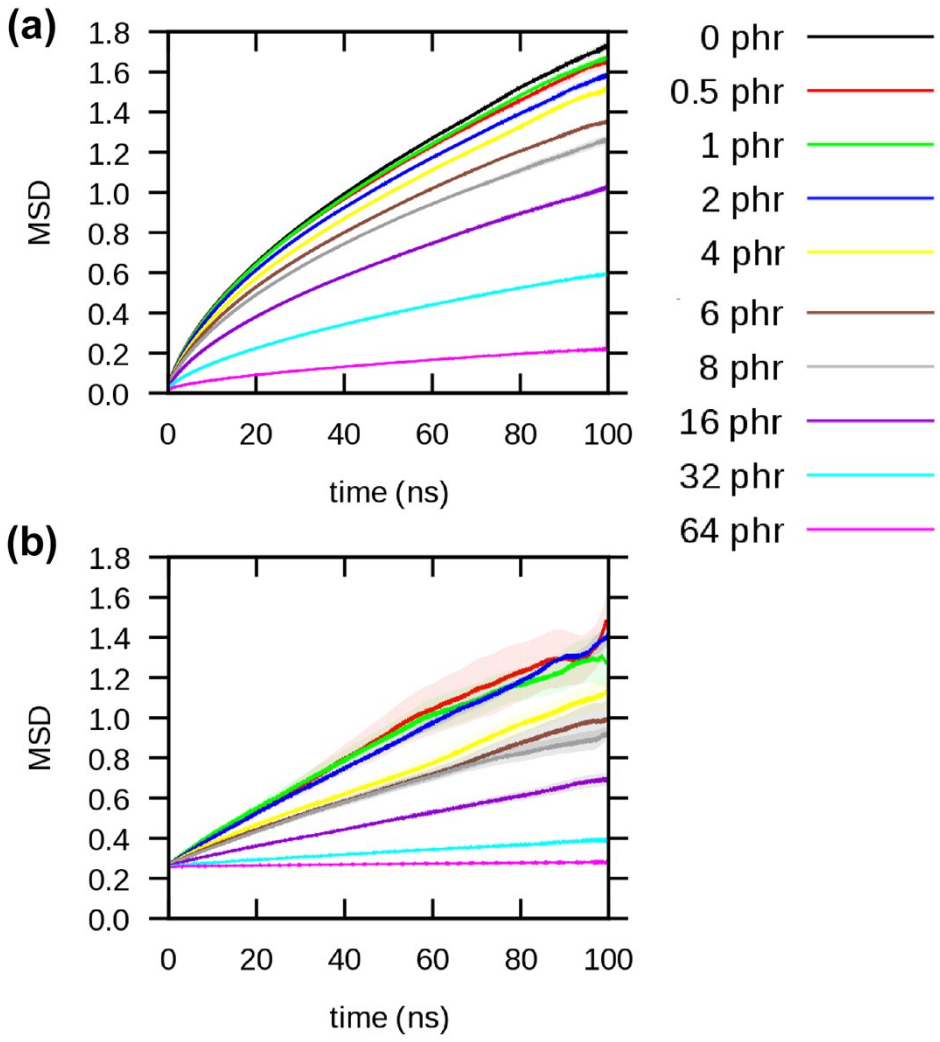


Figure S3: The mean squared displacement (MSD), Eq 6. in the main text, (a) *cis*-PI and (b) C60 is determined by the deviation of the position of a molecule with respect to a reference position over time, $< r^2 >$. The standard deviation is used for error estimate.

References

1. M. Doxastakis, V. G. Mavrantzas and D. N. Theodorou, *The Journal of Chemical Physics*, 2001, **115**, 11339-11351.
2. V. A. Harmandaris, M. Doxastakis, V. G. Mavrantzas and D. N. Theodorou, *The Journal of Chemical Physics*, 2002, **116**, 436-446.
3. D. V. Guseva, P. V. Komarov and A. V. Lyulin, *The Journal of Chemical Physics*, 2014, **140**, 114903.
4. D. V. Guseva, P. V. Komarov and A. V. Lyulin, *Journal of Polymer Science Part B: Polymer Physics*, 2016, **54**, 473-485.
5. M. J. Abraham, T. Murtola, R. Schulz, S. Páll, J. C. Smith, B. Hess and E. Lindahl, *SoftwareX*, 2015, **1**, 19-25.
6. P. Sharma, S. Roy and H. A. Karimi-Varzaneh, *The Journal of Physical Chemistry B*, 2016, **120**, 1367-1379.
7. L. J. Fetters, D. J. Lohse and W. W. Graessley, *Journal of Polymer Science Part B: Polymer Physics*, 1999, **37**, 1023-1033.
8. Y. N. Pandey, A. Brayton, C. Burkhart, G. J. Papakonstantopoulos and M. Doxastakis, *The Journal of Chemical Physics*, 2014, **140**, 054908.
9. B. Holownia, *Rubber Chemistry and Technology*, 1975, **48**, 246-253.
10. A. V. Tobolsky and H. F. Mark, *Polymer science and materials*, John Wiley & Sons1971.
11. J. Brandrup, Polymer Handbook 4th Edition John Wiley & Sons, Inc. New York (1999).