

The Effect of Branching Structure on the Properties of Entangled or Non-covalently Crosslinked Polyisoprene

Chen Mo-Kun, Zhang Rong, Tang Mao-Zhu, Huang Guang-Su, Xu Yun-Xiang

Cite this article as:

Chen Mo-Kun, Zhang Rong, Tang Mao-Zhu, Huang Guang-Su, Xu Yun-Xiang. The Effect of Branching Structure on the Properties of Entangled or Non-covalently Crosslinked Polyisoprene[J]. *Chinese J. Polym. Sci.*, 2021, 39(1): 113-121. doi: 10.1007/s10118-020-2480-0

View online: <https://doi.org/10.1007/s10118-020-2480-0>

Articles you may be interested in

MORPHOLOGY DEPENDENCE OF CRYSTALLIZATION OF NATURAL RUBBER IN BLENDS

Chinese J. Polym. Sci. 2013, 31(10): 1424 <https://doi.org/10.1007/s10118-013-1314-8>

Effect of Long Chain Branching on the Rheological Behavior, Crystallization and Mechanical Properties of Polypropylene Random Copolymer

Chinese J. Polym. Sci. 2016, 34(9): 1158 <https://doi.org/10.1007/s10118-016-1830-4>

SYNTHESIS OF NATURAL RUBBER-g-MALEIC ANHYDRIDE AND ITS USE AS A COMPATIBILIZER IN NATURAL RUBBER/SHORT NYLON FIBER COMPOSITES

Chinese J. Polym. Sci. 2013, 31(8): 1127 <https://doi.org/10.1007/s10118-013-1310-z>

双烯化合物类单体合成支化聚合物的支化结构的研究

STUDIES ON THE BRANCHING STRUCTURE OF POLYMERS USING DIVINYLMONOMERS AS THE BRANCHING AGENT

高分子学报. 2012(7): 749 <https://doi.org/10.3724/SP.J.1105.2012.11356>

P-配合物对异戊二烯负离子聚合中3, 4结构影响的研究

Effect of P-complex on 3, 4-Structure of Polyisoprene during Anionic Polymerization

高分子学报. 2014(9): 1204 <https://doi.org/10.11777/j.issn1000-3304.2014.13474>

冰点下降法研究交联网络结构对天然橡胶力学性能的影响

Studies on Effects of Crosslinking Network Structure on Mechanical Properties of Natural Rubber by Freezing Point Depression Approach

高分子学报. 2014(7): 943 <https://doi.org/10.11777/j.issn1000-3304.2014.13411>

The Effect of Branching Structure on the Properties of Entangled or Non-covalently Crosslinked Polyisoprene

Mo-Kun Chen, Rong Zhang, Mao-Zhu Tang, Guang-Su Huang*, and Yun-Xiang Xu*

College of Polymer Science & Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

 Electronic Supplementary Information

Abstract The branching structures in natural rubber (NR) were believed to be critical for its superior mechanical properties. However, it is challenging to unravel the branching structure-function relationship of NR due to the complexity of the system. Herein, polyisoprene-(polyisoprene-*g*-polylactide) (PI-PLA) as model compound containing branching structure was designed and synthesized, which can improve the modulus, strength and viscoelasticity activation energy compared to those of the pristine polyisoprene (PI). The reason is that the branching structure contributes to the entanglement between polyisoprene chains. In order to probe the effect of branching structure on noncovalently crosslinked system, the polyisoprene block of PI-PLA was epoxidized and mixed with Fe³⁺ ions to introduce coordination bonds. Compared with the linear counterpart, the branching structure obviously enhanced activation energy of coordinated polyisoprenes, remarkably improving the mechanical properties of elastomer.

Keywords Natural rubber; Branching structure; Noncovalent interaction; Polyisoprene

Citation: Chen, M. K.; Zhang, R.; Tang, M. Z.; Huang, G. S.; Xu, Y. X. The effect of branching structure on the properties of entangled or non-covalently crosslinked polyisoprene. *Chinese J. Polym. Sci.* 2021, 39, 113–121.

INTRODUCTION

Natural rubber (NR) possesses excellent comprehensive properties such as high strength and toughness, crack resistance, anti-fatigue property and so on, which is widely used in various fields such as industry, agriculture, medical care and aerospace. The synthetic polyisoprene possesses similar main chain structure (e.g. molecular weight, stereoregularity) to NR, but its properties are still inferior to those of NR.^[1–4] The main reason is ascribed to the nonrubber components in NR which formed natural network in polyisoprene matrix.^[5] Both proteins at the ω -terminal and phospholipids at α -terminal formed branching structures by noncovalent bonding, which influence the entanglement or dynamic bonding between polyisoprene chains.^[6]

In the last decades, many researches have been carried out to study the effects of the nonrubber components on NR network.^[1,7–13] It has been proved that the branching structure in NR makes transient entanglements into permanent entanglements, which can accelerate the strain induced crystallization and stress upturn during the extension. Besides, the curing behavior, crosslinking density, and fatigue resistance of NR are better than those of purified NR as well as the isoprene

rubber. The common method relied on removing nonrubber components hierarchically from NR to obtain deproteinized natural rubber (DPNR) and transesterified deproteinized natural rubber (TEDPNR).^[14,15] Then the differences of the mechanical properties were compared to manifest the effect of the branching structure. However, the treatment of NR with lipase and phosphatase not only changed the topologies but also polyisoprene chain, which hindered the accurate evaluation of the effect of branching structure.^[16] Moreover, the noncovalent bonding in the proteins or phospholipids also contribute to the mechanical properties, which is difficult to decouple with the effect of branching topology. Therefore, it is valuable to design artificial system to reveal the function of the branching structures unambiguously.

Herein, a polyisoprene-(polyisoprene-*g*-polylactide) block copolymer was designed and synthesized. PLA is a well-known polar plastic with glass transition temperature (T_g) around 60 °C, which will phase separate with polyisoprene and form discrete domains. At room temperature, the PLA phases stay at the frozen state and keep the branching structures stable. Therefore, it is ideal to use terminally hydroxyl functionalized polyisoprene to graft PLA and form branching structures. Epoxidation on polyisoprene part was also conducted and Fe³⁺ was added to introduce coordination interaction between polyisoprene chains. The effect of branching cores was revealed by comparing with linear counterparts. The testing results proved that the branching structures

* Corresponding authors, E-mail: guangsu.huang@scu.edu.cn (G.S.H.)
E-mail: yxxu@scu.edu.cn (Y.X.X.)

Received April 24, 2020; Accepted July 13, 2020; Published online September 14, 2020

would strengthen the interactions among the polyisoprene chains, and also improve the modulus and strength in both systems. Furthermore, branching structures showed more stable network than linear ones. Through the study of these model compounds, the function of branching structures could be verified, thus providing theoretical support for designing advanced synthetic rubbers.

EXPERIMENTAL

Materials

Neodymium neodecanoate [Nd(VA)₃] was purchased from Meryer and used as a hexane solution (solid content: 0.69 g/mL). Triisobutylaluminum [Al(*i*-Bu)₃] (1.1 mol/L solution in toluene) and diisobutylaluminum chloride [Al(*i*-Bu)₂Cl] (0.8 mol/L solution in heptanes) were purchased from Acros Chemical. Isoprene was purchased from Alfa and refluxed over CaH₂ for 2 h, and distilled prior to use. Iron(III) chloride and 1,8-diazabicyclo-[5.4.0]-7-undecene (DBU) were purchased from Adamas Chemical. L-lactide was purchased from Jinan Daigang Biomaterial CO., Ltd. Hydroxylmyrcene (HMY) was synthesized by our group. Dichloromethane (Safe dry) was purchased from Adamas Chemical. Other chemicals, unless otherwise specified, were purchased from Aldrich and used as received.

Characterizations

¹H-NMR spectra were collected on a Nuclear magnetic resonance spectrometer (Bruker AV III HD) at room temperature taking CDCl₃ as solvent with TMS as reference.

GPC measurements were performed on an HLC-8320 gel permeation chromatography apparatus (TOSOH, Japan) with polystyrene standard. The samples were dissolved in THF and filtered through 0.45 μm membrane filter.

Fourier transform infrared spectroscopy (FTIR) were recorded on a Thermo Fisher Fourier transform infrared spectrometer with attenuated total reflectance (ATR) mode at room temperature.

Raman spectra were collected on a HORIBA HR evolution Raman spectrometer with an ion laser (632.81 nm) as the source. Spectra were generally accumulated over a spectra range of 150–1800 cm⁻¹ with full-length shot.

TEM images were obtained using a JEOL JEM-1011 transmission electron microscope operated at an accelerating voltage of 100 kV.

DMA measurements were performed on a dynamic mechanical analysis Q800 instrument (TA corporation, America) in tension film mode with the sample dimension about 60 mm × 5 mm × 0.5 mm. Tests were performed in temperature scanning mode in the range of -60–120 °C at a ramping rate of 3 °C/min and a frequency of 1 Hz.

Differential scanning calorimetry (DSC) curves were obtained on Q200 (TA corporation, America). Samples with weight about 4–6 mg was tested in temperature scanning in the range of -70–200 °C at a ramping rate of 10 °C/min.

Rheological experiments were performed on a HAAKE PXR800 rheometer, using a set of 20 mm diameter parallel plates and sample thickness about 1 mm. Frequency dependence of the storage modulus was measured in the frequency range from 0.01 Hz to 100 Hz under a deformation amplitude of 1% and in a temperature range of 10–90 °C. This deformation

was in the range of linear viscoelastic response.

Tensile measurements were performed on a universal testing machine (INSTRON, America) at room temperature with a cross-head speed of 100 mm/min. The initial distance (18 mm) between the two clamps remained constant for each sample and the deformation rate was 0.1 s⁻¹ during stretching. The specimen was a dumbbell shaped thin strip with central dimension of 35 mm × 2 mm × 0.5 mm.

Synthesis

Synthesis of PI

Nd(VA)₃ (197 μL, 0.15 mmol), Al(*i*-Bu)₃ (2.73 mL, 3 mmol) and isoprene (1 mol/L in hexane, 6 mL, 0.6 mmol) were injected into an ampoule *via* pipettes and aged at 50 °C for 10 min. Then Al(*i*-Bu)₂Cl (375 μL, 0.3 mmol) was added into the ampoule and kept aging for 10 min at 50 °C before use. Isoprene (1.5 mol/L in hexane, 55 mL, 8.25 mmol) was placed in a flask and brought to a desired temperature. Then the performed catalyst solution was added into the flask *via* pipette. Polymerization was carried out at 50 °C for 4 h, then quenched by adding 2 mL of ethanol. The product was washed by aqueous solution of hydrochloric acid and methyl alcohol sequentially, and then dried in vacuum at 40 °C to give product (5.61 g, 93.1%). *M_n* = 1.38 × 10⁵ g/mol. ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 5.12 (t, 2H, =CH—), 2.04 (m, 10H, —CH₂C—), 1.67 (s, 3H, —CH₃).

Synthesis of PI-OH

Nd(VA)₃ (197 μL, 0.15 mmol), Al(*i*-Bu)₃ (2.73 mL, 3 mmol) and isoprene (2 mol/L in hexane, 3 mL, 0.6 mmol) were injected into an ampoule *via* pipettes and aged at 50 °C for 10 min. Then Al(*i*-Bu)₂Cl (375 μL, 0.3 mmol) was added into the ampoule and kept aging at 50 °C for 10 min before use. Isoprene (1.5 mol/L in hexane, 55 mL, 8.25 mmol) was placed in a flask and warmed to a desired temperature, then the performed catalyst solution was added into the flask *via* pipette. Polymerization was carried out at 50 °C. After 4 h, HMY (0.4 mol/L in hexane, 8 mL, 3.21 mmol) was added into the flask and was further polymerized at 50 °C for 4 h. Then the polymerization was quenched with ethanol (2 mL). The precipitated product was washed by aqueous solution of hydrochloric acid and methyl alcohol sequentially, and then dried in vacuum at 40 °C to give product (5.39 g, 88.2%). *M_n* = 1.41 × 10⁵ g/mol. ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 5.12 (t, 2H, =CH—), 2.04 (m, 10H, —CH₂C—), 1.67 (s, 3H, —CH₃), 1.20 (s, 6H, —CH₃). The molar ratio between hydroxyl monomer and isoprene is 35 versus 2034.

Synthesis of PI-PLA

PI-OH (2 g) was dissolved with CH₂Cl₂ (70 mL) in a three necked bottle. Then L-lactide (1 g, 6.94 mmol) and DBU (150 μL, 0.984 mmol) were added sequentially. Ring-opening polymerization was carried out at 10 °C for 0.5 h. Then acetic acid (2 mL) was injected into the bottle to quench the polymerization. The polymer was washed by acetone and then dried in vacuum at 40 °C to give product (2.31 g, 76.3%). ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 5.19–5.17 (m, 1H, —CH—), 5.12 (t, 2H, =CH—), 2.04 (m, 10H, —CH₂C—), 1.83 (m, 2H, —CH₂—), 1.59–1.57 (m, 3H, —CH₃).

Synthesis of EPI-PLA (Epoxidized PI-PLA)

PI-PLA (2 g) was dissolved in a flask with cyclohexane (100 mL).

Hydrogen peroxide (7200 μL , 0.064 mol) and formic acid (2880 μL , 0.067 mol) were injected into the flask *via* pipettes when PI-PLA was absolutely dissolved. Then the reaction was kept at 30 $^{\circ}\text{C}$ for 1.5 h to obtain desired epoxidation degree of double bond. The reaction was quenched by saturated salt water and the solution was precipitated in methyl alcohol and dried in vacuum at 30 $^{\circ}\text{C}$ to give product (1.914 g, 95.7%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 5.19–5.17 (m, 1H, $-\text{CH}-$), 5.12 (t, 2H, $=\text{CH}-$), 2.69 (s, 1H, $-\text{OCH}-$), 2.04 (m, 10H, $-\text{CH}_2\text{C}-$), 1.83 (m, 2H, $-\text{CH}_2-$), 1.67 (s, 3H, $-\text{CH}_3$), 1.59–1.57 (m, 3H, $-\text{CH}_3$). Epoxidized degree of EPI-PLA is 31%.

Synthesis of EPI-PLA- Fe^{3+}

EPI-PLA (3.1 g, ED=31%) was dissolved in chloroform before use. FeCl_3 was dissolved in chloroform and then the insoluble solid was removed. The molar concentration of FeCl_3 (0.119 mol/L) in chloroform was determined by gravimetric analysis. Then the FeCl_3 solution was injected into the EPI-PLA solution *via* a pipette (the molar ratio of ferric to epoxy is 1:9, FeCl_3 : 180 mg). After stirring for 10 min, the chloroform was removed by rotary evaporation and 50 mL of toluene was added into the flask. After stirring for 6 h, the solution was poured into polytetrafluoroethylene (PTFE) mould and dried.

Synthesis of EPI (Epoxidized PI)

PI (2 g) was dissolved in a flask with cyclohexane (100 mL). Hydrogen peroxide (7.20 mL, 0.064 mol) and formic acid (2.88 mL, 0.067 mol) were injected into the flask *via* pipettes. Then the reaction was kept at 30 $^{\circ}\text{C}$ for 1.5 h to obtain desired epoxidation degree of double bond. The reaction was quenched by saturated salt water and the polymer was precipitated in methyl alcohol and dried in vacuum at 30 $^{\circ}\text{C}$ to give product (1.922 g, 96.1%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 5.12 (t, 2H, $=\text{CH}-$), 2.69 (s, 1H, $-\text{OCH}-$), 2.04 (m, 10H, $-\text{CH}_2\text{C}-$), 1.67 (s, 3H, $-\text{CH}_3$). Epoxidized degree of EPI is 31.5%.

Synthesis of EPI- Fe^{3+}

EPI (3.1 g) was dissolved in chloroform. Then FeCl_3 (238 mg, 0.119 mol/L) in chloroform was injected into the EPI solution *via* a pipette (the molar ratio of ferric to epoxy is 1:9). The solution was stirred for 10 min, then subjected to rotary evaporation to remove the chloroform. Toluene (50 mL) was then added into the flask and stirred for 6 h, and poured into PTFE mould and dried.

RESULTS AND DISCUSSION

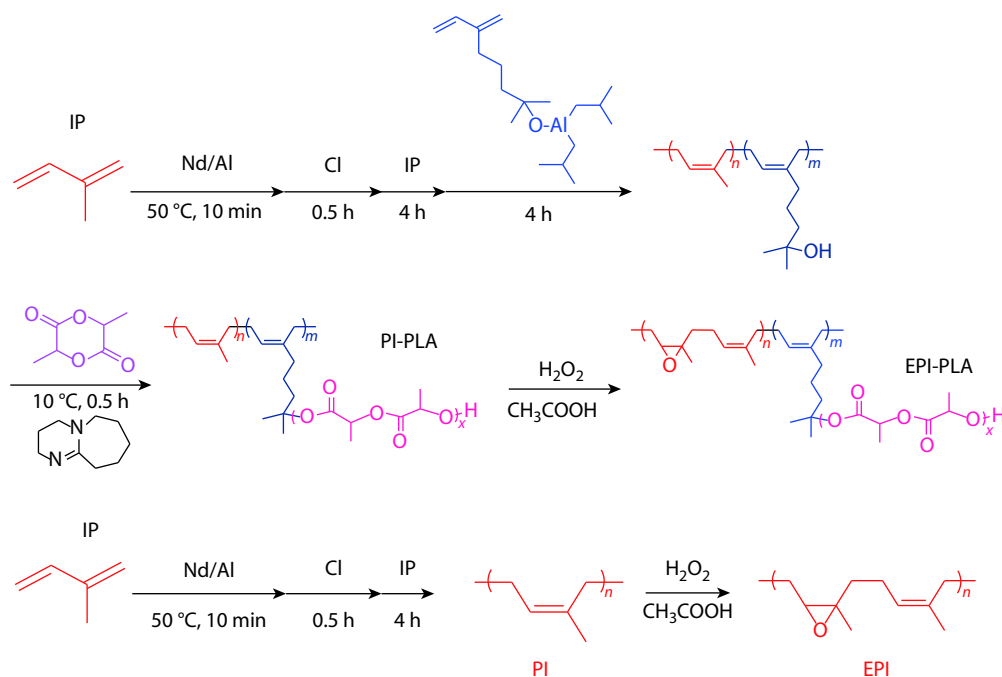
Synthesis

Terminally hydroxyl functionalized polyisoprene was synthesized by coordination copolymerization between isoprene and its polar monomer as shown in Scheme 1. Then the hydroxyl groups were used to initiate the ring-opening polymerization of L-lactide to generate a model compound PI-PLA. Pristine polyisoprene (PI) was prepared as a control polymer. Then epoxidation reactions were carried out on both PI-PLA and PI to generate EPI-PLA and EPI. The detailed synthetic procedures are described in experimental section.

$^1\text{H-NMR}$ spectra of PI-OH, PI-PLA, EPI-PLA, and EPI are shown in Figs. 1(A)–1(D). The characteristic signals have been assigned according to their chemical structures, respectively. The hydroxyl content can be determined according to the methyl groups (1.20 ppm) adjacent to the hydroxyls, which can be calculated by the following formula:

$$\text{OH}\% = \frac{c/6}{(b + b')_{\text{PI-OH}}} \quad (1)$$

where c represents the integral area of the methyl groups (six protons) adjacent to the hydroxy, and $b + b'$ represents the integral area of methylene groups on the main chain. By analysing the $^1\text{H-NMR}$ spectrum (Fig. 1A), the hydroxyl content



Scheme 1 The schematic representation of preparation of the model compounds.

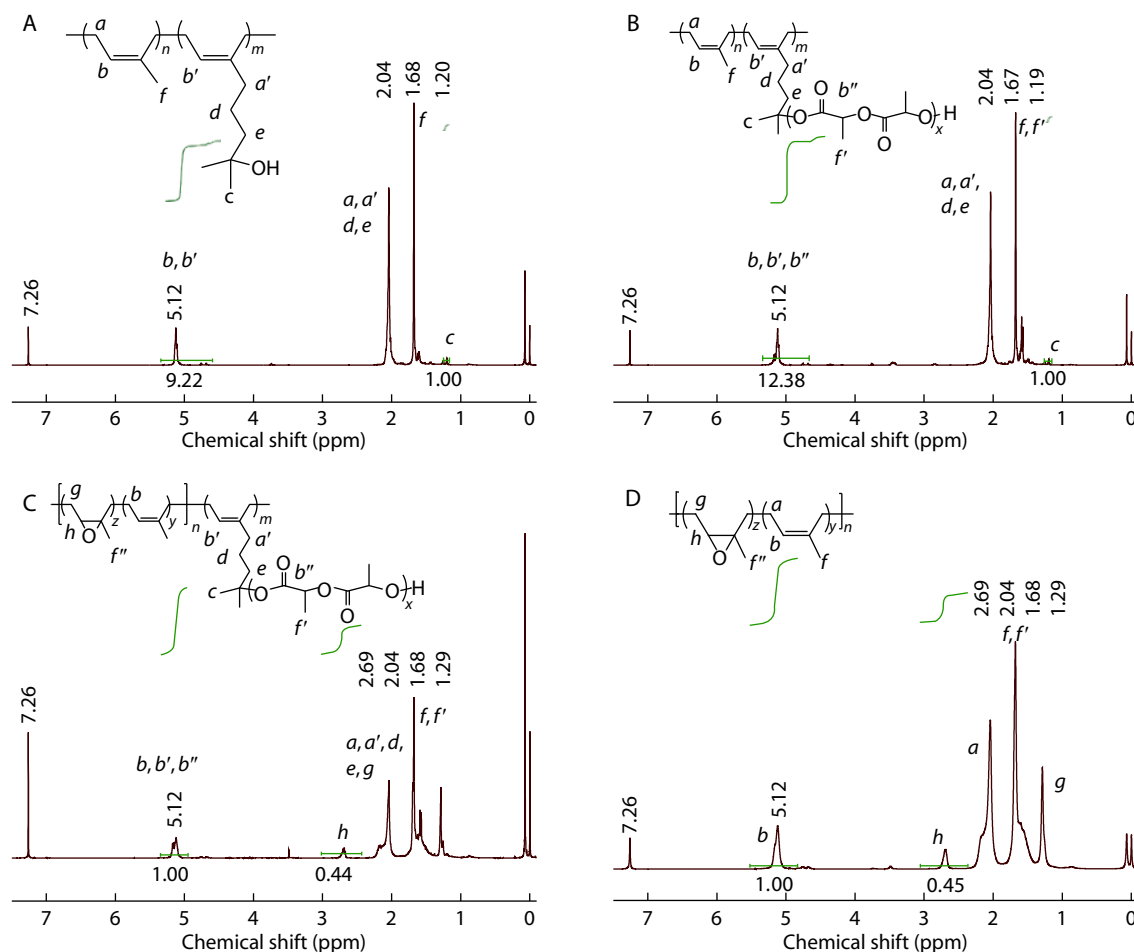


Fig. 1 ^1H -NMR spectra of (A) PI-OH, (B) PI-PLA, (C) EPI-PLA and (D) EPI.

is calculated to be 1.7% related to isoprene unit, about 35 hydroxyl groups each chain.

Then the length of PLA grafted onto polyisoprene was calculated. In ^1H -NMR spectrum (Fig. 1B), the methyl and methenyl signals of PLA ($-\text{CH}_3$ 1.57–1.59 ppm; $-\text{CH}$ 5.15–5.17 ppm) overlapped with those signals of polyisoprene ($-\text{CH}_3$ 1.68 ppm; $-\text{CH}$ 5.12 ppm).^[17] Fortunately, the amount of methylene ($-\text{CH}_2$ 2.04 ppm) in polyisoprene chain is constant. Therefore, the PLA length can be calculated indirectly according to the increment of methenyl protons by taking the methylene protons as reference. The PLA length was calculated by the following formula:

$$\text{DP} = \frac{(b + b' + b'')_{\text{PI-PLA}} - (b + b')_{\text{PI-OH}}}{(a + a' + d + e)} \quad (2)$$

where $b + b'$ is the integral area of methenyl groups on PI-OH and $b + b' + b''$ is the integral area of methenyl groups on PI-PLA by normalizing the integral of methylene groups. $a + a' + d + e$ is the integral area of the constant methylene ($-\text{CH}_2$, 2.04 ppm). The polymerization degree of PLA is about 4.34 lactide units each hydroxyl group.

Finally, epoxidized degrees of EPI and EPI-PLA were calculated according to the chemical shifts of methenyl groups of 5.12 ppm and epoxide groups of 2.69 ppm. Based on this information, the epoxidized degree of EPI and EPI-PLA is calcu-

lated to be 31.5% and 31%, respectively.

Formation of Branching Structure

After synthesizing all samples, the branching structures of all PLA containing samples were investigated. According to the DSC curves in Fig. 2(a), the glass transition temperatures (T_g s) of polyisoprene chains in PI and PI-PLA are at -62°C . And there is another endothermic peak at 120°C for PI-PLA which is ascribed to the melting of the polylactide phase.^[18] The terminal polylactide segments is immiscible with the polyisoprene chain, which will self-aggregate to form separated plastic phase. The TEM images (Figs. 2b and 2c) demonstrate that the polylactide phase formed hard cores surrounded by polyisoprene matrix, which represented branching structures. After epoxidation of polyisoprene chains, the T_g s of rubber chains of EPI and EPI-PLA rose to -42°C , which is about 20°C higher than those of PI and PLA, respectively. This is ascribed to the increased polarity of epoxide groups on the main chains.^[19] The melting temperature of the polylactide phase in EPI-PLA kept at 120°C , which illustrated that the polylactide phase still existed in EPI-PLA. TEM test confirmed that the branching structure was kept in EPI-PLA (Fig. S2 in the electronic supplementary information, ESI).

Formation of Coordination Interactions

After the formation of branching structures for EPI-PLA and EPI, the ferro ions were added to coordination with epoxide

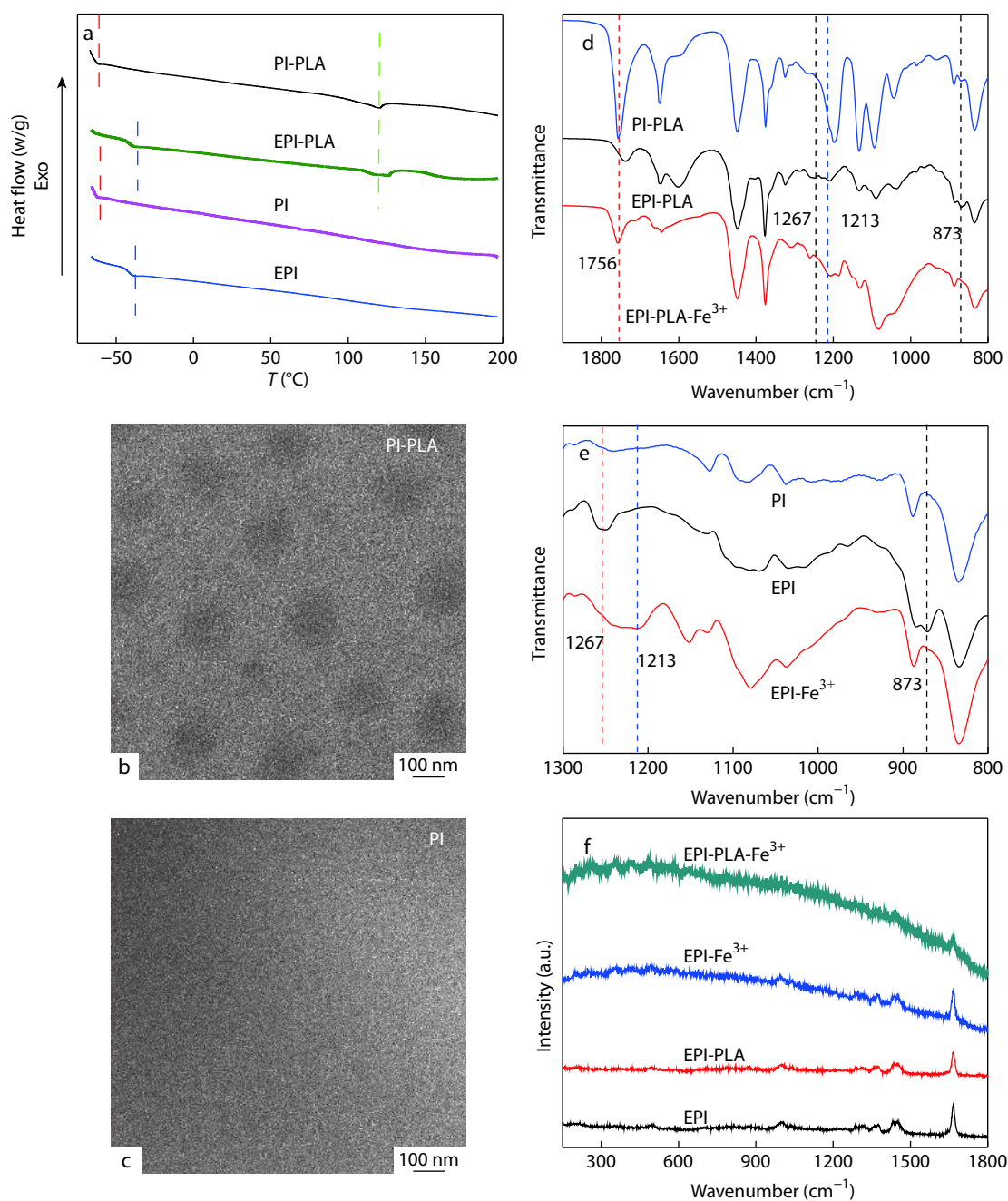


Fig. 2 (a) DSC curves of the model compounds, TEM images of (b) PI-PLA and (c) PI, (d, e) FTIR spectra, and (f) Raman spectra.

groups. FTIR spectra of the model compounds are shown in Figs. 2(d) and 2(e). The band at 1756 cm⁻¹ is assigned to the stretching vibration of C=O of polylactide. The bands at 873 and 1267 cm⁻¹ are related to asymmetric and symmetric stretching vibration of epoxide groups, respectively. After the addition of Fe³⁺ ions, the disappearance of the band at 873 cm⁻¹ indicates the association between the Fe³⁺ ions and the epoxide groups. Furthermore, the band at 1267 cm⁻¹ shifted to 1213 cm⁻¹, demonstrating the existence of Fe³⁺—O coordination in EPI-Fe³⁺ and EPI-PLA-Fe³⁺. The Raman spectra (Fig. 2f) have been recorded to further demonstrate the Fe³⁺—O coordination. The bands at 1020, 1450, 1670 cm⁻¹ are

assigned to the epoxide group, bending vibration of methylene and stretching vibration of double bond, respectively. After the addition of Fe³⁺ ions, The new bands emerging around 330 cm⁻¹ are ascribed to the Fe³⁺—O coordination in EPI-Fe³⁺ and EPI-PLA-Fe³⁺.^[20] Due to the existence of Fe³⁺, the baselines of EPI-Fe³⁺ and EPI-PLA-Fe³⁺ are unsmoothed because of the fluorescence. All the above data convincingly verify the existence of Fe³⁺—O coordination.

The Influence of Branching Structure on the Mechanical Properties

The stress-strain curves of PI and PI-PLA are shown in Fig. 3(a).

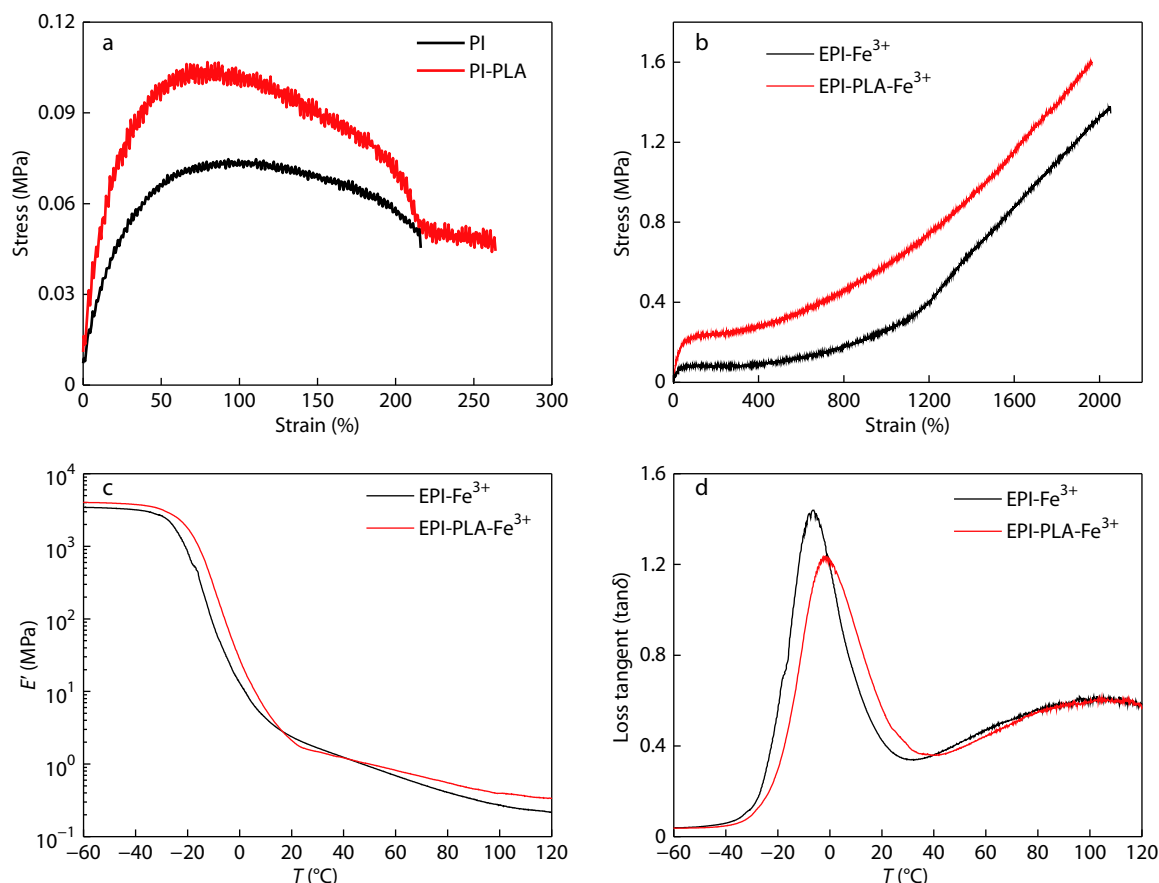


Fig. 3 The stress-strain curves of (a) PI and PI-PLA, (b) EPI-Fe³⁺ and EPI-PLA-Fe³⁺; DMA curves of EPI-Fe³⁺ and EPI-PLA-Fe³⁺: (c) storage modulus (E'), (d) loss tangent ($\tan\delta$).

The initial modulus and ultimate strength of PI-PLA are higher than those of PI. This is because the polylactide block of PI-PLA formed branching structure which anchored the chain and increased the chain entanglement. In contrast, the polyisoprene chain moved more freely and disentangled more rapidly under the external force.

In order to explore the effect of the branching structure on the noncovalent interactions, the Fe³⁺—O coordination was incorporated into the polyisoprene chains. The mechanical properties of the coordination samples are promoted significantly due to increased crosslinking density. Both EPI-Fe³⁺ and EPI-PLA-Fe³⁺ performed the excellent extensibility and much higher strength and modulus compared to those of PI and PI-PLA. Moreover, the branching core also enhanced the mechanical properties. According to the stress-strain curves (Fig. 3b), the initial modulus and ultimate strength of EPI-PLA-Fe³⁺ are higher than those of EPI-Fe³⁺ due to the presence of branching core. Furthermore, the stress upturn phenomenon of EPI-PLA-Fe³⁺ appears in advance compared to EPI-Fe³⁺. A further calculation from stress-strain curves was conducted to disclose the relation between topological structure and modulus of the model compounds. Since the stress-strain curves behave typically nonlinear relations, Mooney-Rivlin laws were applied to describe the elastic behaviors. The Mooney reduced stress can be written by following forms:^[7,21]

$$\sigma_{\text{red}} = \frac{\sigma}{a - a^{-2}} = G_c + G_e f(a), a > 1 \quad (3)$$

$$f(a) = \frac{1}{a} \quad (4)$$

where σ_{red} is the reduced stress, σ is the nominal stress and a is the elongation ratio. G_c represents the elastic modulus, which is derived from the permanent cross-linking, G_e is the modulus due to the contribution of chain interactions. G_c and G_e can be determined from linear fits of $\sigma_{\text{red}}-f(a)$ plots, respectively. The deformation range chosen for the linear fits is $0.4 < 1/a < 0.7$ to avoid the influence of stress upturn and guarantee finite deformation.

The reduced stress σ_{red} decreases in the low strain region because of the slippage or relaxation of coordination interplay. With further stretching, the σ_{red} increases due to the stress upturn. The fitting parameters G_c and G_e are presented in Fig. S3(b) (in ESI). The G_c values of EPI-Fe³⁺ and EPI-PLA-Fe³⁺ are both close to zero, which revealed the transient nature of noncovalent interactions. It is worth noting that G_e value of EPI-PLA-Fe³⁺ is larger than that of EPI-Fe³⁺, which means the Fe³⁺—O coordination is stronger in EPI-PLA-Fe³⁺ than that in EPI-Fe³⁺. The difference is ascribed to the branching structure of the model compounds.

Dynamic mechanical analyses were performed to probe the network robustness and segmental motion. As shown in Figs. 3(c) and 3(d), the storage modulus (E') of EPI-PLA-Fe³⁺ is

larger than that of EPI-Fe³⁺, indicating the branching structure would increase the crosslinking density of the network. The reduced slope of modulus changes along the temperature increase also suggested a more thermally stable network for EPI-PLA-Fe³⁺. The loss tangent peak ($\tan\delta$) of EPI-PLA-Fe³⁺ is at $-2\text{ }^{\circ}\text{C}$, which is $5\text{ }^{\circ}\text{C}$ higher than the value of EPI-Fe³⁺, demonstrating that the branching structure would retard the segment motion.

The Influence of Branching Structure on the Rheological Behavior

Frequency dependent rheological experiments were performed in a temperature range from 283.15 K to 363.15 K. The frequency dependent curves of PI-PLA and PI are shown in Figs. 4(a) and 4(b). The storage moduli (G') represent the energy storage of the model compounds during the deformation and mainly reflect the elasticity. The loss moduli (G'') represent the loss of energy and mainly reflect the viscosity. The relative magnitudes between G' and G'' and the intersect value (f) can reflect the relaxation rate of polymer chains. The f value of PI-PLA is smaller than that of PI at either 283.15 or 363.15 K, indicating that the polyisoprene chains in PI-PLA are prone to entangle due to the branching structure, and the segmental motion is relatively slow under the shear force. From Figs. 4(c) and 4(d), more obvious changes in storage moduli were found due to the temperature dependent relaxation of reversible

Fe³⁺—O coordination in EPI-PLA-Fe³⁺ or EPI-Fe³⁺. And the storage moduli of EPI-PLA-Fe³⁺ are almost an order higher than those of EPI-Fe³⁺ either at 283.15 or 363.15 K, which is ascribed to enhanced entanglement and retarded chain relaxation due to the existence of the branching structure. It is worth noting that the storage modulus follows the time-temperature superposition principle quite well and it is convenient to quantitatively reveal the influence of branching structure in EPI-PLA-Fe³⁺ by comparing with EPI-Fe³⁺.

Therefore, master curves were made by applying horizontal and vertical shift factors on the modulus curves at different temperatures, as shown in Fig. 5. The plot of horizontal shift factors as a function of temperature is shown in Fig. 5, which is fitted via the following Arrhenius equation:^[22]

$$\ln(a_T) = \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \quad (5)$$

where E_a is the activation energy and R is the gas constant, T_{ref} is the reference temperature at 283.15 K. The activation energy of viscous transition for PI-PLA, PI, EPI-PLA-Fe³⁺, and EPI-Fe³⁺ were calculated to be 40.23, 38.01, 46.54, and 38.26 kJ/mol, respectively. It is found that branching structure caused even more energy difference of viscous transitions in coordination compounds. Considering a large family of dynamic crosslinking tools, this phenomenon may give guide to utilizing branching structures in other crosslinking systems of polyisoprene.

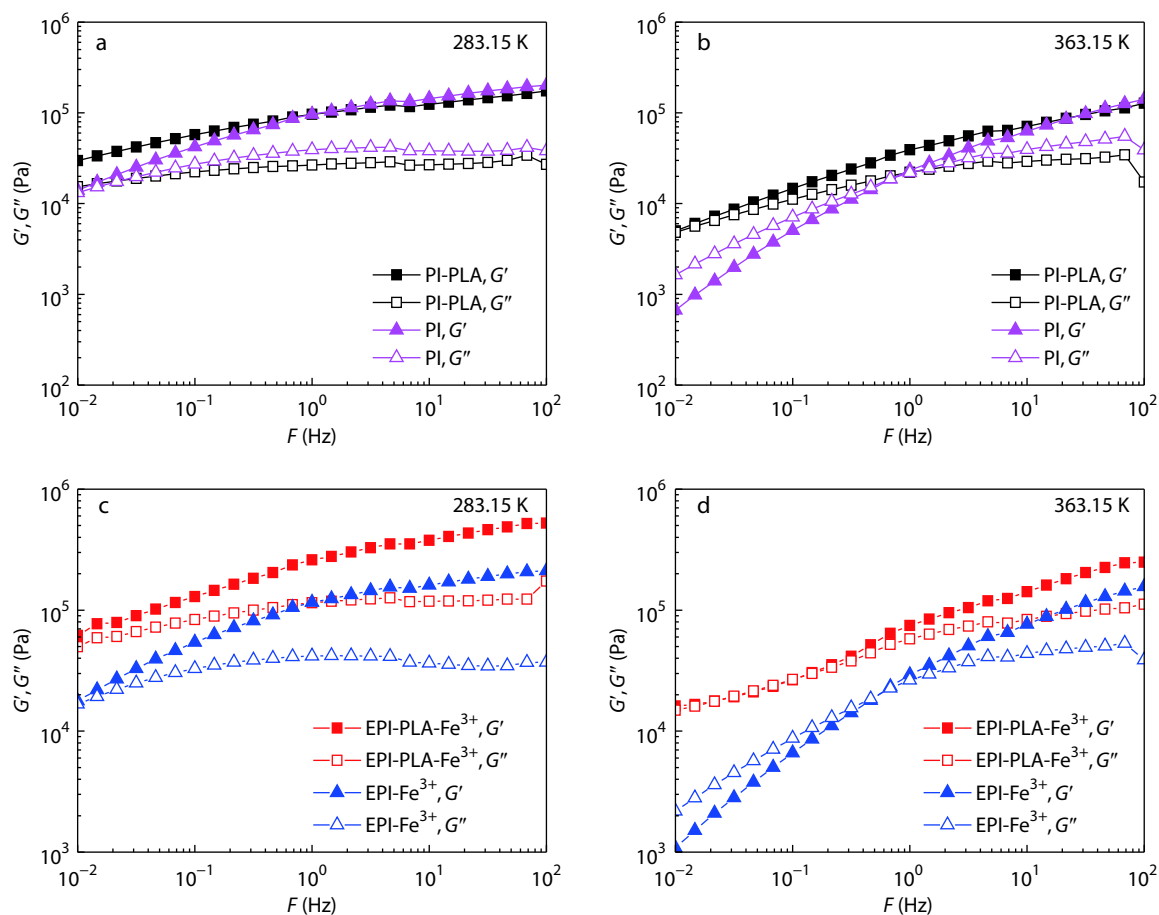


Fig. 4 G' and G'' of PI-PLA, PI, EPI-PLA-Fe³⁺ and EPI-Fe³⁺ versus frequency at different temperatures: (a, c) 283.15 K, (b, d) 363.15 K.

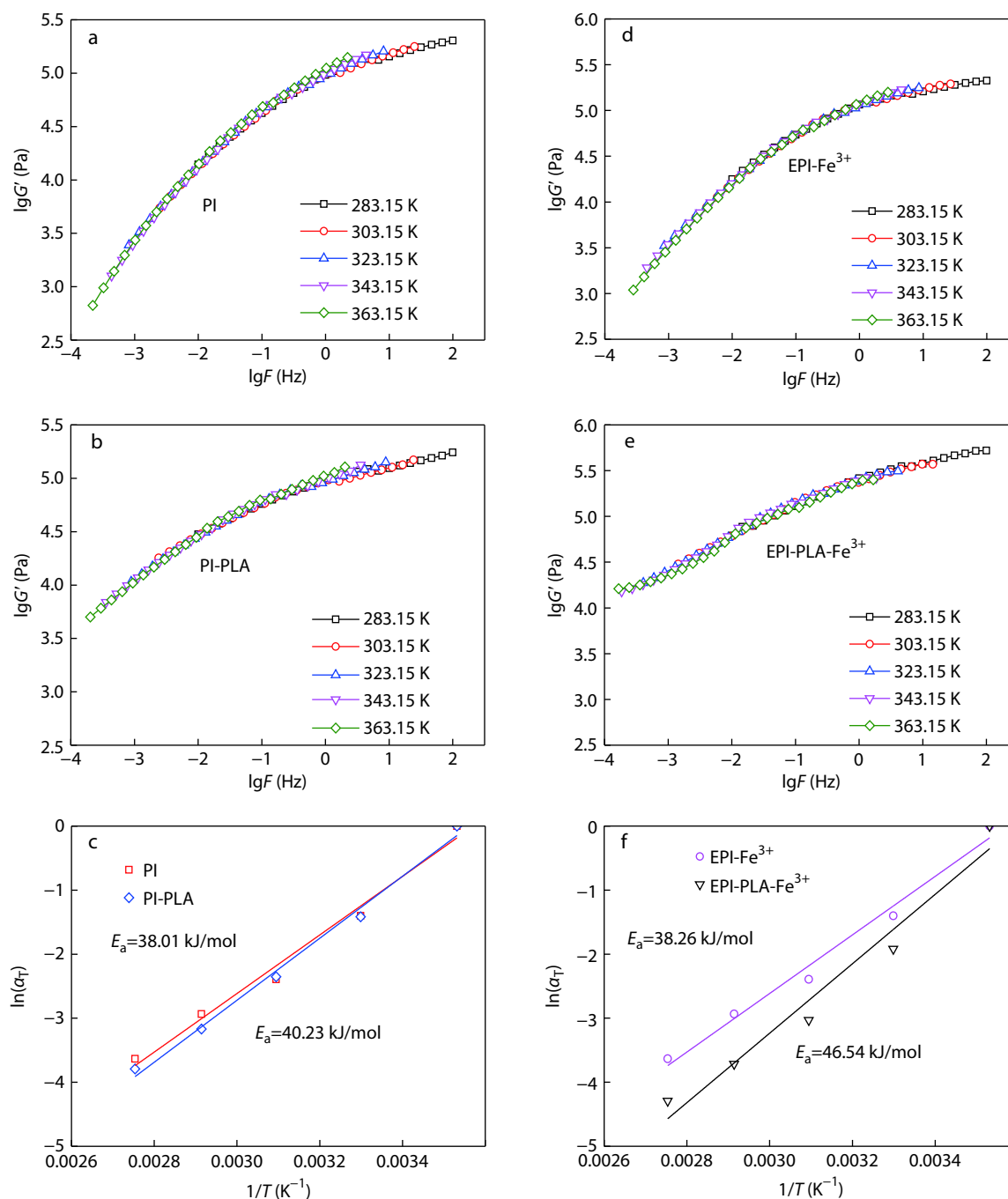


Fig. 5 Master curves were obtained by shifting the frequency sweep curves at different temperatures: (a) PI, (b) PI-PLA, (d) EPI- Fe^{3+} , (e) EPI-PLA- Fe^{3+} ; Arrhenius plots of the horizontal shift factor a_T against temperature variation: (c) PI-PLA and PI, (f) EPI-PLA- Fe^{3+} and EPI- Fe^{3+} .

CONCLUSIONS

In this work, two groups of model compounds with or without branching structures were precisely synthesized. Tensile measurements, DMA, frequency dependent rheological experiments were conducted to disclose the influence of branching structure on chain entanglements. Mooney-Rivlin law reveals that the branching structure would increase the chain entanglements. The rheological experiments show the network of EPI-PLA- Fe^{3+} (PI-PLA) is more stable than EPI- Fe^{3+} (PI) under

shear force due to the branching structure. All the above results verified the contributions of branching structure to the chain entanglements and noncovalent interactions. The principle found here may promote the development of next generation high-performance polyisoprene.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of

charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2480-0>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 51973126 and 51333003).

REFERENCES

- 1 Toki, S.; Che, J.; Rong, L.; Hsiao, B. S.; Amnuaypornsi, S.; Nimpaboon, A.; Sakdapipanich, J. Entanglements and networks to strain-induced crystallization and stress-strain relations in natural rubber and synthetic polyisoprene at various temperatures. *Macromolecules* **2013**, *46*, 5238–5248.
- 2 Le Cam, J. B.; Toussaint, E. The mechanism of fatigue crack growth in rubbers under severe loading: the effect of stress-induced crystallization. *Macromolecules* **2010**, *43*, 4708–4714.
- 3 Amnuaypornsi, S.; Toki, S.; Hsiao, B. S.; Sakdapipanich, J. The effects of endlinking network and entanglement to stress-strain relation and strain-induced crystallization of un-vulcanized and vulcanized natural rubber. *Polymer* **2012**, *53*, 3325–3330.
- 4 Rattanasom, N.; Thammasiripong, U.; Suchiva, K. Mechanical properties of deproteinized natural rubber in comparison with synthetic cis-1,4 polyisoprene vulcanizates: gum and black-filled vulcanizates. *J. Appl. Polym. Sci.* **2005**, *97*, 1139–1144.
- 5 Toki, S.; Burger, C.; Hsiao, B. S.; Amnuaypornsi, S.; Sakdapipanich, J.; Tanaka, Y. Multi-scaled microstructures in natural rubber characterized by synchrotron X-ray scattering and optical microscopy. *J. Polym. Sci., Part B: Polym. Phys.* **2008**, *46*, 2456–2464.
- 6 Kitaura, T.; Kobayashi, M.; Tarachiwin, L.; Kum-ourm, H.; Matsuura, A.; Fushihara, K.; Ute, K. Characterization of natural rubber end groups using high-sensitivity NMR. *Macromol. Chem. Phys.* **2018**, *219*.
- 7 Huang, C.; Huang, G.; Li, S.; Luo, M.; Liu, H.; Fu, X.; Qu, W.; Xie, Z.; Wu, J. Research on architecture and composition of natural network in natural rubber. *Polymer* **2018**, *154*, 90–100.
- 8 Wu, J.; Qu, W.; Huang, G.; Wang, S.; Huang, C.; Liu, H. Super-resolution fluorescence imaging of spatial organization of proteins and lipids in natural rubber. *Biomacromolecules* **2017**, *18*, 1705–1712.
- 9 Li, S.; Tang, M.; Huang, C.; Zhang, R.; Wu, J.; Ling, F.; Xu, Y. X.; Huang, G. Branching function of terminal phosphate groups of polyisoprene chain. *Polymer* **2019**, *174*, 18–24.
- 10 Liu, J.; Wu, S.; Tang, Z.; Lin, T.; Guo, B.; Huang, G. New evidence disclosed for networking in natural rubber by dielectric relaxation spectroscopy. *Soft Matter* **2015**, *11*, 2290–2299.
- 11 Wei, Y. C.; Liu, G. X.; Zhang, L.; Xu, W. Z.; Liao, S.; Luo, M. C. Mimicking the mechanical robustness of natural rubber based on a sacrificial network constructed by phospholipids. *ACS Appl. Mater. Interfaces* **2020**, *12*, 14468–14475.
- 12 Tang, M.; Zhang, R.; Li, S.; Zeng, J.; Luo, M.; Xu, Y. X.; Huang, G. Towards a supertough thermoplastic polyisoprene elastomer based on a biomimic strategy. *Angew. Chem. Int. Ed.* **2018**, *57*, 15836–15840.
- 13 Ling, F.; Luo, M.; Chen, M.; Zeng, J.; Li, S.; Yin, H.; Wu, J.; Xu, Y.; Huang, G. Terminally and randomly functionalized polyisoprene lead to distinct aggregation behaviors of polar groups. *Polymer* **2019**, *178*, 121629.
- 14 Chaikumpollert, O.; Yamamoto, Y.; Suchiva, K.; Nghia, P. T.; Kawahara, S. Preparation and characterization of protein-free natural rubber. *Polym. Adv. Technol.* **2012**, *23*, 825–828.
- 15 Rattanasom, N.; Suchiva, K. Rheological and processing properties of purified natural rubber. *J. Appl. Polym. Sci.* **2005**, *98*, 456–465.
- 16 Nawamawat, K.; Sakdapipanich, J. T.; Ho, C. C. Effect of deproteinized methods on the proteins and properties of natural rubber latex during storage. *Macromol. Symp.* **2010**, *288*, 95–103.
- 17 Yokoyama, N.; Kanazawa, A.; Kanaoka, S.; Aoshima, S. Synthesis of highly defined graft copolymers using a cyclic acetal moiety as a two-stage latent initiating site for successive living cationic polymerization and ring-opening anionic polymerization. *Macromolecules* **2018**, *51*, 884–894.
- 18 Uehara, H.; Karaki, Y.; Wada, S.; Yamanobe, T. Stereo-complex crystallization of poly(lactic acid)s in block-copolymer phase separation. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2707–2710.
- 19 Xia, W.; Ketten, S. Coupled effects of substrate adhesion and intermolecular forces on polymer thin film glass-transition behavior. *Langmuir* **2013**, *29*, 12730–12736.
- 20 Zhang, X.; Tang, Z.; Guo, B.; Zhang, L. Enabling design of advanced elastomer with bioinspired metal-oxygen coordination. *ACS Appl. Mater. Interfaces* **2016**, *8*, 32520–32527.
- 21 Xie, Z.; Luo, M.; Huang, C.; Wei, L.; Liu, Y.; Fu, X.; Huang, G.; Wu, J. Effects of graphene oxide on the strain-induced crystallization and mechanical properties of natural rubber crosslinked by different vulcanization systems. *Polymer* **2018**, *151*, 279–286.
- 22 Zou, X.; Kui, X.; Zhang, R.; Zhang, Y.; Wang, X.; Wu, Q.; Chen, T.; Sun, P. Viscoelasticity and structures in chemically and physically dual-cross-linked hydrogels: insights from rheology and proton multiple-quantum NMR spectroscopy. *Macromolecules* **2017**, *50*, 9340–9352.