

Investigation of Homogeneous and Heterogeneous Cluster Formation in Mixtures of Ester and Hydroxy-Terminated *cis*-1,4-Polyisoprene Chains in Oligomers of Natural Rubber

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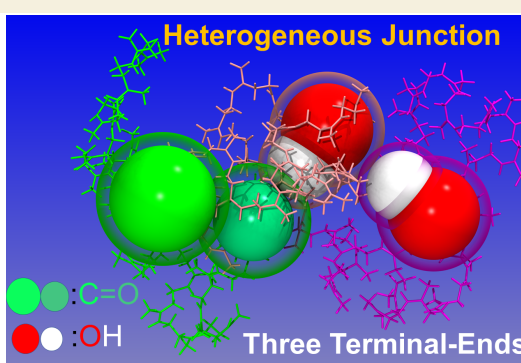
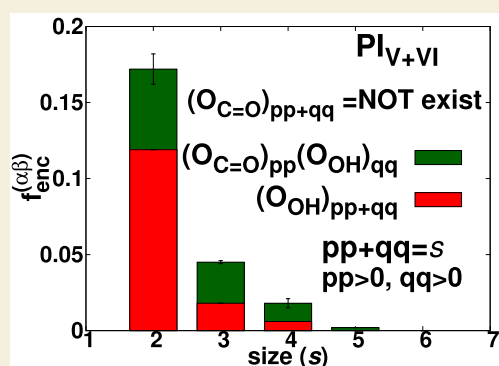
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ABSTRACT: The terminal structures of *cis*-1,4-polyisoprene (PI) chains significantly influence the exceptional mechanical properties of Hevea natural rubber (NR), including high toughness, wet skid resistance, and strain-induced crystallization. We conducted all-atom molecular dynamics simulations to investigate the structural and dynamic properties of PI melt systems with various terminal group combinations. These included single-component melts and binary mixtures of chains with ester- and hydroxy-terminated α -terminal groups. The study revealed that hydrogen bonding between α -terminal groups drive the formation of stable homogeneous and heterogeneous clusters. In single-component systems, hydroxy-terminal groups promoted homogeneous clusters, while in binary mixtures, heterogeneous clusters formed between ester and hydroxy terminals. These clusters, ranging in size from 2 to 5 chains, serve as physical junction points, slowing chain dynamics and enhancing network stability. Dynamic properties, such as rotational relaxation, Rouse mode times, and stress–stress autocorrelation, were significantly influenced by cluster formation, particularly in mixed systems. The stress–stress autocorrelation function, $G(t)$, exhibits a Rouse-type relaxation behavior ($G(t) \sim t^{-1/2}$) in the intermediate time range for PI_0 . In contrast, the mixed melt systems PI_0 show a slower relaxation compared to the pure components. This slower relaxation is attributed to the formation of stable, well-ordered heterogeneous clusters, driven by hydrogen bonding between ester and hydroxy-terminal groups. These findings provide evidence for the formation of physical junction points between hydroxy- and ester-terminated polyisoprene chains through their respective α_1 , α_2 , α_3 , α_4 , α_5 , and α_6 terminals. These physical junction points might be crucial for superior properties of NR such as high toughness, crack growth resistance, and strain-induced crystallization.

KEYWORDS: ester terminal group, hydroxy terminal group, homogeneous cluster, heterogeneous cluster, potentials of mean force, hydrogen bond, physical junction points

1. INTRODUCTION

Natural rubber finds widespread application in commonplace items such as vehicle tires, rubber bands, hoses, gloves, boots, and various industrial components that may not necessarily feature prominently in everyday use. The distinctive properties exhibited by natural rubber products are characterized by their exceptional attributes, notably elevated toughness, superior tensile strength, and remarkable resistance to crack propagation. These superior characteristics are believed to be intricately associated with the nuanced effects arising from the terminal

ends of polyisoprene molecules within natural rubber compositions.^{1–4}

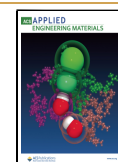
Hevea natural rubber (NR) exhibits a plethora of high-performance attributes, including remarkable malleability,

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impact resistance, elasticity, resilience, efficient heat dispersion, and cold temperature abrasion resistance. These characteristics are not solely reliant on the high molecular weight of the *cis*-1,4-polyisoprene chain and the quantity of *cis* isoprene, but are intricately linked to the structural configurations of the end groups within the polymer chain of NR.^{1,3,6} Despite over eight decades of manufacturing research, synthetic rubber has been unable to replicate the distinctive chemical and mechanical properties of natural rubber.⁵ Due to its exceptional attributes, natural rubber remains indispensable across a diverse array of industries, including tire manufacturing, medical devices, and engineering applications.⁶ Synthetic polyisoprene rubber (IR) has emerged as an alternative source in response to the escalating demand for natural rubber. While the main chain structure of synthetic polyisoprene closely resembles that of natural rubber, the mechanical properties of IRs, including tensile strength, and tearing strength, notably lag behind those of NRs.⁷ The polar terminal ends of NR have been identified as significant contributors to the mechanical performance of natural rubber.⁸ Consequently, in pursuit of enhancing the chemical and mechanical attributes of IRs, a deeper understanding of the molecular interactions governing the association of terminal ends within polyisoprene chains of natural rubber is imperative.

The unprocessed latex of natural rubber, derived from the *Hevea brasiliensis* tree, encompasses a complex mixture of constituents, including rubber particles, proteins, metal ions, carbohydrates, lipids, and various other compounds.^{9,10} Hevea natural rubber primarily consists of *cis*-polyisoprene as its main chain, accompanied by two distinct types of end functional groups.¹¹ The primary structure of the polymer chain in natural rubber comprises *cis*-1,4-polyisoprene as its main chain, alongside distinctive ω -end and α -end groups. The ω -end group typically consists of a single unit of dimethylallyl combined with two to three *trans*-1,4-isoprene units.^{1,11} Conversely, the α -end group exhibits variability, encompassing hydroxy, ester,^{1,11} and phosphate functionalities.¹⁰ The mechanical property of rubber's ability to resist deformation and fracture before undergoing vulcanization is commonly known as its green strength.¹ The presence of specific functional groups within Hevea natural rubber leads to an augmented sigmoidal stress response as strain increases. This characteristic behavior serves as a reliable indicator of its robust green strength and its capacity to endure deformation under strain.¹⁰ There is conjecture regarding the binding of protein to the ω -terminal and lipid to the α -terminal of the polymer, leading to the formation of branch points within the structure.¹⁰ These branch points play a pivotal role in facilitating polymer chain elongation during deformation. A comprehensive investigation conducted by Tanaka et al. utilizing NMR spectroscopy has yielded significant insights into the behavior of these functional groups.¹⁰ Their findings suggest a plausible association between lipid molecules and the α -terminal, possibly mediated by hydrogen bonds or ionic interactions.¹⁰ A recent experimental investigation has proposed that the formation of physical junction points via the terminal groups of polyisoprene chains within natural rubber plays a pivotal role in facilitating strain-induced crystallization in NR.^{12,13} Oouchi et al.¹¹ documented the occurrence of a mixture comprising various types of ester- and hydroxy-terminated *cis*-1,4-polyisoprene chains in the Hevea natural rubber sample. Their findings delineated six distinct types of *an* terminal ends (*an*-terminal groups, where *n* ranges from 1 to 6), with odd-numbered α terminals

representing ester terminal groups (α_1 , α_3 , α_5), and even-numbered α terminal groups corresponding to hydroxy terminal groups (α_2 , α_4 , α_6). In our prior investigations on melt systems composed only of PI with ω and a single type of *an* terminals, we demonstrated the absence of cluster formation between ester-terminal ends within pure melt systems of ester-terminated *cis*-1,4-polyisoprene. Conversely, hydroxy-terminal ends in hydroxy-terminated *cis*-1,4-polyisoprene pure melt systems facilitated the establishment of stable clusters.¹⁴ Consequently, the precise structural mechanism governing the formation of physical junction points via ester-terminal ends remains unresolved. In this study, we aim to elucidate the impact of both ω -terminal and α -terminal groups on the formation of physical junction points through the terminal groups of polyisoprene chains in mixtures of ester- and hydroxy-terminated *cis*-1,4-polyisoprene chains, in other words, to investigate synergy effects by mixing two types chains with ester- and hydroxy-terminal ends. Notably, our investigation excludes any involvement of carbohydrates, metal ions, proteins, and lipids. To achieve this objective, we employ a multiscale method which we have used in our previous studies.^{14–16} Molecular modeling and molecular dynamics simulations have become essential methodologies in polymer science, enabling the exploration of molecular complexities inherent in the mechanical and chemical characteristics of polymers. These computational approaches offer invaluable insights into polymer behavior, complementing experimental investigations by providing a deeper understanding of phenomena that may be difficult to discern solely through experimental means.^{14–24} *Cis*-1,4 polyisoprene (PI) melts have served as a prototypical system for understanding polymer dynamics and their influence on macroscopic properties for over five decades.^{14–16,19,22,25–33} To understand the polymer dynamics and dielectric relaxation spectroscopy is extensively utilized to explore the dynamic behavior of polyisoprene.^{19,22,27–29,31–33} The inherent asymmetry in the repeat unit of *cis*-1,4-polyisoprene results in dipole moment components aligned both parallel and perpendicular to the polymer chain contour. This structural feature gives rise to two distinct relaxation processes: the dielectric normal-mode relaxation, associated with chain-scale dynamics, and the α -relaxation, which corresponds to segmental motions.^{19,22,27–29,31–33} The normal-mode relaxation is governed by the dipole moment component parallel to the polymer backbone, whereas the α -relaxation predominantly arises from localized fluctuations of the perpendicular dipole moment component. Adachi et al.³⁴ reported the observation of two distinct dielectric relaxation processes in *cis*-polyisoprene (*cis*-PI) samples with varying molecular weights: the normal mode, linked to fluctuations in the end-to-end distance, and the segmental mode. The relaxation time for the normal mode exhibited a significant dependence on molecular weight (*M*). Below the critical molecular weight ($M_c = 10^4$), the relaxation time for the normal mode followed a M^2 dependence, in accordance with Rouse theory. However, above M_c , the dependence shifted to $M^{3.7}$, consistent with the tube disengagement mechanism proposed by de Gennes.³⁵ Furthermore, the distribution of relaxation times became broader as molecular weight increased, with a shift toward higher frequencies, in line with predictions based on tube theory.³⁶ Subsequent investigations have refined the scaling laws governing viscosity and relaxation times while considering the effects of temperature, polydispersity, and microstructure.^{19,21,22,25,26,28,29,31–33} Theoretical and mesoscopic models of *cis*-1,4-polyisoprene (PI)

Table 1. Melt Systems Utilized in the Investigation^a

system	chain	cis-isoprene	terminal 1	terminal 2	N	M	NVT (ns)	sim. annl. (ns)	NPT (ns)	NVT production run (ns)
PI ₀	HPI _H	24	isoprene	isoprene	24	512	20	20	100	1100
PI _I	ω PI _{α1}	21	ω	α 1	24	512	20	20	100	1100
PI _{II}	ω PI _{α2}	21	ω	α 2	24	512	20	20	100	1100
PI _{III}	ω PI _{α3}	21	ω	α 3	24	512	20	20	100	1100
PI _{IV}	ω PI _{α4}	21	ω	α 4	24	512	20	20	100	1100
PI _V	ω PI _{α5}	21	ω	α 5	24	512	20	20	100	1100
PI _{VI}	ω PI _{α6}	21	ω	α 6	24	512	20	20	100	1100
PI _{I+II}	ω PI _{α1} + ω PI _{α2}	21	ω	α 1	24	256	20	20	100	1100
		21	ω	α 2	24	256				
PI _{III+IV}	ω PI _{α3} + ω PI _{α4}	21	ω	α 3	24	256	20	20	100	1100
		21	ω	α 4	24	256				
PI _{V+VI}	ω PI _{α5} + ω PI _{α6}	21	ω	α 5	24	256	20	20	100	1100
		21	ω	α 6	24	256				

^aThe parameter *N* indicates the total number of monomers constituting each polymer chain, while *M* denotes the number of chains present within each melt system. To ensure thorough analysis, full-atom molecular dynamics (MD) simulations were conducted, following a predefined sequence comprising NVT equilibration, simulated annealing, NPT equilibration, and NVT production run.

predominantly adopt a top-down framework, utilizing experimental data to define phenomenological parameters and predict macroscopic properties. However, these models often derive from data sets obtained under diverse conditions, such as varying microstructures, polydispersities, and temperatures, employing techniques like rheology or dielectric relaxation spectroscopy (DRS). This variability introduces potential limitations in the universality and consistency of these approaches. In contrast, molecular simulations offer the advantage of directly probing well-defined polymer models without assumptions about underlying mechanisms. Pioneering simulations by Kremer and Grest on bead-spring models¹⁷ provided insights into the transition from Rouse to reptation dynamics, revealing that while inner chain segments exhibit restricted mobility consistent with reptation, chain ends retain faster motion independent of molecular weight (*M*). Subsequent studies, such as those by Hou and colleagues,³⁷ integrated stress relaxation and primitive-path analysis to demonstrate that constraint-release (CR) and contour-length fluctuation (CLF) effects persist until extensive entanglement is achieved. Building on these foundational efforts, recent simulations of polyethylene (PE) and polybutadiene (PB) melts have enabled the investigation of system-specific effects and facilitated comparisons with experimental data. For PI, however, the slower dynamics relative to PE and PB have limited the application of atomistic models to low molecular weights (*M* < 2000 g/mol). To address this challenge, systematically developed coarse-grained (CG) models have emerged as an efficient alternative, balancing computational feasibility with predictive accuracy.^{38–40} Li et al.⁴¹ proposed coarse-grained (CG) models utilizing the Inverse Boltzmann Method⁴² for polyisoprene (PI), which facilitate the prediction of dynamic moduli, shear viscosities, and relaxation moduli for *cis*-1,4-polyisoprene and polyethylene.⁴³ Extensions of these models to longer chains facilitated mapping of primitive-path statistics to mean-field slip-link frameworks.⁴⁴ More recently, Okhuma et al.²⁴ introduced a two-bead-per-monomer CG model for *cis*-1,4-polyisoprene with pressure corrections based on Inverse Boltzmann Method, achieving robust predictions of viscoelastic behavior and stress relaxation for *cis*-1,4-polyisoprene melt systems. In our recent investigations,^{14–16,45} we employed a multiscale methodology to examine the association among terminal groups within the *cis*-1,4-polyisoprene chain. In this

investigation, our focus lies on *cis*-1,4-polyisoprene, wherein we specifically analyze the presence of ω -terminal and α -terminal groups (*n* = 1, 2, ..., 6). Oouchi's investigation into natural polyisoprene revealed the fractions of chains with different terminal groups (α n) as follows: α 1: 24%, α 2: 2%, α 3: 53%, α 4: 13%, α 5: 8%, and α 6: <0.5%. This entails the scrutiny of ten distinct melt systems, each distinguished by a unique ω -terminal group, as well as six different types of α -terminal groups (refer to Figure S1): ester-terminated isopentene [–CH₂ – C(CH₂) – CH₂ – CH₂ – O – CO – CH₃] (α 1), hydroxy-terminated isopentene [–CH₂ – C(CH₂) – CH₂ – CH₂ – OH] (α 2), ester-terminated isobutane [–CH₂ – CH(CH₃) – CH₂ – O – CO – CH₃] (α 3), hydroxy-terminated isobutane [–CH₂ – CH(CH₃) – CH₂ – OH] (α 4), ester-terminated 1,4-*cis*-isoprene [–CH₂ – C(CH₃) = CH – CH₂ – O – CO – CH₃] (α 5) and hydroxy-terminated 1,4-*cis*-isoprene [–CH₂ – C(CH₃) = CH – CH₂ – OH] (α 6) terminal groups. We have employed the same model as detailed in our previous study.^{14–16} Although the main components of natural rubber consist of the six types of *cis*-polyisoprene with different chemical structures of α terminal ends and with different fractions, in the present work, we focus on the synergy effect of mixtures composed of PI's with ester- and hydroxy-groups in α terminals, i.e., 50:50 mixtures of PI's with odd-numbered and even-numbered α terminals. From the nine combinations, we have chosen three typical mixtures, i.e., PI_{I+II}, PI_{III+IV}, and PI_{V+VI}. Comprehensive details of each PI melt system are provided in Table 1.

2. METHODOLOGY AND COMPUTATIONAL PROCEDURES

Our investigation encompasses ten unique *cis*-1,4-polyisoprene melt systems, distinguished by diverse combinations of ω -terminal and α -terminal groups (see Figure S1 and Table 1). Each melt system comprises a total of 512 polymer chains, with each chain composed of 24 monomers (*M* = 512, *N* = 24). This methodology remains consistent with our prior investigations, where we undertook a comparable approach albeit with exclusive attention directed toward the six variations of α -terminals.^{14–16,46} Prior findings suggest that natural rubbers featuring lower molecular weights tend to exhibit enhanced mechanical and rheological properties, largely attributed to a higher prevalence of shorter chains.⁴⁷ The terminal groups of

Table 2. This Table Presents the Mean-Square End-to-End Distance, $\langle R_{ee}^2 \rangle$ [nm²], and Mean Square Radius of Gyration, $\langle R_g^2 \rangle$ [nm²], alongside the Kuhn Length, b [nm], and the Number of Kuhn Segments, N_{RB} , for All Melt Systems at 360 K and 1 Bar

system	chain	type of α terminal	$\langle R_{ee}^2 \rangle$ [nm ²]	$\langle R_g^2 \rangle$ [nm ²]	$\langle R_{ee}^2 \rangle / \langle R_g^2 \rangle$	b [nm]	N_{RB}
PI ₀	HPI _H		8.73 ± 0.25	1.43 ± 0.02	6.11	0.80	13.50
PI _I	ω PI _{α1}	ester	9.93 ± 0.30	1.55 ± 0.02	6.39	0.91	12.03
PI _{I+II}	ω PI _{α1}		9.93 ± 0.39	1.55 ± 0.04	6.39	0.92	11.89
PI _{III}	ω PI _{α3}		9.67 ± 0.28	1.54 ± 0.03	6.27	0.85	13.28
PI _{III+IV}	ω PI _{α3}		9.49 ± 0.42	1.51 ± 0.04	6.31	0.85	13.33
PI _V	ω PI _{α5}		9.36 ± 0.27	1.49 ± 0.02	6.28	0.84	13.30
PI _{V+VI}	ω PI _{α5}	hydroxy	9.13 ± 0.36	1.47 ± 0.03	6.23	0.83	13.38
PI _{II}	ω PI _{α2}		9.60 ± 0.29	1.50 ± 0.02	6.38	0.88	12.45
PI _{I+II}	ω PI _{α2}		9.74 ± 0.41	1.52 ± 0.03	6.42	0.89	12.36
PI _{IV}	ω PI _{α4}		9.56 ± 0.28	1.52 ± 0.03	6.31	0.86	12.90
PI _{III+IV}	ω PI _{α4}		9.76 ± 0.42	1.55 ± 0.04	6.28	0.86	12.94
PI _{VI}	ω PI _{α6}		9.00 ± 0.30	1.44 ± 0.03	6.23	0.81	13.59
PI _{V+VI}	ω PI _{α6}		9.10 ± 0.44	1.45 ± 0.04	6.27	0.82	13.42

shorter chains are thought to readily establish associations, potentially interacting with nonrubber components such as proteins, lipids, and sugars, thereby facilitating aggregate formation.⁴⁷ In the realm of natural rubber, longer molecular chains have been observed to manifest inferior mechanical and physical attributes. This phenomenon is ascribed to the reduced density of chain end groups, which may contribute to a diminished propensity for aggregate formation. Consequently, to achieve a deeper understanding of aggregate formation involving terminal groups, we have chosen to concentrate on shorter polyisoprene chains. The molecular weight distribution of naturally occurring polyisoprene, sourced from rubber trees, spans an extensive range from 100 to 2000 kDa, as documented in prior investigations.⁴⁸ This broad spectrum poses a formidable challenge for computational simulations, given its substantial magnitude and varying chain lengths. Consequently, our primary research objective centers on elucidating the influence of end groups on the formation dynamics of both polar and nonpolar aggregates. To achieve this, we focus on a representative polyisoprene chain with a molecular weight of 1.6 kDa, deemed adequate for the specific aims of our study.

2.1. Details of All-Atom Molecular Dynamics Simulations

The initial configuration for each melt system is established using a multiscale methodology. Here we briefly describe how to prepare the initial equilibrium state of a melt system. The details of the methodology can be referred to in our prior papers.^{14–16,46} Each melt system underwent NPT and NVT coarse-grained molecular dynamics (MD) simulations to relax the polymer chains, utilizing the OPENMM software package.⁴⁹ The relaxed coarse-grained structures were then converted to all-atom representations (Figure S2), which were subsequently used to conduct all-atom MD simulations with GROMACS (version 2019.2)⁵⁰ All-atom molecular dynamics simulations were conducted using the CHARMM general all-atom force field,⁵¹ which has been extensively validated for various types of polymer melt systems.⁵²

The temperature and pressure are maintained at 360 K and 1 bar, respectively, mirroring the conditions established in our previous investigations.^{15,16,46} To prepare the systems for simulation, initial configurations undergo energy minimization followed by successive stages of NVT equilibration, NPT simulated annealing, and NPT equilibration processes (refer to Table 1 for the corresponding classical MD simulation durations for each phase). The resultant equilibrium structure is

subsequently subjected to a production run extending over 1100 ns. The trajectories derived from these simulations facilitate the calculation of fundamental properties such as the radius of gyration, end-to-end distance, and radial distribution function between terminal groups. These analyses offer insights into the intricate local structure of branching physical junction points formed between or among polyisoprene chain ends. To ensure temperature stability throughout the simulations, we utilize the Nosé–Hoover thermostat with a coupling constant of 1 ps. To maintain system pressure at 1 bar throughout equilibration and production runs, both the Berendsen barostat and Parrinello–Rahman barostat⁵³ are employed, with time constants of 5 ps. The compressibility is set at 4.5×10^{-5} bar⁻¹ (4.5×10^{-10} Pa⁻¹) for the Parrinello–Rahman barostat. The neighbor list is constructed using the Verlet cutoff scheme, with a cutoff radius of 1.2 nm for all-atom MD simulations. Hydrogen bond lengths are constrained using the LINCS algorithm,⁵⁴ and a time step of 2 fs is utilized for all-atom molecular dynamics. Electrostatic interactions are computed using the particle mesh Ewald method.⁵⁵

3. RESULTS

3.1. Equilibration of *cis*-1,4-Polyisoprene Chain: All-Atom Molecular Dynamics

In this section, we present an in-depth analysis of findings derived from our extensive all-atom molecular dynamics simulations. Our investigation is centered on a detailed exploration of static and dynamic characteristics, encompassing parameters such as end-to-end distances, radii of gyration, mean square internal distance, end-to-end vector autocorrelation functions, and Rouse mode analysis. These properties are specifically pertained to elucidate the behavior of polyisoprene chains across ten melt systems as enumerated in Table 1. To evaluate the equilibrated states of the polymer chains, our analysis focuses on the end-to-end distance R_{ee} and radius of gyration R_g . Time-dependent profiles of R_{ee} and R_g , depicted in Figure S3 (provided in the Supporting Information), reveal their stability throughout the simulation period, indicative of the attainment of equilibrium by the polymer chains. Furthermore, we determine the mean square end-to-end distance $\langle R_{ee}^2 \rangle$ and mean square radius of gyration $\langle R_g^2 \rangle$ for the equilibrated systems. The resultant ratio of $\langle R_{ee}^2 \rangle$ to $\langle R_g^2 \rangle$ is tabulated in Table 2. Remarkably, the observed ratio, proximate to 6 (Table 2),

corroborates the typical behavior of random Gaussian coil conformations demonstrated by the polyisoprene chains.

The Kuhn length, denoted as b , serves as a fundamental descriptor of polymer behavior, representing the ratio between the mean square end-to-end distance, $\langle R_{ee}^2 \rangle$, and the maximum achievable length of the polymer chain when the chain is fully extended, R_{max} (eq 1).

$$b = \frac{\langle R_{ee}^2 \rangle}{R_{max}} \quad (1)$$

$$R_{max} = bN_{RB}$$

The parameters b , representing the Kuhn length of the polymer chain, N_{RB} , signifying the count of Kuhn segments, and R_{max} indicative of the fully extended length of the polymer chain, constitute pivotal variables in our study.

Our investigation encompasses the comprehensive estimation of both the Kuhn length and the number of Kuhn segments for the polymer chain within each melt system, with exhaustive findings elucidated in Table 2. Notably, the determined values for the Kuhn lengths demonstrate notable agreement with experimental observations.⁵⁶

The structural features of polymer chains in each melt system are characterized by analyzing the mean square internal distances, C , as presented in Figure S4 of the Supporting Information. For all ten melt systems, C is evaluated as a function of repeat unit separation (ΔN), using the scaled parameter $C = \Delta R_{CM-CM}^2 / [(\Delta N - 1)^2]$, with the mean square monomer length defined as $l^2 = 0.09 \text{ nm}^2$. This analysis confirms that the simulation times employed are sufficient, as the polymer chains undergo displacements significantly larger than their own dimensions multiple times. The computation of the end-to-end vector autocorrelation function, represented by $C(t)$, was conducted for each melt system, varying with simulation time. This analysis was carried out employing the subsequent expression (eq 2).

$$C(t) = \frac{\langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle}{\langle \mathbf{R}(0) \cdot \mathbf{R}(0) \rangle} \quad (2)$$

Here, $\mathbf{R}(0)$ and $\mathbf{R}(t)$ symbolize the end-to-end vectors at time $t = 0$ and at time t , respectively. The angular brackets denote the ensemble average. Visual representation of the end-to-end vector autocorrelation functions $C(t)$ for the ten systems, labeled as 0, I, II, ..., VI, I+II, III+IV, and V+VI, is presented in Figure 1. Additionally, we ascertained the average relaxation time by fitting the time correlation function to a Kohlrausch–Williams–Watts stretched exponential function (eq 3):⁵⁷

$$C(t) = \exp \left[- \left(\frac{t}{\tau_{rot}} \right)^{\beta_{rot}} \right] \quad (3)$$

The rotational relaxation times, designated as τ_{rot} along with the corresponding stretching exponents, denoted as β_{rot} are visualized in Table 3 for the ten distinct systems under consideration. Notably, in the context of the simple exponential function, β_{rot} assumes a value of 1, whereas for the stretched exponential function, β_{rot} is constrained to values less than 1. Table 3 illustrates the values of the stretching exponent β_{rot} and the rotational relaxation time τ_{rot} across the ten different melt systems. The order of average relaxation time τ_{rot} is ${}^H\text{PI}_H < {}^\omega\text{PI}_{\alpha 3}$ (in PI_{III}) $< {}^\omega\text{PI}_{\alpha 3}$ (in PI_{III+IV}), ${}^\omega\text{PI}_{\alpha 1}$ (in PI_I) $< {}^\omega\text{PI}_{\alpha 1}$ (in PI_{I+II}), ${}^\omega\text{PI}_{\alpha 5}$ (in PI_V) $< {}^\omega\text{PI}_{\alpha 5}$ (in PI_{V+VI}) which shows that ester-

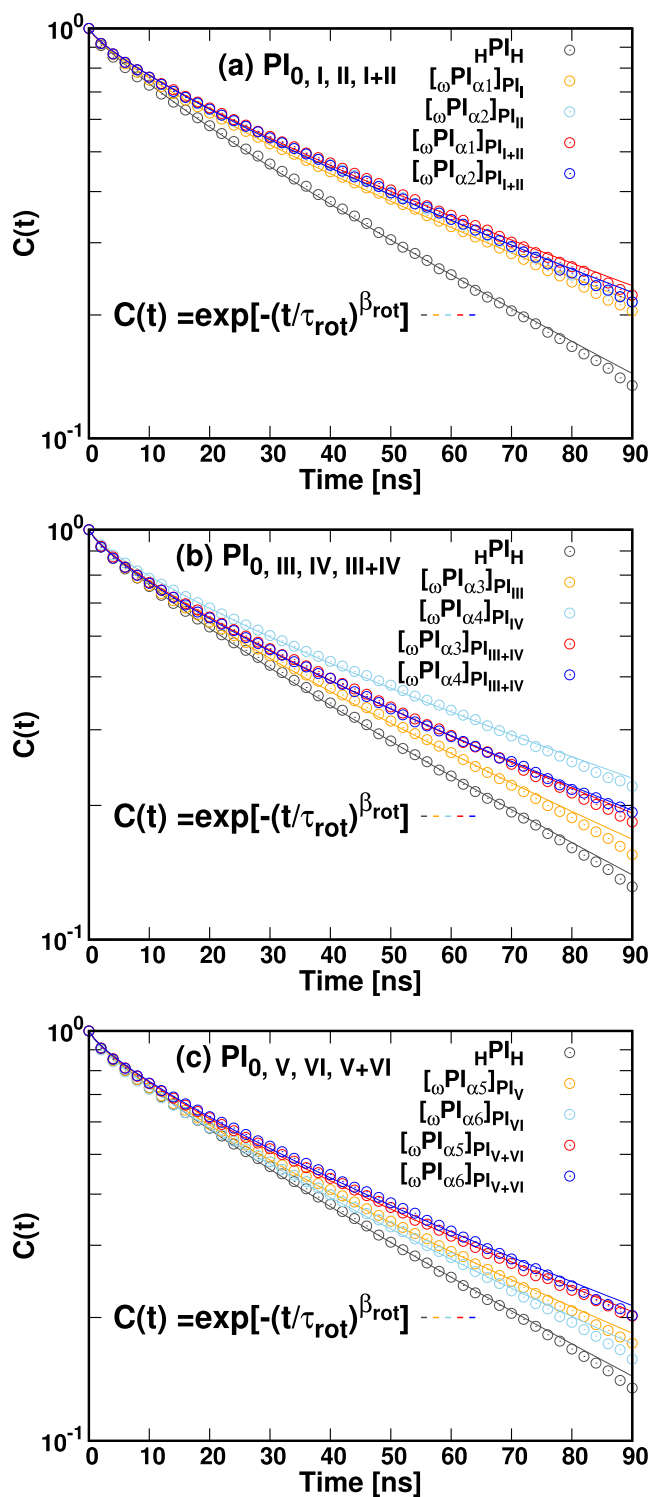


Figure 1. Rotational correlation functions as a function of time for (a) PI_0 , I, II, I+II; (b) PI_0 , III, IV, III+IV; and (c) PI_0 , V, VI, V+VI melt systems. The empty circle stands for a fit to a stretched exponential ($C(t) = \exp[-(t/\tau_{rot})^{\beta_{rot}}]$) function.

terminated polyisoprene chains are more strongly associated with each other in mixed melt systems than that of ester terminated polyisoprene chains in pure melt systems. In the case of PI_{I+II} , PI_{III+IV} , PI_{V+VI} mixed melt systems, the average relaxation time for ester-terminated PI chains is higher than that of ester-terminated PI chains in PI_I , PI_{III} , PI_V single-component melt systems.

Table 3. Showcases the Corresponding Rotational Relaxation Times, Denoted as τ_{rot} , Computed by Fitting the End-to-End Vector Autocorrelation Functions, $C(t)$, to Both the Simple Exponential ($C(t) = \exp(-t/\tau_{\text{rot}})$) and Stretched Exponential ($C(t) = \exp[-(t/\tau_{\text{rot}})^{\beta_{\text{rot}}}]$) Functions

system	chain	type of α terminal	average relaxation time τ_{rot} [ns]	
			$\beta_{\text{rot}} = 1$	$\beta_{\text{rot}} \neq 1$
PI ₀	HPI _H		45.41 ± 0.01	40.43 ± 0.01 ($\beta_{\text{rot}} = 0.84$)
PI _I	ω PI _{α1}	ester	57.04 ± 0.02	51.28 ± 0.01 ($\beta_{\text{rot}} = 0.79$)
PI _{I+II}	ω PI _{α1}		64.67 ± 0.02	55.18 ± 0.01 ($\beta_{\text{rot}} = 0.79$)
PI _{III}	ω PI _{α3}		53.10 ± 0.01	44.58 ± 0.01 ($\beta_{\text{rot}} = 0.82$)
PI _{III+IV}	ω PI _{α3}		57.17 ± 0.02	48.97 ± 0.01 ($\beta_{\text{rot}} = 0.79$)
PI _V	ω PI _{α5}		56.79 ± 0.02	45.07 ± 0.01 ($\beta_{\text{rot}} = 0.79$)
PI _{V+VI}	ω PI _{α5}		64.31 ± 0.02	49.75 ± 0.01 ($\beta_{\text{rot}} = 0.78$)
PI _{II}	ω PI _{α2}	hydroxy	65.71 ± 0.03	53.92 ± 0.01 ($\beta_{\text{rot}} = 0.80$)
PI _{I+II}	ω PI _{α2}		61.66 ± 0.02	53.61 ± 0.01 ($\beta_{\text{rot}} = 0.81$)
PI _{IV}	ω PI _{α4}		64.14 ± 0.03	57.31 ± 0.01 ($\beta_{\text{rot}} = 0.78$)
PI _{III+IV}	ω PI _{α4}		58.86 ± 0.02	49.33 ± 0.01 ($\beta_{\text{rot}} = 0.77$)
PI _{VI}	ω PI _{α6}		57.23 ± 0.01	43.06 ± 0.01 ($\beta_{\text{rot}} = 0.80$)
PI _{V+VI}	ω PI _{α6}		59.91 ± 0.02	50.65 ± 0.01 ($\beta_{\text{rot}} = 0.79$)

3.2. Rouse Mode Analysis

We perform Rouse mode analysis on the all-atom chains, employing a coarse-grained representation consisting of 12–15 Rouse beads as delineated in Table 2. Following the principles outlined in the Rouse model,³⁶ we calculate the normal coordinate denoted as X_p specifically for the free chain termini. This coordinate is defined as (eqs 4 and 5):

$$X_p(t) = \frac{2}{N_{\text{RB}}} \int_0^{N_{\text{RB}}} \cos\left(\frac{\pi p n}{N_{\text{RB}}}\right) \mathbf{r}_n(t) dn, \quad (p = 1, 2, \dots) \quad (4)$$

$$X_0(t) = \frac{1}{N_{\text{RB}}} \int_0^{N_{\text{RB}}} \mathbf{r}_n(t) dn, \quad (p = 0) \quad (5)$$

Here, N_{RB} represents the numerical count of Rouse beads comprising a chain, with $\mathbf{r}_n$ denoting the spatial coordinate of the n -th Rouse bead, as referenced in literature.^{58,59} Within the framework of a Rouse chain featuring free terminal ends, the anticipated theoretical outcome prescribes the relation $\tau_p/\tau_R = 1/p^2$. Here, $\tau_R(\equiv \tau_1)$ denotes the longest chain relaxation time. The Rouse mode analysis for a polymer chain with fully immobilized chain ends can be conducted through the utilization of the subsequent normal coordinate. The analysis of Rouse modes for a polymer chain with completely immobilized terminal ends can be executed by employing the following normal coordinate (eq 6):⁶⁰

$$X_p(t) = \frac{1}{N_{\text{RB}}} \int_0^{N_{\text{RB}}} \sin\left(\frac{(p - 1/2)n\pi}{N_{\text{RB}}}\right) \mathbf{r}_n(t) dn \quad (6)$$

When considering fixed termini of the chain, the expected theoretical expression of the relaxation time τ_p for a mode p is given as $\tau_p/\tau_R = 1/(p - 1/2)^2$. The time autocorrelation function $\langle X_p(t) \cdot X_p(0) \rangle / \langle X_p(0) \cdot X_p(0) \rangle$ was computed for Rouse modes $p = 1, 2, 3, \dots, 6$, derived from all-atom molecular dynamics (MD) simulations. The resultant time autocorrelation functions are depicted in Figure S5 of the Supporting Information. Table 4 presents the longest relaxation time,

Table 4. Rouse Relaxation Time τ_R Evaluated by the Fittings of the Time Autocorrelation Function $\langle X_1(t) \cdot X_1(0) \rangle / \langle X_1(0) \cdot X_1(0) \rangle$ with a Simple Decay Exponential Function

system	chain	type of α terminal	τ_R [ns]	$\tau_R(\text{system})/\tau_R(\text{HPI}_H)$
PI ₀	HPI _H	hydrogen	48.88 ± 0.01	1.00
PI _I	ω PI _{α1}	ester	66.99 ± 0.02	1.37
PI _{I+II}	ω PI _{α1}		70.07 ± 0.02	1.43
PI _{III}	ω PI _{α3}		56.56 ± 0.01	1.16
PI _{III+IV}	ω PI _{α3}		59.64 ± 0.01	1.22
PI _V	ω PI _{α5}		64.83 ± 0.02	1.32
PI _{V+VI}	ω PI _{α5}		66.42 ± 0.02	1.35
PI _{II}	ω PI _{α2}	hydroxy	72.55 ± 0.04	1.48
PI _{I+II}	ω PI _{α2}		66.10 ± 0.04	1.35
PI _{IV}	ω PI _{α4}		72.70 ± 0.03	1.48
PI _{III+IV}	ω PI _{α4}		61.30 ± 0.03	1.25
PI _{VI}	ω PI _{α6}		57.07 ± 0.01	1.17
PI _{V+VI}	ω PI _{α6}		64.10 ± 0.01	1.31

$\tau_R(\equiv \tau_1)$, associated with the primary Rouse mode ($p = 1$) for each melt system. Concurrently, Table 3 showcases τ_{rot} derived from fitting a simple exponential decay function to the rotational correlation function $C(t)$ for individual melt systems. A consistent correlation emerges between the relaxation time of the primary Rouse mode τ_1 (refer to Table 4) and the rotational relaxation time τ_{rot} (given in Table 3).

Theoretical underpinnings stipulate that in the absence of constrained chain terminal, the scaling relationship is articulated as $\tau_p/\tau_R = 1/p^2$, while under fixed chain terminal conditions, this relationship transforms to $\tau_p/\tau_R = 1/(p - 1/2)^2$.⁶⁰ Figure 2 visually elucidates the dependency of τ_p on the normal mode p . The determination of relaxation times τ_p for polymer chains in each melt system entails fitting the time autocorrelation function $\langle X_p(t) \cdot X_p(0) \rangle / \langle X_p(0) \cdot X_p(0) \rangle$ with a simple exponential function, specifically $\exp(-t/\tau_p)$. If Rouse scaling is valid, all curves depicted in Figure 2 are expected to converge onto a unified trajectory, reflecting $\tau_p/\tau_R = 1/p^2$ for unconfined chain ends and $\tau_p/\tau_R = 1/(p - 1/2)^2$ for fixed chain ends. In the case of PI₀ (HPI_H), where polyisoprene chains feature unbound termini, adherence to Rouse scaling is apparent (as depicted by the gray-colored solid circle symbol in Figure 2 for Rouse modes $p = 1, 2, 3, \dots, 6$). Likewise, for the PI_{I-to-VI} and PI_{I+II, III+IV, V+VI} melt systems, the polyisoprene chains also adhere to the Rouse scaling with free chain ends, indicating that any deviation in higher modes is not induced by intermittent associations among chain termini. In Table 4, we provide the relaxation time τ_R for the polymer chains within each analyzed melt system.

The observations from Figure 2 and Table 4 collectively suggest that the systems (PI_{0, I-to-VI} and PI_{I+II, III+IV, V+VI}), characterized by end-group associations, maintains adherence to the scaling principles of the Rouse model with free ends. However, it manifests a prolonged relaxation time scale due to the intermittently constrained dynamics of chain ends.

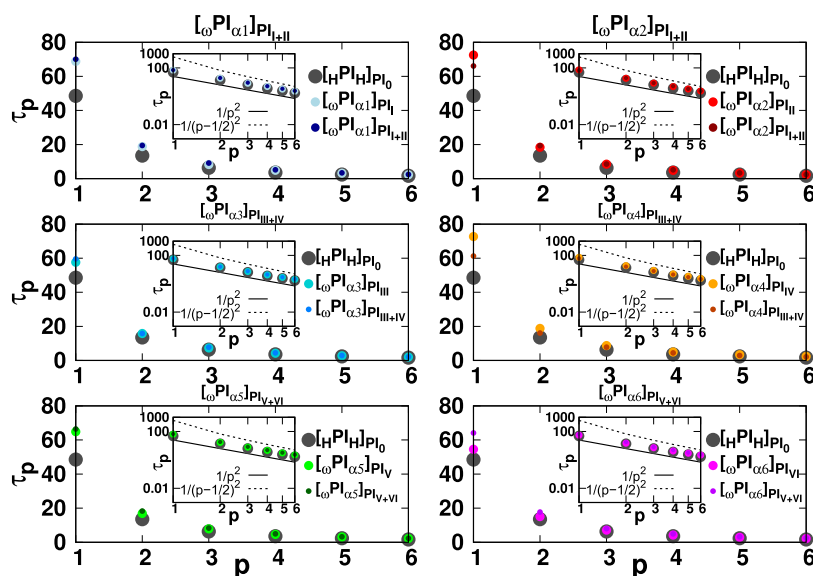


Figure 2. Plot of τ_p vs p . The figure illustrates the relaxation times corresponding to distinct normal modes p of the polymer chains, elucidating the dynamic characteristics of the melt system. In the inset of the plot, we have shown the log–log plot of τ_p -vs- p .

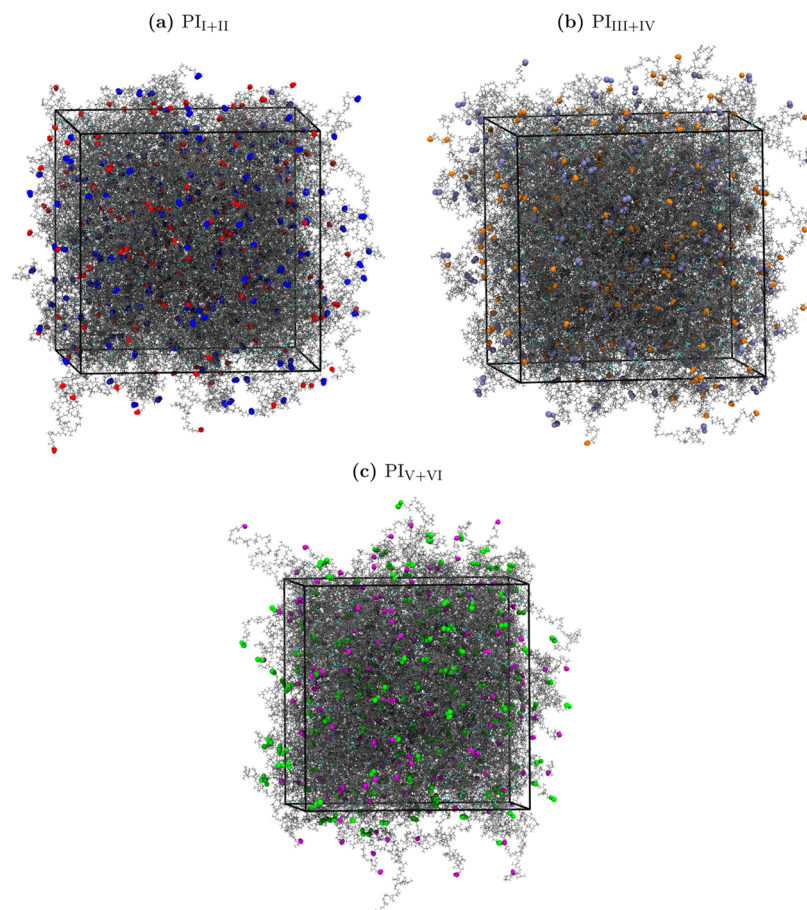


Figure 3. Snapshots depict (a) PI_{I+II} , (b) PI_{III+IV} , (c) PI_{V+VI} melt systems following a 1 μ s production-run of all-atom MD simulations. Cyan coloring is utilized to denote the dimethyl allyl group of ω terminals (comprising a Dimethyl allyl group and two *trans*-1,4-isoprene units), while $\alpha 1$, $\alpha 2$, $\alpha 3$, $\alpha 4$, $\alpha 5$, and $\alpha 6$ terminals are represented by blue, red, web-blue, orange, green, and magenta colors, respectively. Backbone carbon and hydrogen atoms are rendered in gray color.

Furthermore, an examination of Table 4 reveals that the extension of relaxation time can be augmented through the association between ester and hydroxy terminal ends. Based on the data gleaned from our analyses, it is evident that the

association among α -terminals does not alter the dynamics of Rouse behavior but significantly affects the time scale of Rouse relaxation.

3.3. Association of Ester and Hydroxy-Terminated Polyisoprene Chains

In this section, we undertake an exploration of the associations between H – H, ω – ω , and α – α terminals in the PI_{0, I–VI, I+II, III+IV, V+VI} melt systems. Visual representations of PI_{I+II, III+IV, V+VI} melt systems following a 1 μ s production-run are presented in Figure 3.

In order to unveil the localized structural configuration of terminal groups surrounding a specified terminal group, a comprehensive investigation was conducted utilizing radial distribution functions (RDFs). These RDFs, denoted as $g_{\alpha\beta}(r)$, were determined by scrutinizing the distribution of distances between the centers of mass of terminal groups originating from various *cis*-1,4-polyisoprene chains. The formulation governing the RDFs is delineated as follows (eq 7):

$$g_{\alpha\beta}(r) = \frac{\langle \rho_{\beta}(r) \rangle_{\text{local},\alpha}}{\langle \rho_{\beta}(r_c) \rangle_{\alpha}} \quad (7)$$

The formulation of $\langle \rho_{\beta}(r) \rangle_{\text{local},\alpha}$ encapsulates the mean density of β particles proximal to α particles at a specified distance r and r_c is defined as half of the box length. The computation of this density proceeds as follows (eq 8):

$$\langle \rho_{\beta}(r) \rangle_{\text{local},\alpha} = \frac{1}{N_{\alpha}(\delta_{\alpha\beta} + 1)} \sum_{i_{\alpha}=1}^{N_{\alpha}} \langle \rho_{\beta}(r) \rangle_{\text{local},i_{\alpha}} \quad (8)$$

where N_{α} denotes the total number of α particles, and $\delta_{\alpha\beta}$ is the Kronecker delta, 1 when $\alpha = \beta$ and 0 otherwise. To prevent redundancy in the case of $\alpha = \beta$, the denominator incorporates the term $(\delta_{\alpha\beta} + 1)$. In eq 8, $\langle \rho_{\beta}(r) \rangle_{\text{local},i_{\alpha}}$ signifies the density of β particles adjacent to the i -th type α particle at a given distance r . This localized density is characterized as follows (eq 9):

$$\langle \rho_{\beta}(r) \rangle_{\text{local},i_{\alpha}} = \sum_{j_{\beta}=1}^{N_{\beta}} \delta(r_{i_{\alpha}j_{\beta}} - r) \quad (9)$$

In eq 9, the primed summation notation introduces a differentiation based on the interrelationship between α and β . Specifically, when α and β represent distinct particle types, the summation, indicated as $\sum'$, ranges from $j_{\beta} = 1$ to N_{β} . Conversely, if α and β denote identical particle types, the summation, denoted as $\sum'$, excludes contributions from the i_{α} -th particle and spans from $j_{\beta} = 1$ to N_{β} , with the exclusion of $j_{\beta} \neq i_{\alpha}$.

The denominator on the right-hand side of eq 7, $\langle \rho_{\beta}(r_c) \rangle_{\alpha}$, delineates the mean density of particle type β within a sphere of radius r_c , which is centered around the α particle. It is expressed as follows (eq 10):

$$\langle \rho_{\beta}(r_c) \rangle_{\alpha} = \frac{1}{N_{\alpha}} \sum_{i_{\alpha}=1}^{N_{\alpha}} \langle \rho_{\beta}(r_c) \rangle_{i_{\alpha}} \quad (10)$$

where the term $\langle \rho_{\beta}(r_c) \rangle_{i_{\alpha}}$ denotes the density of particle type β constrained within a sphere of radius r_c centered around the i -th type α particle. This parameter is defined as follows (eq 11):

$$\langle \rho_{\beta}(r_c) \rangle_{i_{\alpha}} = \frac{1}{V} \int_0^{r_c} \langle \rho_{\beta}(r) \rangle_{\text{local},i_{\alpha}} 4\pi r^2 dr \quad (11)$$

where V represents the volume of the sphere and r_c is defined as half of the box length. In this context, our primary emphasis lies in the investigation of the solvation structure encompassing

terminal groups surrounding a designated terminal group. We have estimated the radial distribution functions in between terminals, i.e., [ISO] – [ISO] (ISO represents Hydrogen terminated 1,4-*cis*-isoprene) in PI₀, [DMA] – [DMA] in PI_{I–to–VI, I+II, III+IV, V+VI}, [C_{C=O}] – [C_{C=O}], [C_{C=O}] – [DMA] in PI_{I, III, V, I+II, III+IV, V+VI}, [O_{OH}] – [O_{OH}], [O_{OH}] – [H_{OH}], and [O_{OH}] – [DMA] in PI_{II, IV, VI, I+II, III+IV, V+VI}. Here the notation [A] represents the center of mass of the functional group A. For clarity, it is essential to emphasize that throughout this study, the notation [A]–[B] is utilized as a symbolic representation of the spatial arrangement of a chemical functional group B around a functional group A. However, the RDFs of [A]–[B] and [B]–[A] always gave the same result in all the simulation. In computing the radial distribution functions for [DMA] – [DMA], the center of mass of the dimethyl allyl residue (DMA) was employed as mentioned above. Here, the ω terminal encompasses the Dimethyl allyl residue along with two *trans*-1,4-isoprene residues. The radial distribution functions depicted in Figures 4 and S6 illustrate the interactions between dimethyl-allyl residues within PI_{0, I–VI, I+II, III+IV, V+VI}. A subtle enhancement in the association between dimethyl-allyl residues is observed compared to that of [ISO] – [ISO] (Figure S6). This observation aligns with trends reported in our earlier investigations.^{14,16,46} Specifically, we estimated the RDFs of [C_{C=O}] around [C_{C=O}] (representing the RDF of the carbon atom of carbonyl groups around carbon atom of carbonyl groups of ester-terminated polyisoprene chains, denoted as α_{2m-1}) in PI_{I, III, V, I+II, III+IV, V+VI}, and [H_{OH}] around [O_{C=O}] (representing the RDF of the hydrogen atom of hydroxy groups of hydroxy-terminated polymer chains around oxygen atom of carbonyl group of ester terminal groups of ester-terminated polymer chains) in PI_{I+II, III+IV, V+VI}. The emergence of the first peak in the [O_{C=O}] – [H_{OH}] radial distribution functions in PI_{I+II, III+IV, V+VI} is noted at a distance of 0.2 nm, thereby affirming the establishment of hydrogen bonding interactions between α_1 – α_2 , α_3 – α_4 , and α_5 – α_6 terminal groups. These interactions facilitate the formation of heterogeneous polar aggregates between ester- and hydroxy-terminated PI chains. In the case of PI_{II, IV, VI, I+II, III+IV, V+VI}, the radial distribution functions of the hydrogen atom (bound to an oxygen atom) from one polymer chain surrounding the oxygen atom of hydroxy group of another polymer chain are represented by the black color. The occurrence of the first peak in the [O_{OH}] – [H_{OH}] RDFs in PI_{II, IV, VI, I+II, III+IV, V+VI} is observed at a distance of 0.2 nm which confirms the formation of hydrogen bond between α_2 – α_2 , α_4 – α_4 , and α_6 – α_6 terminal groups and that facilitate the formation of homogeneous polar aggregates between hydroxy-terminated PI chains. The peaks observed in the radial distribution functions [O_{C=O}] $_{\alpha_{2m-1}}$ – [H_{OH}] $_{\alpha_{2m}}$ ($m = 1, 2, 3$) exhibit notably higher intensities compared to those of [O_{OH}] – [H_{OH}], [C_{C=O}] – [C_{C=O}], [ISO] – [ISO], and [DMA] – [DMA] RDFs peaks. This observation underscores the pronounced association between ester-terminated polyisoprene chains and hydroxy-terminated polyisoprene chains, surpassing the associations observed between hydroxy- and hydroxy-terminated polyisoprene chains. The correlation tendencies observed in the three mixtures can be generalized to any combinations of PI_{ODD} + PI_{EVEN}, i.e., one can expect high first RDF peaks of [O_{C=O}] $_{\alpha_{\text{odd}}}$ – [H_{OH}] $_{\alpha_{\text{even}}}$ and [H_{OH}] $_{\alpha_{\text{even}}}$ – [O_{C=O}] $_{\alpha_{\text{odd}}}$ in the mixture of ω PI $_{\alpha_{\text{odd}}}$ + ω PI $_{\alpha_{\text{even}}}$. In the case of I_{V+VI}, the intensity of the [O_{C=O}] – [H_{OH}] RDF peak surpasses those observed in PI_{I+II} and PI_{III+IV}. This heightened intensity

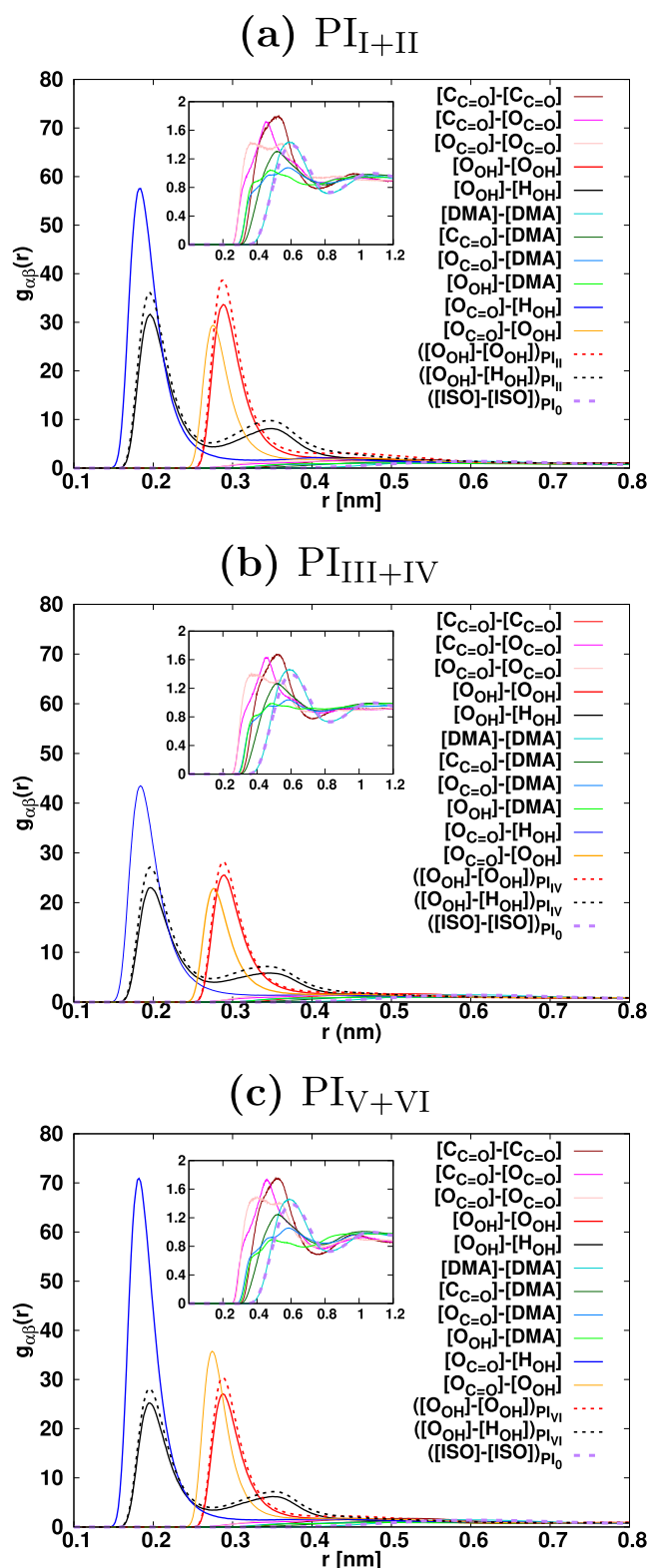


Figure 4. Radial distribution functions (RDFs) depict the spatial distributions of terminals around terminals across ten distinct *cis*-polyisoprene systems, (a) PI_{I+II}, (b) PI_{III+IV}, and (c) PI_{V+VI}. As a point of reference, the ISO around ISO RDF (gray line) in the pure PI system (PI₀) is included in all graphs, denoted by “[ISO]” representing the center of mass of isoprene residues of the terminals. The notation “[DMA]” designates the centroid of the dimethyl allyl group, specifically representing the dimethyl allyl residue of the ω terminal. Similarly, “[C_{C=O}]” expresses the carbon atom in the ester group in $\alpha 1$, $\alpha 3$, and $\alpha 5$ -terminals. [O] and [H] denote the oxygen and hydrogen

Figure 4. continued

atoms of the hydroxy group in $\alpha 2$, $\alpha 4$, and $\alpha 6$ -terminals. In the RDFs represented by $g_{\alpha\beta}$, α and β symbolize various terminal groups, including [C_{C=O}], [O_{C=O}], [ISO], [DMA], [O_{OH}], and [H_{OH}]. The RDFs of β around α symbolically expressed by $[\alpha] - [\beta]$, and the RDFs of α around β is expressed as $[\beta] - [\alpha]$. In the current investigation $[\alpha] - [\beta]$ and $[\beta] - [\alpha]$ are same. These RDFs are represented by using specific colors: purple for [ISO] – [ISO], dark-cyan for [DMA] – [DMA], red color dashed lines for ([C_{C=O}] – [C_{C=O}]), dark-green for [C_{C=O}] – [DMA], black for [O_{OH}] – [H_{OH}], red color for [O_{OH}] – [O_{OH}], and dark-green color for [O] – [DMA]. Additionally, dark-blue color solid lines depict [O_{C=O}] – [H_{OH}], while dark-blue color dashed lines represent [O_{C=O}] – [O_{OH}].

facilitates the formation of robust associations between the –C=O and –OH groups of $\alpha 5$ and $\alpha 6$ terminal ends, respectively.

The intensities of the first peaks observed for $[\alpha 1] - [\alpha 2]$, $[\alpha 3] - [\alpha 4]$, and $[\alpha 5] - [\alpha 6]$ substantially surpass those of [ISO] – [ISO], $[\alpha 1] - [\alpha 1]$, $[\alpha 2] - [\alpha 2]$, $[\alpha 3] - [\alpha 3]$, $[\alpha 4] - [\alpha 4]$, $[\alpha 5] - [\alpha 5]$, and $[\alpha 6] - [\alpha 6]$. Conversely, the peak intensities observed for $[\alpha 2] - [\alpha 2]$, $[\alpha 4] - [\alpha 4]$, and $[\alpha 6] - [\alpha 6]$ exhibit notably higher magnitudes in comparison to those of $[\alpha 1] - [\alpha 1]$, $[\alpha 3] - [\alpha 3]$, $[\alpha 5] - [\alpha 5]$, and [ISO] – [ISO]. Hence, the association between ester and hydroxy terminal ends exhibits greater strength than that between hydroxy terminal ends in a mixture of ester- and hydroxy-terminated polyisoprene chains. Nonetheless, the propensity for hydroxy–hydroxy association markedly exceeds that of ester–ester, ISO–ISO, and DMA–DMA interactions. In all the mixtures, we observed narrow RDF peaks in between α terminal groups of hydroxy-terminated polyisoprene chains while the first RDF peaks of α terminal groups of ester-terminated polyisoprene chains are very low and broader. The first coordination shell of hydroxy- around ester-terminal ends and hydroxy- around hydroxy- α terminal ends are more structured than that in ester around ester α terminals. The coordination shell of ester around ester is more ordered than that of DMA around DMA. In the primary coordination shell, the arrangement of hydroxy terminals around ester-terminal ends and hydroxy terminals around other hydroxy α terminal ends exhibits a higher degree of organization compared to the configuration observed for ester terminals around ester α terminals. Additionally, the coordination shell formed by ester terminals around ester α terminals demonstrates greater structural regularity in comparison to the arrangement of DMA terminals around DMA. Through the examination of running coordination numbers (RCNs) (Figure S7), it becomes evident that within the first coordination shell, the count of hydroxy α terminals surrounding the ester α terminal, as well as the count of hydroxy α terminals surrounding other hydroxy α terminals, markedly exceeds those of ester terminals around ester α terminals, DMA terminals around DMA, and ISO terminals around ISO.

Utilizing the single linkage algorithm, we conducted an association analysis as outlined in previous studies.⁶¹ Subsequently, we introduced the notion of an “encountering-state” for an end-group in a polymer chain, which signifies its interaction with end-groups from other polymer chains. At any given time step, if the distance between end-groups originating from distinct polyisoprene (PI) chains falls below a predefined threshold distance r_{th} , we identify these end-groups as being in an “encountering-state”. Furthermore, if either of the two ends is

in an encountering-state with an end-group from another chain, we deduce that the third end-group is also in an encountering-state with the first two end-groups. This iterative process enables the determination of the size s of the encountering end-groups by aggregating the number of encountering end-groups. Consequently, we can compute the count n_s for each size s .

The end-groups involved in an encountering-state consist exclusively of a single type of end-group, designated as α type. We denote the count of encountering end-groups with size s in this scenario as $n_s^{\alpha\alpha}$. However, when encountering end-groups encompass two distinct types of ends, namely α and β , we employ the notation $n_s^{\alpha\beta}$. Although the occurrence of encountering-events involving three different types of terminal groups is theoretically possible, our investigations of the mixed systems did not reveal any such events. Therefore, we limit our focus to encountering-events that involve either one or two distinct types of terminal groups. The calculation of $n_s^{\alpha\beta}$ was performed by considering the center of mass of the α -type end group relative to the center of mass of the β -type end group. The count of encountering end-groups with size s is computed across K intervals during the final 100 ns of the 1000 ns simulation trajectories. Here, K represents the number of frames within the 100 ns simulation period, denoted as $n_s^{\alpha\beta}(k)$ with $k = 1, \dots, K = 50,000$. Utilizing the values of $n_s^{\alpha\beta}(k)$, we determine the encountering-event-fraction $f_{\text{enc}}^{\alpha\beta}(s)$ for a given size s as follows (eq 12):

$$f_{\text{enc}}^{\alpha\beta}(s) = \frac{1}{M} \frac{1}{K} \sum_{k=1}^K n_s^{\alpha\beta}(k) \quad (12)$$

The parameter M signifies the total count of chains within the system. In Figure 5, the encountering-event-fraction $f_{\text{enc}}^{\alpha\beta}(s)$ is depicted as a function of the encountering-event-size s for each melt system.

The value $f_{\text{enc}}^{\alpha\beta}(s = 2)$ denotes the proportion of end-group encounters with another end-group. For example, when $\sum_{\beta} f_{\text{enc}}^{\alpha\beta}(s = 2) = 1$, it signifies that every α end-group is linked with a β end-group of another chain. Consequently, all the α end-groups exist as dimers with β -end groups, constituting 100% of the total. The encountering-event-fraction of end-groups exhibits a decreasing trend as the size increases. In the pure ester-terminated polyisoprene melt systems (PI_{I, III, V}), encountering-end-groups are predominantly observed in size two, with fewer instances of size three, and very rare occurrences of size four.^{14–16} However, in mixed melt systems PI_{I+II, III+IV, V+VI}, larger-sized encountering-end-groups also emerge. Additionally, ester-terminal ends facilitate the encountering of ester terminal end-groups with hydroxy terminal end-groups of sizes two, three, and four. For the pure melt systems, namely PI_{II}, PI_{IV}, and PI_{VI}, encountering-events of size two and three are observed, alongside larger-sized encountering-events due to strong hydrogen bond interactions between α_2 , α_4 , and α_6 terminals.^{14–16} Furthermore, in mixed melt systems PI_{I+II, III+IV, V+VI}, the fraction of encountering-events involving ester around hydroxy terminals notably increases. However, these events are less pronounced compared to those involving hydroxy around ester terminals. Although encountering-events between ester-hydroxy end-groups are observed with certain fractions, the stability of the formed clusters, referred to as stable physical junctions, cannot be conclusively determined. The heterogeneous and homogeneous encountering-event-size s is denoted by (OH) _{s} , (DMA) _{s} , (O_{C=O}) _{s} , (OH)_{pp}(DMA)_{qq}, (O_{C=O})_{pp}(DMA)_{qq} or (O_{C=O})_{pp}(OH)_{qq} where pp = 1, 2, ...

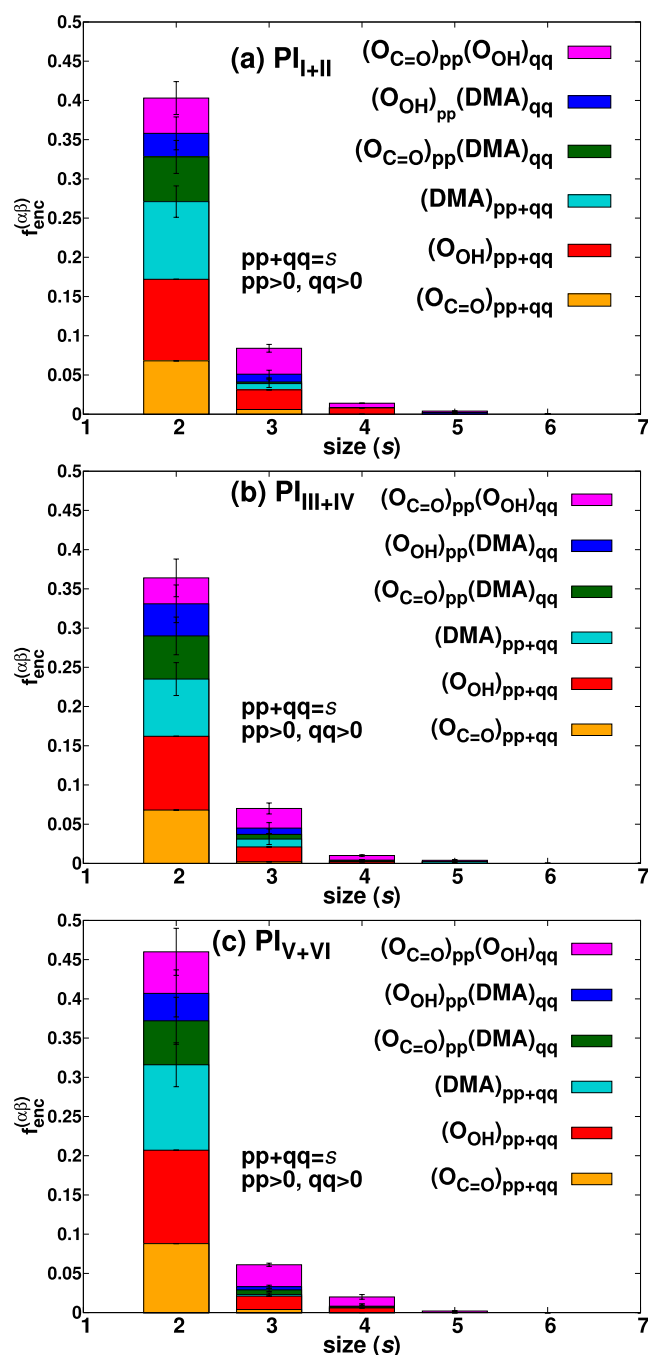


Figure 5. Encountering-event-fraction of end-groups as a function of size s for the (a) PI_{I+II}, (b) PI_{III+IV}, and (c) PI_{V+VI} systems. The designated cut threshold length, r_{thr} , is established at 0.6 nm. It is important to note that in an encountering-event involving DMA, the DMA may originate from both PI_{even} and PI_{odd}. No encountering-events involving three distinct types of terminal groups were observed. The fractions corresponding to $s = 1$ are not represented in the plot.

and qq = 1, 2, ... with $s = \text{pp} + \text{qq}$. It should be noted that the DMA involved in the encounter events of (DMA) _{s} , (OH)_{pp}(DMA)_{qq}, and (O_{C=O})_{pp}(DMA)_{qq} can originate from both PI_{even} and PI_{odd}. Regarding encountering-event-fractions of size two, occurrences of (OH)₂ are substantially larger to those of (O_{C=O})₁(OH)₁. Additionally, (OH)₂, and (O_{C=O})₁(OH)₁ encounters are slightly more frequent than (OH)₁(DMA)₁ and (DMA)₂. Similarly, for size three, (O_{C=O})₁(OH)₂, and (OH)₃ dominate over (DMA)₃, (OH)₂(DMA)₁, and (OH)₁(DMA)₂.

(Other possibility like $(\text{O}_{\text{C}=\text{O}})_2(\text{OH})_1$ are not present.). For size four, contributions from $(\text{O}_{\text{C}=\text{O}})_1(\text{OH})_3$, and $[(\text{OH})_4]$ are significant, while the contribution of $(\text{OH})_1(\text{DMA})_3$ is minor (Other possibility like $(\text{OH})_2(\text{DMA})_2$, and $(\text{O}_{\text{C}=\text{O}})_3(\text{OH})_1$ is not observed). For size five, $(\text{O}_{\text{C}=\text{O}})_1(\text{OH})_4$, $(\text{O}_{\text{C}=\text{O}})_2(\text{OH})_3$, and $(\text{OH})_5$ are observed. Namely, for example, $[(\text{OH})_5]$ should be replaced with $(\text{OH})_5$. Although the observation of end-group encounters occurs with a discernible fraction, it remains inadequate for determining whether the encountered end-groups establish stable physical junctions or clusters. Evaluating the stability of such clusters typically involves the utilization of potentials of mean force (PMFs).⁶² (The potentials of mean force is computed between terminal ends by using eq S1, given in the Supporting Information. More details are provided in the Supporting Information) Figure 6 depicts the potentials of mean force (PMFs) between the two terminal groups as a function of their separation distance. Notably, each PMF profile exhibits a distinct minimum indicative of contact pairs, hereby designated as the contact minimum (CM). In PI_0 , we identified a slight energy minimum for contact pairs comprising the ISO – ISO terminals (where ISO denotes hydrogen-terminated 1,4-*cis*-isoprene) at a distance of 0.6 nm. For the $\text{PI}_{\text{I+II}}$, $\text{PI}_{\text{III+IV}}$, $\text{PI}_{\text{V+VI}}$ melt systems, we observed a subtle decrease in free energy for contact pairs involving $(\text{C}_{\text{C}=\text{O}})_{\alpha_{2n-1}} - (\text{C}_{\text{C}=\text{O}})_{\alpha_{2n-1}}$ ($n = 1, 2, 3$) terminals at a distance of 0.5 nm, as well as between DMA- and DMA-terminals at a distance of 0.6 nm. The interaction free energies between ISO- and ISO-terminals in the PI_0 system (depicted as the gray line in Figure 6), as well as among $(\text{C}_{\text{C}=\text{O}})_{\alpha_{2n-1}} - (\text{C}_{\text{C}=\text{O}})_{\alpha_{2n-1}}$ ($n = 1, 2, 3$) in the $\text{PI}_{\text{I+II}}$, $\text{PI}_{\text{III+IV}}$, $\text{PI}_{\text{V+VI}}$ systems, along with DMA- and DMA-terminals in the $\text{PI}_{\text{I+II}}$, $\text{PI}_{\text{III+IV}}$, $\text{PI}_{\text{V+VI}}$ systems, are comparable to thermal energy. Consequently, these interactions cannot be deemed as stable associations. In contrast, in the $\text{PI}_{\text{I+II}}$, $\text{PI}_{\text{III+IV}}$, $\text{PI}_{\text{V+VI}}$ melt systems, distinct deep minima are evident for contact pairs comprising $\alpha_1 - \alpha_2$, $\alpha_2 - \alpha_2$, $\alpha_3 - \alpha_4$, $\alpha_4 - \alpha_4$, $\alpha_5 - \alpha_6$, and $\alpha_6 - \alpha_6$ terminals. These contact pairs demonstrate significantly greater stabilities than the thermal energy. The stabilities of the $\alpha_1 - \alpha_2$, $\alpha_2 - \alpha_2$, $\alpha_3 - \alpha_4$, $\alpha_4 - \alpha_4$, $\alpha_5 - \alpha_6$, and $\alpha_6 - \alpha_6$ interactions are notably higher in comparison to those involving ISO – ISO, $\omega - \omega$, $\alpha_1 - \alpha_1$, $\alpha_3 - \alpha_3$, and $\alpha_5 - \alpha_5$ terminals. To establish a stable cluster formation, the magnitude of free energy $|W|$ at the contact minimum (CM) must notably exceed thermal energy. Therefore, we defined the criterion for cluster formation as $|W| > 2k_{\text{B}}T$ at the contact minimum. Upon analyzing the data depicted in Figure 6, we determined dissociation barriers for the $(\text{O}_{\text{C}=\text{O}})_{\alpha_{2m-1}} - (\text{H}_{\text{OH}})_{\alpha_{2m}}$ ($m = 1, 2, 3$) contact minimum as $4.05 k_{\text{B}}T$, $3.77 k_{\text{B}}T$, and $4.26 k_{\text{B}}T$ for the $\text{PI}_{\text{I+II}}$, $\text{PI}_{\text{III+IV}}$, and $\text{PI}_{\text{V+VI}}$ mixed PI melt systems, respectively. The dissociation barriers at the $(\text{O}_{\text{OH}})_{\alpha_{2m}} - (\text{O}_{\text{OH}})_{\alpha_{2m}}$ ($m = 1, 2, 3$) contact minimum are quantified as $3.51 k_{\text{B}}T$, $3.24 k_{\text{B}}T$, and $3.29 k_{\text{B}}T$ for the $\text{PI}_{\text{I+II}}$, $\text{PI}_{\text{III+IV}}$, and $\text{PI}_{\text{V+VI}}$ mixed melt systems, respectively.

Based on the PMF results, we establish a criterion for determining a stable association between two terminal groups in the following manner. When the PMF (W) between two terminal groups satisfies the inequality $(|W(r_{\text{CM}})| > 2k_{\text{B}}T)$, where r_{CM} represents the distance at the contact minimum, it indicates that the two terminal groups are in a state of stable association and can form a cluster. The count of terminal groups participating in a cluster is determined based on two criteria: (i) the distance criterion described in eq 12, and (ii) the criterion for stable association $(|W(r_{\text{CM}})| > 2k_{\text{B}}T)$. The number of clusters

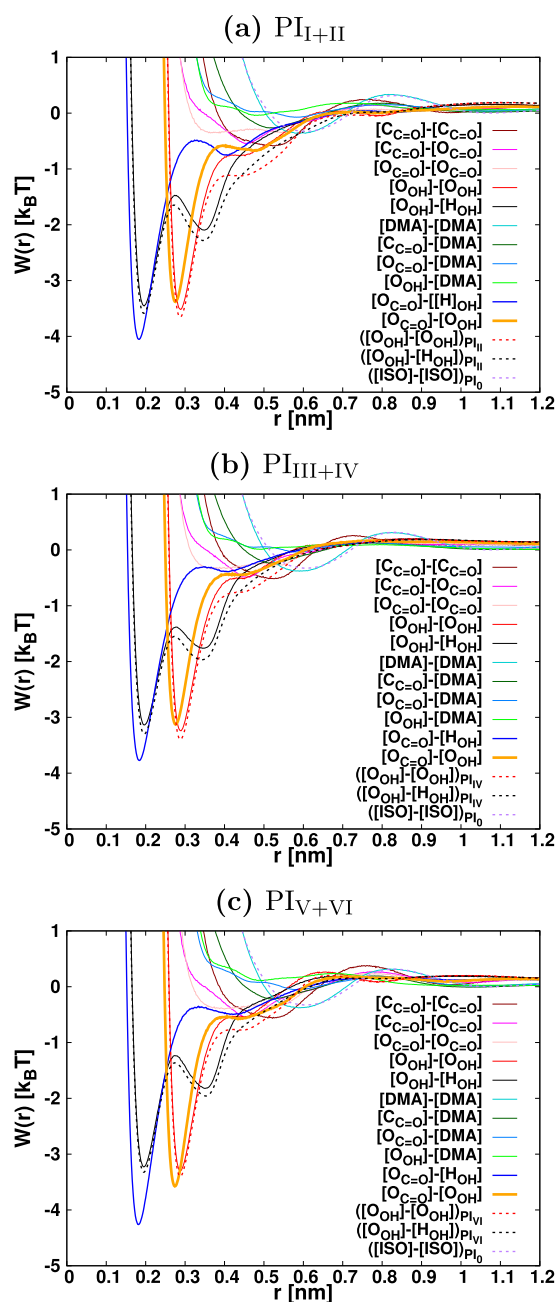


Figure 6. Potential of mean force $W(r)$, defined by $W(r) = -k_{\text{B}}T \log(g(r))$ where k_{B} represents the Boltzmann constant in units of $\text{kJ mol}^{-1}/\text{K}$, T the system temperature, and $g(r)$ the radial distribution function between the terminal groups. The potentials of mean force between the terminal ends are shown for (a) $\text{PI}_{\text{I+II}}$, (b) $\text{PI}_{\text{III+IV}}$, and (c) $\text{PI}_{\text{V+VI}}$. The error bars of each PMF profile is below $0.2 k_{\text{B}}T$. Note that $W(r)$ for $[\text{Y}]-[\text{X}]$ means the potential of the mean force between “Y” and “X”. In addition, $[\text{X}]-[\text{Y}]$ is same as $[\text{Y}]-[\text{X}]$. The gradient of $W(r)$ gives the force between “Y” and “X” averaged over the equilibrium distribution for all the other atoms. The [DMA] in PMF’s involving [DMA] can originate both from the ω terminal of PI with α_{2m-1} terminal and the one of PI with α_{2m} ($m = 1, 2, 3$).

of size s is determined and denoted as $n_s^{(\alpha\beta)}(k; |W(r_{\text{CM}})| > 2k_{\text{B}}T)$, where α and β correspond to O_{OH} , $\text{O}_{\text{C}=\text{O}}$ or DMA. The superscript α and β in this context carry the same significance as the notation used for the count of encountering end-groups. As an illustration, $n_s^{(\text{O}_{\text{C}=\text{O}}-\text{OH})}$ signifies the count of clusters with a size of s that encompass both $(\text{O}_{\text{C}=\text{O}})$ and OH residues of the

terminals, and $n_s^{(\text{OH}-\text{OH})}$ ($n_s^{(\text{O}_{\text{C}=\text{O}}-\text{O}_{\text{C}=\text{O}})}$ or $n_s^{(\text{DMA}-\text{DMA})}$) represents the count of clusters with a size of s that exclusively consist of OH ($\text{O}_{\text{C}=\text{O}}$ or DMA) terminal groups. By utilizing the aforementioned quantities, we establish the cluster formation fraction $f_{\text{cluster}}^{(\alpha\beta)}(s)$ as follows (eq 13):

$$f_{\text{cluster}}^{(\alpha\beta)}(s) = \frac{1}{M} \frac{1}{K} \sum_{k=1}^K n_s^{(\alpha\beta)}(k; |W(r_{\text{CM}})| > 2k_B T) \quad (13)$$

Figure 7 displays the cluster-formation-fraction, $f_{\text{cluster}}^{(\alpha\beta)}(s)$, revealing the extent of cluster formation. In the mixed polyisoprene melt systems $\text{PI}_{\text{I+II}}$, $\text{PI}_{\text{III+IV}}$, and $\text{PI}_{\text{V+VI}}$, we note the occurrence of clusters with sizes of two, three, four, and five units, with no clusters of size $s \geq 6$ detected. However, in the pure systems composed only of HPI_{H} , $\text{PI}_{\alpha 1}$, $\text{PI}_{\alpha 3}$ and $\text{PI}_{\alpha 5}$, the formation of clusters by the terminal groups is notably absent.^{14,16} This absence of cluster formation specifically precludes the association between terminal groups such as DMA – DMA, $\text{O}_{\text{C}=\text{O}}$ – DMA, and OH – DMA. A similar pattern was previously reported in our earlier investigations.^{14,16} The observed fractions of cluster formation, with sizes ranging from two to five, for $(\text{O}_{\text{C}=\text{O}})_1(\text{OH})_{1-\text{to}-4}$ closely resemble those of $(\text{OH})_{2-\text{to}-4}$. In addition, any clusters composed of three distinct types of terminal ends are not formed.

3.4. Analyzing Terminal Groups Survival Probability in Heterogeneous and Homogeneous Cluster

The survival probability $P_{[\text{Y}]-[\text{X}]}(\tau)$ represents the probability of X particles around Y particle in a spherical region centered at the geometric center of Y, with a radius of r_{thrd} .^{63,64} Computation of the survival probability for terminal groups has been accomplished using the subsequent equation (eq 14).

$$P_{[\text{Y}]-[\text{X}]}(\tau) = \frac{1}{M_{\text{tot}}} \sum_{t=1}^{M_{\text{tot}}} \frac{N_{[\text{Y}]-[\text{X}]}(t, t + \tau)}{N_{[\text{Y}]-[\text{X}]}(t)} \quad (14)$$

Here, $N_{[\text{Y}]-[\text{X}]}(t)$ denotes the count of X terminal groups around Y terminal group at time t in a spherical region centered at the geometric center of Y, with a prescribed radius (r_{thrd}). Similarly, $N_{[\text{Y}]-[\text{X}]}(t, t + \tau)$ signifies the number of X-terminal groups persistently occupying the same spherical region, defined by a specified radius, from time t to a subsequent time $t + \tau$. Additionally, M_{tot} represents the cumulative count of time steps considered for computing $P_{[\text{Y}]-[\text{X}]}(\tau)$, while τ indicates the time interval between consecutive configurations under examination. To determine the radius r_{thrd} of the defined region utilized in computing $P_{[\text{Y}]-[\text{X}]}(\tau)$ for X around Y where $X, Y = \{[\text{O}_{\text{OH}}], [\text{O}_{\text{C}=\text{O}}]\}$, the radial distribution functions (RDFs) between $[\text{O}_{\text{OH}}] - [\text{O}_{\text{C}=\text{O}}]$, $[\text{O}_{\text{OH}}] - [\text{O}_{\text{OH}}]$, and $[\text{O}_{\text{C}=\text{O}}] - [\text{O}_{\text{OH}}]$ were analyzed (refer to Figure 4). Based on the resultant RDF, we determined the radius of these selected regions to be equivalent to that of the first coordination shells surrounding [ISO] (where ISO denotes Hydrogen-terminated 1,4-*cis*-isoprene), [DMA], $[\text{O}_{\text{OH}}]$, and $[\text{C}_{\text{C}=\text{O}}]$.

The survival probability was determined through the utilization of the MDAnalysis software package.⁶⁵ These probabilities were derived from the final 10 ns of 1000 ns independent molecular dynamics (MD) simulations. Each survival probability was obtained by averaging over time windows at specified intervals spanning from 1 to 200 ps. From Figure 8, it is observed that the survival probabilities exhibit a gradual decay of hydroxy groups around ester group in hydroxy-terminated polyisoprene than those in hydroxy groups around hydroxy. In addition, the behavior of $P_{[\text{Y}]-[\text{X}]}(\tau)$ is

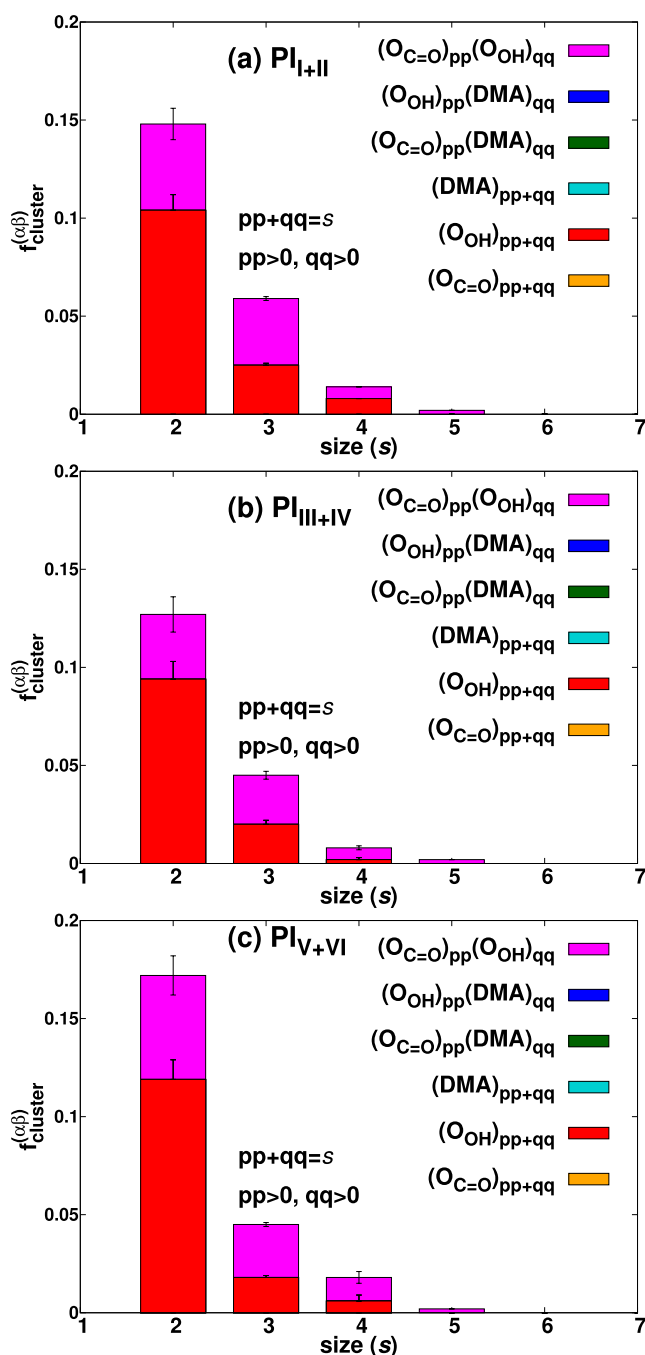


Figure 7. Cluster-formation-fraction as a function of cluster size s in the (a) $\text{PI}_{\text{I+II}}$, (b) $\text{PI}_{\text{III+IV}}$, and (c) $\text{PI}_{\text{V+VI}}$ systems. An additional criterion utilizing the magnitude of potentials of mean force between terminal groups to determine stable cluster formation. Note that $\sum_{s=1}^{\infty} f_{\text{cluster}}^{(\alpha\beta)}(s) = 1$ for each system, and the fractions for $s = 1$ are not shown.

almost the same as that of $P_{[\text{X}]-[\text{Y}]}(\tau)$ in the three mixtures. The decay times of the survival probability curves $P_{[\text{Y}]-[\text{X}]}(\tau)$ were determined through fitting using the Kohlrausch–Williams–Watts stretched exponential function, we estimated the characteristic decay times τ_{sp} and show them in Table 5. Consequently, the relaxation times of hydroxy terminal groups surrounding ester groups exhibits slower kinetics compared to those of hydroxy terminal groups adjacent to hydroxy groups. This observation suggests that the physical junction points (PJPs) between ester and hydroxy α terminal groups, possess higher structural integrity and stability than those involving

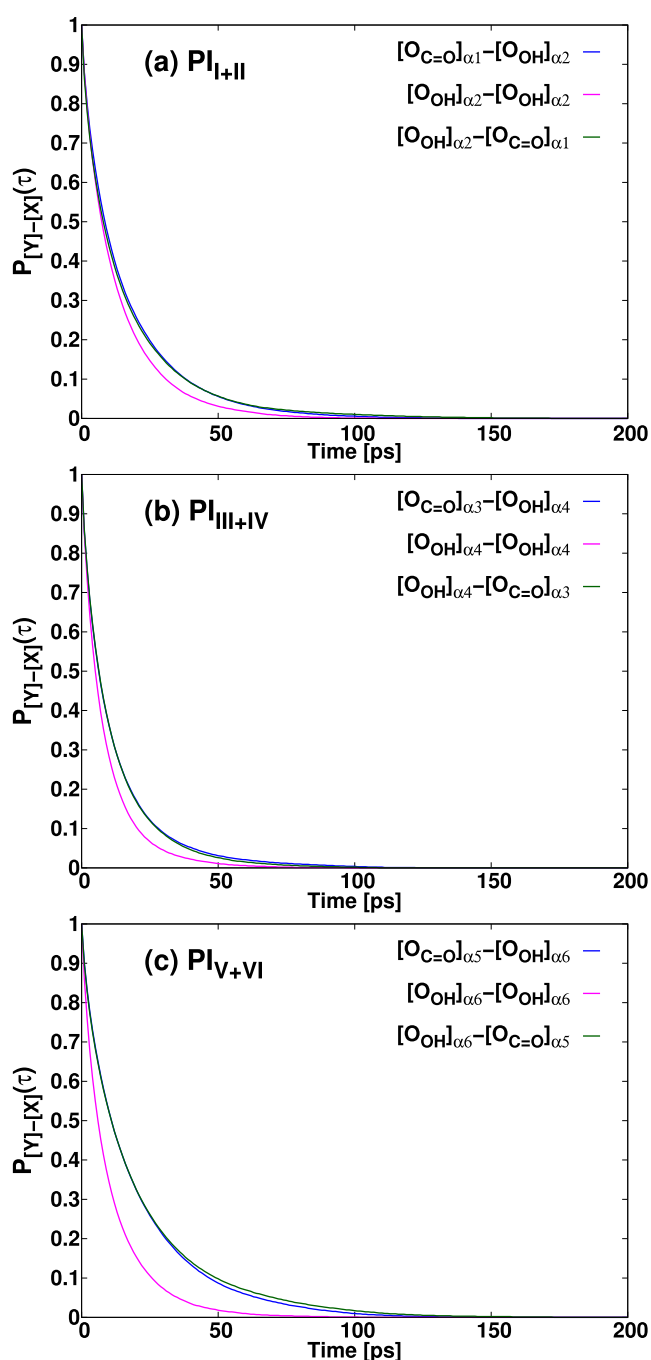


Figure 8. Survival probabilities $P_{[Y]-[X]}(\tau)$ for terminal groups located within the first coordination shell of each terminal group as functions of the time duration τ in the systems (a) PI_{I+II} , (b) PI_{III+IV} , and (c) PI_{V+VI} . $[O_{C=O}]$ and $[O_{C=O}]$ groups do not form any clusters; hence, the survival probabilities $P_{[Y]-[X]}(\tau)$ for $[O_{C=O}] - [O_{C=O}]$ are not presented in (a–c).

hydroxy and hydroxy α terminal groups. Further details, including relaxation times and stretching exponents are provided in Table 5.

3.5. Self-Diffusion Characteristics of Ester- and Hydroxy-Terminated Polymer Chains in a Mixed PI Melt System

We investigate the diffusion characteristics of individual polyisoprene chains within each melt system. Utilizing the final 1000 ns of the production-run trajectories, we calculate the

Table 5. Survival Probability $P_{[Y]-[X]}(\tau)$ is Analyzed through Fitting with the Kohlrausch–Williams–Watts Stretched Exponential Function, Enabling the Determination of both the Average Survival Time τ_{sp} and β_{sp} Parameters

systems	association pair		τ_{sp} [ps]	β_{sp}
PI_{I+II}	$[O_{C=O}]$	$[O_{OH}]$	13.519 ± 0.008	0.802 ± 0.001
	$[O_{OH}]$	$[O_{OH}]$	11.436 ± 0.004	0.838 ± 0.001
	$[O_{OH}]$	$[O_{C=O}]$	12.811 ± 0.008	0.762 ± 0.001
PI_{III+IV}	$[O_{C=O}]$	$[O_{OH}]$	9.870 ± 0.011	0.785 ± 0.001
	$[O_{OH}]$	$[O_{OH}]$	7.704 ± 0.007	0.847 ± 0.001
	$[O_{OH}]$	$[O_{C=O}]$	9.893 ± 0.004	0.809 ± 0.001
PI_{V+VI}	$[O_{C=O}]$	$[O_{OH}]$	17.078 ± 0.016	0.823 ± 0.001
	$[O_{OH}]$	$[O_{OH}]$	9.334 ± 0.003	0.677 ± 0.003
	$[O_{OH}]$	$[O_{C=O}]$	17.217 ± 0.010	0.789 ± 0.001

mean square displacement (MSD) of the center of mass for each polyisoprene chain (eq 15):

$$\langle (\Delta R_{cm}(t))^2 \rangle \sim D_{diff} t^{\alpha_{msd}} \quad (15)$$

where $\Delta R_{cm}(t) \equiv R_{cm}(t) - R_{cm}(0)$ and $\langle (\Delta R_{cm}(t))^2 \rangle$ represents the mean square displacement of the center of mass of a polyisoprene chain at time t . We have shown the mean square displacements for the centers of mass of polymer chains in each melt system in Figure 9.

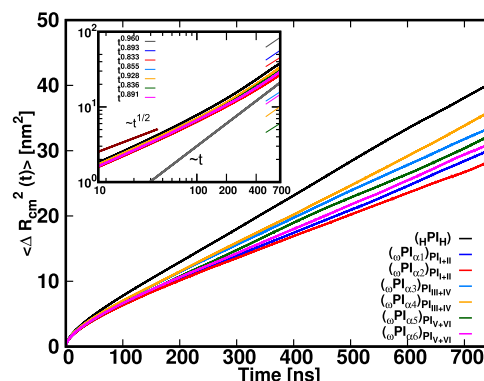


Figure 9. Mean square displacements for the centers of mass of polymer chains in each melt system. The inset stands for the log–log plot of the main graph.

We have observed that the center of mass motion of polymer chains exhibits subdiffusive behavior, characterized by $\langle (\Delta R_{cm}(t))^2 \rangle$, across all melt systems PI_{I+II} , $(PI_{\alpha 1})PI_{I+II}$, $(PI_{\alpha 2})PI_{I+II}$, $(PI_{\alpha 3})PI_{III+IV}$, $(PI_{\alpha 4})PI_{III+IV}$, $(PI_{\alpha 5})PI_{V+VI}$, and $(PI_{\alpha 6})PI_{V+VI}$, with exponents shown in Table 6. We determined the exponent α_{msd} by fitting the data in the 400–700 ns time range. Similarly, the self-diffusion coefficients, D_{diff} were derived by linearly fitting the same time range which is corresponding to the Fickian regime $\langle (\Delta R_{cm}(t))^2 \rangle \sim D_{diff} t$. In the case of PI_0 melt system, the Self-diffusion coefficients D_{diff} are in good agreement with the reported values.^{21,22,66} From the data in Table 6, one can see the clear slowing down of a single chain diffusion in the three mixtures than that in PI_0 . The decreasing of the self-diffusion coefficients can be attributed to the formation of stable associations among terminals in the mixed systems.

Table 6. Exponent α_{msd} and Self-Diffusion Coefficients D_{diff} for Ester and Hydroxy-Terminated PI Chain in Mixed Melt Systems^a

system	chain	type of α terminal	α_{msd}	D_{diff} [10^{-8} cm ² /s]	$(D_{\text{diff}})_{\text{system}}/(D_{\text{diff}})_{\text{PI}_0}$
PI ₀	HPI _H	hydrogen	0.960 ± 0.001	9.528	1
PI _{I+II}	ω PI _{α_1}	ester	0.893 ± 0.001	6.891	0.7232
PI _{III+IV}	ω PI _{α_3}		0.855 ± 0.001	7.793	0.8179
PI _{V+VI}	ω PI _{α_5}		0.836 ± 0.001	7.436	0.7804
PI _{I+II}	ω PI _{α_2}	hydroxy	0.833 ± 0.001	6.595	0.6921
PI _{III+IV}	ω PI _{α_4}		0.928 ± 0.001	8.147	0.8550
PI _{V+VI}	ω PI _{α_6}		0.891 ± 0.001	7.135	0.7488

^aBecause the diffusion behavior shows a sub-diffusive one in a short time range, then changes to a diffusive one, the exponent α_{msd} for a sub-diffusive one is estimated by fitting the data into 400–700 ns. As a long-time behavior, the self-diffusion coefficients D_{diff} is estimated by fitting the data into 400–700 ns.

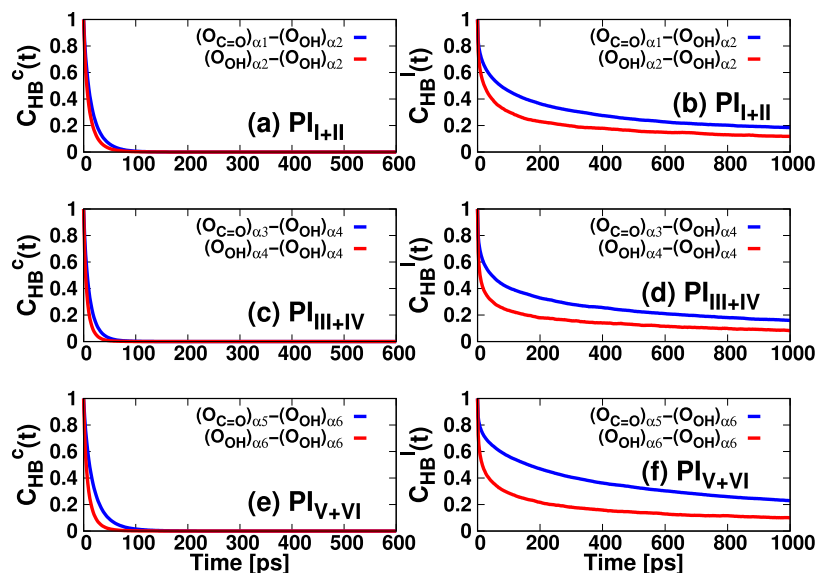


Figure 10. Continuous $C_{\text{HB}}^c(t)$ (a, c, and e) and intermittent $C_{\text{HB}}^I(t)$ (b, d, f) hydrogen bond correlation functions $(\text{O}_{\text{C=O}})_{\alpha_1} - (\text{O}_{\text{OH}})_{\alpha_2}$, $(\text{O}_{\text{OH}})_{\alpha_2} - (\text{O}_{\text{OH}})_{\alpha_2}$, $(\text{O}_{\text{C=O}})_{\alpha_3} - (\text{O}_{\text{OH}})_{\alpha_4}$, $(\text{O}_{\text{OH}})_{\alpha_4} - (\text{O}_{\text{OH}})_{\alpha_4}$, and $(\text{O}_{\text{C=O}})_{\alpha_5} - (\text{O}_{\text{OH}})_{\alpha_6}$, $(\text{O}_{\text{OH}})_{\alpha_6} - (\text{O}_{\text{OH}})_{\alpha_6}$ for the (a) and (b) PI_{I+II}, (c) and (d) PI_{III+IV}, and (e) and (f) PI_{V+VI} melt systems. The pairs $\alpha_1 - \alpha_2$, $\alpha_3 - \alpha_4$, and $\alpha_5 - \alpha_6$ are shown by solid blue lines and $\alpha_2 - \alpha_2$, $\alpha_4 - \alpha_4$, and $\alpha_6 - \alpha_6$ are shown by solid red lines.

3.6. Investigating Heterogeneous and Homogeneous Cluster Dynamics: Insights into Hydrogen-Bond Dynamics

To explore the dynamics of hydrogen bonds within the polymer melt systems, we conducted an analysis focusing on the hydrogen bond (HB) time correlation function $C_{\text{HB}}(t)$ for pairs of hydrogen-bonded polymer chains labeled as i and j . This correlation function, crucial for elucidating hydrogen bond dynamics, adheres to the definition established in prior investigations^{67,68} and shown below (eq 16):

$$C_{\text{HB}}^x(t) = \left\langle \frac{\sum h_{ij}(t_0)h_{ij}(t_0 + t)}{\sum (h_{ij}(t_0))^2} \right\rangle \quad (16)$$

Here, the variable $h_{ij}(t)$ quantifies whether a pair i, j of polymer chains satisfies the geometric criteria of a hydrogen bond at time t , with $h_{ij}(t) = 1$ indicating satisfaction and $h_{ij}(t) = 0$ otherwise. For a hydrogen bond to form between donor and acceptor atoms, the donor–acceptor–acceptor (D–H...A) angle must exceed 130.0°. We have observed the RDF peak around 2.8 Å for $[\text{O}_{\text{C=O}}] - [\text{O}_{\text{OH}}]$ and around 3.0 Å for $[\text{O}_{\text{OH}}] - [\text{O}_{\text{OH}}]$ in the PI_{I+II}, PI_{III+IV}, and PI_{V+VI} (Figure 4). Therefore, we have used the maximum distance 3.0 Å between the donor (O_{OH}) and acceptor (O_{OH}) or ($\text{O}_{\text{C=O}}$) atoms to calculate the hydrogen bond. The summation encompasses all potential hydrogen-

bonded pairs i, j of polymer chains, while angular brackets denote an ensemble average across multiple initial time points within the trajectory. The superscript (“c” or “I”) distinguishes between two approaches for assessing $h_{ij}(t)$ at subsequent time points: continuous ($C_{\text{HB}}^c(t)$) and intermittent ($C_{\text{HB}}^I(t)$). The hydrogen bond dynamics are characterized by both the continuous hydrogen bond correlation function $C_{\text{HB}}^c(t)$ and the intermittent hydrogen bond correlation function $C_{\text{HB}}^I(t)$, offering unique insights into the diverse facets of hydrogen bond dynamics. In alignment with the continuous hydrogen bond correlation definition, the rupture of a specific hydrogen bond entails its permanent classification as broken, irrespective of potential reformation. Thus, this definition enables the quantification of the average duration during which a hydrogen bond pair remains intact, offering an estimation of the average hydrogen bond lifetime. Regarding intermittent HB correlation, the analysis centers on the persistence probability at time t of a hydrogen bond initially established at $t = 0$, without consideration of multiple bond disruptions and subsequent reformations within the time span $[0, t]$. Within the framework of continuous hydrogen bond correlation $C_{\text{HB}}^c(t)$, the concept of lifetime is denoted as continuous lifetime τ_{HB}^c . Conversely, the lifetime associated with intermittent hydrogen bond correlation $C_{\text{HB}}^I(t)$ is termed intermittent lifetime or hydrogen bond

Table 7. Table Presents the Hydrogen Bond (HB) Relaxation Times τ_{HB} and Stretching Exponents β_{HB} of (O_{C=O}) – (O_{OH}) and (O_{OH}) – (O_{OH}) in the Melt Systems PI_{I+II,III+IV,V+VI}

system	pair		continuous		intermittent		
			$\tau_{\text{HB}}^{\text{c}}[\text{ps}]$	$\beta_{\text{HB}}^{\text{c}}$	$\tau_{\text{HB}}^{\text{i}}[\text{ps}]$	$\beta_{\text{HB}}^{\text{i}}$	P_{HB}^{i}
PI _{I+II}	O _{C=O}	O _{OH}	14.500 ± 0.005	0.8403 ± 0.0003	143.50 ± 1.09	0.3583 ± 0.0006	0.0429 ± 0.0009
	O _{OH}	O _{OH}	9.623 ± 0.006	0.7945 ± 0.0006	38.27 ± 0.29	0.3185 ± 0.0012	0.0543 ± 0.0008
PI _{III+IV}	O _{C=O}	O _{OH}	10.739 ± 0.004	0.8577 ± 0.0004	127.91 ± 0.89	0.3182 ± 0.0004	0.0146 ± 0.0007
	O _{OH}	O _{OH}	6.105 ± 0.004	0.8062 ± 0.0007	19.61 ± 0.15	0.2655 ± 0.0010	0.0279 ± 0.0008
PI _{V+VI}	O _{C=O}	O _{OH}	17.525 ± 0.007	0.8418 ± 0.0004	443.27 ± 2.92	0.4034 ± 0.0003	0.0190 ± 0.0008
	O _{OH}	O _{OH}	7.948 ± 0.006	0.7899 ± 0.0007	32.21 ± 0.09	0.3150 ± 0.0005	0.0478 ± 0.0003

relaxation time $\tau_{\text{HB}}^{\text{i}}$. The hydrogen bond correlation functions $C_{\text{HB}}^{\text{c}}(t)$ and $C_{\text{HB}}^{\text{i}}(t)$ were computed for the $\alpha 1 - \alpha 2$, $\alpha 2 - \alpha 2$, $\alpha 3 - \alpha 4$, $\alpha 4 - \alpha 4$, $\alpha 5 - \alpha 6$, and $\alpha 6 - \alpha 6$ pairs using the MDAnalysis software package.^{65,69} The resulting data are depicted in Figure 10.

We conducted an assessment of the continuous $C_{\text{HB}}^{\text{c}}(t)$ and intermittent $C_{\text{HB}}^{\text{i}}(t)$ hydrogen bond correlation functions for specific pairs, including $\alpha 1 - \alpha 2$, $\alpha 2 - \alpha 2$, $\alpha 3 - \alpha 4$, $\alpha 4 - \alpha 4$, $\alpha 5 - \alpha 6$, and $\alpha 6 - \alpha 6$, as illustrated in Figure 10. Furthermore, the determination of the hydrogen bond relaxation time τ_{HB} was achieved by fitting the hydrogen bond autocorrelation functions $C_{\text{HB}}^{\text{c}}(t)$ and $C_{\text{HB}}^{\text{i}}(t)$ using the Kohlrausch–Williams–Watts (KWW) stretched exponential function. The hydrogen bond relaxation time τ_{HB} was determined via fitting the hydrogen bond autocorrelation function $C_{\text{HB}}^{\text{c}}(t)$ with the KWW stretched exponential function, expressed as $C_{\text{HB}}^{\text{c}}(t) = C_{\text{HB}}^{\text{c}}(0) \exp[-(t/\tau_{\text{HB}}^{\text{c}})^{\beta_{\text{HB}}^{\text{c}}}]$. The values of $\tau_{\text{HB}}^{\text{c}}$ and the stretching exponent $\beta_{\text{HB}}^{\text{c}}$ are detailed in Table 7. In analyzing the intermittent hydrogen bond correlation function, we utilized a KWW stretched exponential function with an offset, represented as $C_{\text{HB}}^{\text{i}}(t) = P_{\text{HB}}^{\text{i}} + C_{\text{HB}}^{\text{i}}(0) \exp[-(t/\tau_{\text{HB}}^{\text{i}})^{\beta_{\text{HB}}^{\text{i}}}]$. The calculated values of $\tau_{\text{HB}}^{\text{i}}$, the stretching exponent $\beta_{\text{HB}}^{\text{i}}$ and the offset P_{HB}^{i} are provided in Table 7. These results support the formation of stable clusters between $\alpha 1 - \alpha 2$, $\alpha 2 - \alpha 2$, $\alpha 3 - \alpha 4$, $\alpha 4 - \alpha 4$, $\alpha 5 - \alpha 6$, and $\alpha 6 - \alpha 6$.

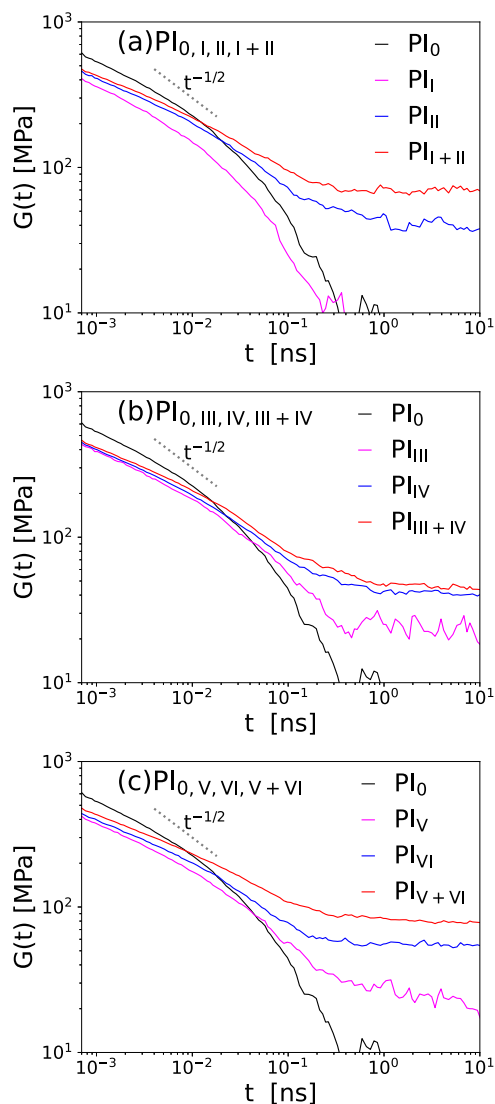
Based on the findings, it is evident that both continuous and intermittent HB lifetimes (see Figure 10 and Table 7) demonstrate notably higher values for $\alpha 1 - \alpha 2$, $\alpha 3 - \alpha 4$, and $\alpha 5 - \alpha 6$ compared to $\alpha 2 - \alpha 2$, $\alpha 4 - \alpha 4$, and $\alpha 6 - \alpha 6$. This observation provides compelling evidence for the presence of a significantly stronger correlation between hydrogen-bonded terminal ends $\alpha 1 - \alpha 2$ in PI_{I+II}, $\alpha 3 - \alpha 4$ in PI_{III+IV}, $\alpha 5 - \alpha 6$ in PI_{V+VI} in comparison to those of $\alpha 2 - \alpha 2$ in PI_{I+II} and PI_{II}, $\alpha 4 - \alpha 4$ in PI_{III+IV} and PI_{IV}, $\alpha 6 - \alpha 6$ in PI_{V+VI} and PI_{VI}.

3.7. Viscoelastic Properties

Viscoelastic properties of the pure and mixed melt systems were calculated based on the stress–stress autocorrelation which is defined as follows (eq 17).

$$G(t) = \frac{1}{6k_{\text{B}}T} \left\{ \langle \sigma_{xy}(t)\sigma_{xy}(0) \rangle + \langle \sigma_{yz}(t)\sigma_{yz}(0) \rangle + \langle \sigma_{zx}(t)\sigma_{zx}(0) \rangle + \frac{1}{4} [\langle N_{xy}(t)N_{xy}(0) \rangle + \langle N_{yz}(t)N_{yz}(0) \rangle + \langle N_{zx}(t)N_{zx}(0) \rangle] \right\} \quad (17)$$

where the normal stress difference is defined as $N_{\alpha\beta} = \sigma_{\alpha\alpha} - \sigma_{\beta\beta}$. The stress–stress autocorrelation function was evaluated by the multiple-tau method.⁷⁰ The stress–stress autocorrelation function is shown in Figure 11 for each melt system. The

**Figure 11.** Relaxation moduli $G(t)$ of the ten melt systems (a) PI_{0, I, II, I+II} (b) PI_{0, III, IV, III+IV}, and (c) PI_{0, V, VI, V+VI}. $G(t)$ is evaluated from the autocorrelation function of the stress tensor at equilibrium through eq 17. The gray dotted line stands for guideline, $t^{-1/2}$.

Rouse relaxation behavior ($G(t) \sim t^{-1/2}$) is observed in the middle time range for PI₀. However, the mixed melt systems PI_{I+II}, PI_{III+IV}, and PI_{V+VI} demonstrate noticeably slower relaxation dynamics relative to their respective pure components. This deviation is primarily attributed to the strong intermolecular associations formed between the ester and hydroxy terminal groups. The presence of stable, hydrogen-bond-mediated heterogeneous clusters in the mixed melts

further slows their relaxation dynamics compared to their pure counterparts, underscoring the influence of intermolecular interactions on the relaxation process.

4. DISCUSSION AND CONCLUDING REMARKS

We conducted all-atom MD simulations to investigate ten different types of *cis*-1,4-polyisoprene (PI) melt systems, each containing various combinations of dimethyl allyl- (*Trans*-1,4-isoprene₂) (ω) and different terminal groups, including ester-terminated isopentene ($\alpha 1$), hydroxy-terminated isopentene ($\alpha 2$), ester-terminated isobutane ($\alpha 3$), hydroxy-terminated isobutane ($\alpha 4$), ester-terminated 1,4-*cis*-isoprene ($\alpha 5$), and hydroxy-terminated 1,4-*cis*-isoprene ($\alpha 6$). Our investigation delves into the static and dynamic attributes of polyisoprene chains, encompassing parameters such as end-to-end distance R_{ee} , radius of gyration R_g , mean square internal distances, end-to-end vector autocorrelation function $C(t)$, average relaxation time τ_{rov} , Rouse mode analysis, survival probability $P(t)$ of terminal groups, hydrogen bond correlation functions of terminal groups, and self-diffusion behavior of polyisoprene chains.

From our analysis of Figure 1, we have observed a distinct slow relaxation behavior in mixed PI melt systems composed of polymer chains with hydroxy-group and ones with ester-group in α terminals, i.e., ω PI $_{\alpha 1}$ + ω PI $_{\alpha 2}$ (PI $_{I+II}$), ω PI $_{\alpha 3}$ + ω PI $_{\alpha 4}$ (PI $_{III+IV}$), and ω PI $_{\alpha 5}$ + ω PI $_{\alpha 6}$ (PI $_{V+VI}$). The investigation revealed a decreased mobility of polymer chains in the mixed PI melt systems as compared with those in single-component systems (see Figure 9 in the literature¹⁴ for the data of pure systems). This observation substantiates the existence of heterogeneous and homogeneous clustering of the terminal groups of ester- and hydroxy-terminated polyisoprene chains.

The rotational relaxation time τ_{rot} (Table 3) of ester-terminated PI chains across all three cases: PI $_{I+II}$, PI $_{III+IV}$, and PI $_{V+VI}$ is longer than that of the single-component system. This increase in the relaxation time is attributed to the strong association of ester groups with hydroxy terminal ends. In contrast, the relaxation time of hydroxy-terminated PI chains is shorter in the mixed system compared to the pure system, except for PI $_{V+VI}$. This exception is due to the lower radial distribution function (RDF) peak intensity of $[O_{C=O}]_{\alpha 1} - [O_{OH}]_{\alpha 2}$ compared to $[O_{OH}]_{\alpha 2} - [O_{OH}]_{\alpha 2}$, and the lower first RDF peak intensity of $[O_{C=O}]_{\alpha 3} - [O_{OH}]_{\alpha 4}$ compared to $[O_{OH}]_{\alpha 4} - [O_{OH}]_{\alpha 4}$, although the trend is reversed for PI $_{V+VI}$. The relaxation time of hydroxy-terminated PI chains is higher in the PI $_{V+VI}$ system compared to the single-component system. This increase is due to the higher RDF peak intensity of $[O_{C=O}]_{\alpha 5} - [O_{OH}]_{\alpha 6}$ compared to $[O_{OH}]_{\alpha 6} - [O_{OH}]_{\alpha 6}$. We have calculated the radial distribution functions between the terminal groups, namely $[ISO] - [ISO]$ in PI $_0$ (Shown in Figure S6 of Supporting Information), $[DMA] - [DMA]$ in PI $_{I+II}$, PI $_{III+IV}$, and PI $_{V+VI}$, $[\alpha 1] - [\alpha 1]$, $[\alpha 1] - [\alpha 2]$ and $[\alpha 2] - [\alpha 2]$ in PI $_{I+II}$, $[\alpha 3] - [\alpha 3]$, $[\alpha 3] - [\alpha 4]$, and $[\alpha 4] - [\alpha 4]$ in PI $_{III+IV}$, $[\alpha 5] - [\alpha 5]$, $[\alpha 5] - [\alpha 6]$, and $[\alpha 6] - [\alpha 6]$ in PI $_{V+VI}$ (refer to Figures 4 and S6). The observed low intensity and broad first peaks in the RDF of $[ISO] - [ISO]$ (where ISO represents Hydrogen terminated 1,4-*cis*-isoprene) and $[DMA] - [DMA]$ indicate a weak association between the $[ISO] - [ISO]$ and $[\omega] - [\omega]$ terminal groups. In the mixed PI melt systems considered in the present work, the first peak intensities in the RDF of $[O_{C=O}] - [H_{OH}]$, and $[O_{OH}] - [H_{OH}]$ in the PI $_{I+II}$, PI $_{III+IV}$, PI $_{V+VI}$ notably surpass those of $[\alpha 1] - [\alpha 1]$ in PI $_{I+II}$, $[\alpha 3] - [\alpha 3]$ in PI $_{III+IV}$, $[\alpha 5] - [\alpha 5]$ in PI $_{V+VI}$, $[ISO] - [ISO]$ in the single-component

PI system, and $[\omega] - [\omega]$ in the PI $_{I+II}$, PI $_{III+IV}$, PI $_{V+VI}$ systems. Hence, the interactions between $\alpha_{2m-1} - \alpha_{2m}$, $\alpha_{2m} - \alpha_{2m+1}$ ($m = 1, 2, 3$) terminals in PI $_{I+II}$, PI $_{III+IV}$, PI $_{V+VI}$ exhibit notably greater strength compared to $\alpha_{2m-1} - \alpha_{2m-1}$ and $ISO - ISO$ in the PI $_0$ melt system, along with $\omega - \omega$ in the PI $_{I+II}$, PI $_{III+IV}$, PI $_{V+VI}$ systems. In the three mixed melt systems PI $_{I+II}$, PI $_{III+IV}$, PI $_{V+VI}$, the first peak intensities in the RDFs of $[O_{C=O}] - [H_{OH}]$ are notably higher compared to those of $[O_{OH}] - [H_{OH}]$ in the same systems. Hence, the affinity between $\alpha 1 - \alpha 2$, $\alpha 3 - \alpha 4$, and $\alpha 5 - \alpha 6$ terminals in PI $_{I+II}$, PI $_{III+IV}$, PI $_{V+VI}$ significantly surpasses that of $\alpha 2 - \alpha 2$, $\alpha 4 - \alpha 4$, and $\alpha 6 - \alpha 6$ terminals in the same systems. This observation is underscored by the prolonged decay of hydrogen bond relaxation between $\alpha 1$ and $\alpha 2$, $\alpha 3$ and $\alpha 4$, and $\alpha 5$ and $\alpha 6$ terminals, as illustrated in Figure 10. The intensity of the peak in the RDF for $[O_{OH}] - [O_{OH}]$ is observed to surpass that of $[O_{OH}] - [H_{OH}]$ in PI $_{I+II}$, PI $_{III+IV}$, PI $_{V+VI}$. This trend aligns with findings reported in prior studies.^{14,16} In PI $_{I+II}$, a more robust hydrogen bond interaction is observed between $[O_{OH}]_{\alpha 2} - [H_{OH}]_{\alpha 2}$ compared to PI $_{III+IV}$ and PI $_{V+VI}$. This difference arises from structural disparities among the terminal groups. Specifically, the hydroxy-terminated isopentene ($\alpha 2$) features a methylene side chain, whereas the hydroxy-terminated isobutane ($\alpha 4$) and hydroxy-terminated 1,4-*cis*-isoprene ($\alpha 6$) incorporate a methyl side chain. The larger steric repulsion between methyl–methyl interactions compared to methylene–methylene interactions contributes to this difference. Additionally, the linear configuration of hydroxy-terminated isopentene stands in contrast to the globular nature of hydroxy-terminated isobutane ($\alpha 4$) and hydroxy-terminated 1,4-*cis*-isoprene ($\alpha 6$).

We have calculated the encountering-event-fraction $f_{enc}^{(\alpha\beta)}(s)$ for the terminal groups in the ten different melt systems (Figure 5). Additionally, we have determined the potentials of the mean force between these terminal groups (Figure 6) and the cluster formation fraction of the terminal groups (Figure 7). Notably, the encountering-event fraction for size two is significantly higher than that for other sizes in each of the melt systems. The ester-terminated and hydroxy-terminated polyisoprene chains led to a higher occurrence of encountering-events with larger sizes in the single-component PI $_{II}$, PI $_{IV}$ and PI $_{VI}$ melt systems than those of the single-component PI $_0$, PI $_I$, PI $_{III}$ and PI $_V$ systems. The encountering-event-fractions for the dimer, trimer, tetramer, pentamer, and hexamer follow the order of $f_{enc}^{(\alpha\beta)}(\text{dimer}) > f_{enc}^{(\alpha\beta)}(\text{trimer}) > f_{enc}^{(\alpha\beta)}(\text{tetramer}) > f_{enc}^{(\alpha\beta)}(\text{pentamer}) > f_{enc}^{(\alpha\beta)}(\text{hexamer})$. A similar trend is reported previously for hydroxylated polyisoprene.¹⁶ The potentials of mean force $W(r)$ are utilized to assess the interaction free energy between these encountered end-groups. In the PI $_0$, the PMF profile for $[ISO] - [ISO]$ exhibits a shallow contact minimum (CM) located at approximately 0.6 nm. In pure PI $_I$, PI $_{III}$, and PI $_V$, a shallow contact minimum for $[O_{C=O}]_{\alpha_{2m-1}} - [O_{C=O}]_{\alpha_{2m-1}}$ ($m = 1, 2, 3$) is located around 0.5 nm.¹⁴ The depths of the free energies at these contact minima are on the same order as the thermal energy, which is 2.99 kJ/mol at a temperature of 360 K. In the mixtures PI $_{I+II}$, PI $_{III+IV}$, PI $_{V+VI}$, a distinct contact minimum for $[O_{C=O}]_{\alpha_{2m-1}} - [O_{OH}]_{\alpha_{2m}}$ is observed at a distance of approximately 0.28 nm, and the depths of the free energy minima at these contact points are significantly larger than the thermal energy. A distinct contact minimum for $[O_{OH}]_{\alpha_{2m}} - [O_{OH}]_{\alpha_{2m}}$ is observed at a distance of approximately 0.30 nm, and the depths of the free energy minima at these contact points are significantly larger than the thermal energy. This indicates that the association between ester-terminated and hydroxy-terminated, and hydroxy-termin-

nated and hydroxy-terminated polyisoprene chains are more stable compared to $\alpha_{2m-1} - \alpha_{2m-1}$, ISO – ISO and $\omega - \omega$. The survival probabilities for the terminal groups further validate this enhanced stability. Additionally, we explored the cluster-formation-fraction $f_{\text{cluster}}^{(ab)}(s)$ using an additional criterion ($|W(r_{\text{CM}})| > 2k_{\text{B}}T$) to further understand the formation of clusters. In the single-component melt systems PI_0 , PI_{I} , PI_{III} , and PI_{V} , the absence of cluster formation is evident due to the weak association between the terminal groups ($|W(r_{\text{CM}})| \lesssim k_{\text{B}}T$). In the single-component melt systems PI_{II} , PI_{IV} and PI_{VI} , it is observed that terminals with α_{2m} form stable clusters satisfying the condition ($|W(r_{\text{CM}})| \gg k_{\text{B}}T$).^{14,16} In the mixtures $\text{PI}_{\text{I+II}}$, III+IV , V+VI , the presence of both heterogeneous clusters, involving interactions between ester- and hydroxy terminals, and homogeneous clusters, formed exclusively between hydroxy terminals, is evident. These stable clusters, which include dimers, trimers, and tetramers, emerge due to the pronounced interaction between the terminal groups, characterized by $|W(r_{\text{CM}})| \gg 2k_{\text{B}}T$. The stress–stress autocorrelation function, $G(t)$ (Figure 11), demonstrates a Rouse-type relaxation behavior, $G(t) \sim t^{-1/2}$, in the intermediate time regime for PI_0 . Conversely, the $\text{PI}_{\text{I+II,III+IV,V+VI}}$ mixed melt systems demonstrate a relaxation process that is slower compared to their respective pure components. This deviation is attributed to the formation of highly stable and ordered heterogeneous clusters, facilitated by hydrogen bonding between the ester- and hydroxy-terminal groups. The proportions of cluster formation for both heterogeneous clusters (involving ester- and hydroxy terminals) and homogeneous clusters (involving only hydroxy terminals) exhibit comparable fractions. The identification of size two, three, and four clusters, both heterogeneous and homogeneous (as depicted in Figure 7), substantiates the presence of multiple physical junction points between polyisoprene chains terminated with ester and hydroxy groups. Notably, the absence of homogeneous clusters exclusively between ester-terminal ends (α_{2m-1}) in the mixtures is evident as well as in the single-component melt systems PI_{I} , PI_{III} , and PI_{V} . This observation is supported by previous research.^{14,16} The spatial distribution of these junction points is depicted in Figure 12, while dynamic visualizations of the junctions are available in Videos S1, S2, and S3 corresponding to the $\text{PI}_{\text{I+II}}$, $\text{PI}_{\text{III+IV}}$, and $\text{PI}_{\text{V+VI}}$ melt systems, respectively. The presence of multiple physical junction points significantly hinders the mobility of both ester-terminated and hydroxy-terminated *cis*-1,4-polyisoprene chains. In the mixtures we observed the absence of cluster formation between DMA – DMA residues of ω terminal groups. This absence can be attributed to the interaction free energy between DMA and DMA residues falling within the range of thermal energy. A similar trend was previously reported in our earlier work (Dixit et al.,^{14,16}). We identified the formation of both heterogeneous and homogeneous stable clusters between ester- and hydroxy-terminated isopentene terminal groups ($\alpha_1 - \alpha_2$ and $\alpha_2 - \alpha_2$), ester- and hydroxy-terminated isobutane groups ($\alpha_3 - \alpha_4$ and $\alpha_4 - \alpha_4$), as well as between ester- and hydroxy-terminated 1,4-*cis*-isoprene groups ($\alpha_5 - \alpha_6$ and $\alpha_5 - \alpha_6$). Conversely, no cluster formation was observed for ester-terminated isopentene ($\alpha_1 - \alpha_1$), ester-terminated isobutane ($\alpha_3 - \alpha_3$), and ester-terminated 1,4-*cis*-isoprene ($\alpha_5 - \alpha_5$) groups (Dixit et al.¹⁴). These results can be generalized to the possibility of heterogeneous cluster formation consisting of any combinations of α_{odd} and α_{even} terminals, and those of α_{even} and α_{even} terminals.

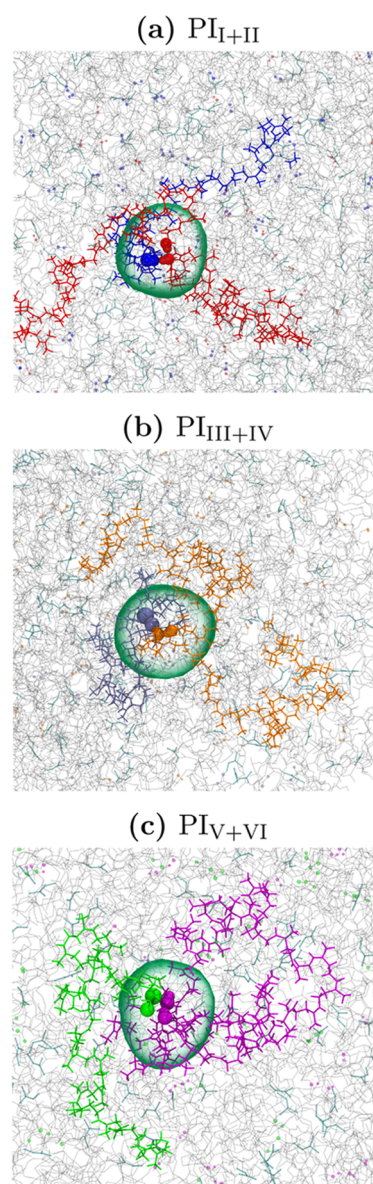


Figure 12. Physical junction points of α_2 around α_1 , α_4 around α_3 , and α_6 around α_5 terminals in (a) $\text{PI}_{\text{I+II}}$, (b) $\text{PI}_{\text{III+IV}}$, and (c) $\text{PI}_{\text{V+VI}}$ melt systems, respectively. Dimethyl allyl group of ω terminals are shown by cyan color and α_2 , α_4 , and α_6 terminals are shown by red, orange, and magenta colors, respectively. The backbone carbon and hydrogen atoms are represented in gray, while the oxygen and hydrogen atoms of $-\text{OH}$ are depicted in red and white, respectively.

5. CONCLUSIONS

In summary, this study explored the impact of both the ω and all six α terminals on the interplay of end-terminal associations and the dynamic properties of polyisoprene chains in mixed polyisoprene melt systems. Significantly, we observed weaker affinities between isoprene-isoprene and ester–ester terminals, resulting in the absence of discernible stable clusters. As a consequence, no evident branching points were identified between ISO – ISO in PI_0 and $\alpha_1 - \alpha_1$ in PI_{I} , $\alpha_3 - \alpha_3$ in PI_{III} , and $\alpha_5 - \alpha_5$ in PI_{V} . Conversely, robust hydrogen-bond interactions between $\alpha_1 - \alpha_2$, $\alpha_2 - \alpha_2$, $\alpha_3 - \alpha_4$, $\alpha_4 - \alpha_4$, $\alpha_5 - \alpha_6$, and $\alpha_6 - \alpha_6$ terminals effectively facilitated the formation of heterogeneous and homogeneous stable clusters characterized by larger sizes ($s \geq 2$). The radial distribution

function (RDF) $[O_{C=O}] - [H_{OH}]$ provides insight into the stability and structural organization of heterogeneous clusters, while the RDF $[O_{OH}] - [H_{OH}]$ characterizes the stability and structural arrangement of homogeneous clusters. Notably, the intensity of the primary peak in $[O_{C=O}] - [H_{OH}]$ is significantly higher than that observed in $[O_{OH}] - [H_{OH}]$ (Figure 4), indicating stronger interactions within heterogeneous clusters. The first peak of $[O_{C=O}] - [H_{OH}]$ occurs at approximately 0.18 nm, compared to 0.20 nm for $[O_{OH}] - [H_{OH}]$. This suggests that the hydrogen bonding between the ester oxygen atom ($[O_{C=O}]$) of the ester terminal ends and the hydroxyl hydrogen ($[H_{OH}]$) of the hydroxy terminal ends is considerably stronger than the hydrogen bonding between hydroxyl groups ($[H_{OH}]$) in homogeneous clusters (Figure 10). Additionally, the free energy profiles for $[O_{C=O}] - [H_{OH}]$ and $[O_{OH}] - [H_{OH}]$ across all melt systems are presented in Figure 6. The contact minimum free energy of $[O_{C=O}] - [H_{OH}]$ is substantially greater than that of $[O_{OH}] - [H_{OH}]$, further emphasizing the enhanced stability of heterogeneous clusters relative to homogeneous clusters. As a result, the heterogeneous clusters substantially reduce the dynamic mobility of ester-terminated PI chains in the mixed melt systems compared to the corresponding pure components, as the ester-terminated PI chains exclusively participate in the formation of heterogeneous clusters. This discovery provides corroborative evidence supporting the presence of multiple physical cross-linked points in ester- and hydroxy-terminated polyisoprene chains. Notably, the stability of heterogeneous clusters formed between $\alpha 1 - \alpha 2$, $\alpha 3 - \alpha 4$, $\alpha 5 - \alpha 6$ terminals surpasses that of homogeneous clusters formed between $\alpha 2 - \alpha 2$, $\alpha 4 - \alpha 4$, $\alpha 6 - \alpha 6$. The stress–stress autocorrelation function, $G(t)$ (Figure 11), exhibits Rouse-type relaxation ($G(t) \sim t^{-1/2}$) for PI_0 . In contrast, the mixed melt systems ($PI_{I+II,III+IV,V+VI}$) show slower relaxation behavior in comparison to their respective pure components due to the formation of stable heterogeneous clusters mediated by hydrogen bonding between ester and hydroxy terminal groups. We have verified the existence of hydrogen-bonded heterogeneous as well as homogeneous polar aggregates between the hydroxy and ester terminals of polyisoprene chains, which could potentially contribute to the phenomenon of strain-induced crystallization in natural rubber. In our forthcoming investigations, we plan to conduct all-atom MD simulations of polyisoprene melt systems containing nonrubber components such as proteins, lipids, fatty acids, and sugars. This approach aims to elucidate the influence of these nonrubber components on the formation of polar or nonpolar physical junction points with terminal groups, which may play a pivotal role in conferring superior properties to NR, including high toughness, resistance to crack growth, and strain-induced crystallization.

6. LIMITATIONS

Our multiscale modeling approach demonstrates robustness and practical applicability for simulating complex polymer melt systems, though certain limitations should be acknowledged. Using this framework, coarse-grained (CG) equilibration for melt systems composed of unentangled polymer chains can be efficiently achieved within a reasonable time frame. However, the present approach still requires a lot of computational costs even when using our multiscale approach to prepare the initial equilibrium structure. This high computational cost restricts us from performing the simulation for a melt composed of long polymer chains having many entanglement points on them.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaenm.4c00679>.

Figures S1–S7; the initial structures of mixed *cis*-1,4-polyisoprene melt systems; end-to-end distance (R_{ee}); radius of gyration (R_g); mean square internal distances; the time autocorrelation function of Normal Coordinate of different Rouse modes; radial distribution function (RDFs); running coordination number (RCN) (PDF)

The formation of physical junction point between $\alpha 1$ and $\alpha 2$ terminal groups in the mixture PI_{I+II} (Video S1) (MP4)

The formation of physical junction point between $\alpha 3$ and $\alpha 4$ terminal groups in the mixture PI_{III+IV} (Video S2) (MP4)

The formation of physical junction point between $\alpha 5$ and $\alpha 6$ terminal groups in the mixture PI_{V+VI} (Video S3) (MP4)

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Notes

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