The Relationship between Pendant Phosphate Groups and Mechanical Properties of Polyisoprene Rubber

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Abstract It is still a great challenge to mimic the structure and function of natural rubber by introducing polar components into synthetic polyisoprene. In order to explore the function of phosphate groups on the mechanical properties of polyisoprene rubber, a terminally functionalized compound (PIP-P) containing phosphate groups was synthesized and further vulcanized to prepare the model compound V-PIP-P. Through analyzing the test results, it was found that these phosphate groups formed polar aggregates in non-polar polyisoprene rubber matrix, serving as an additional dynamic cross-linking sites, which increases the cross-linking density and improves mechanical properties. The influence of the phosphate groups on the strain-induced crystallization (SIC) was further investigated via synchrotron wide-angle X-ray diffraction (WAXD) experiment. These phosphate group aggregates not only reduced the onset strain of SIC, but also slowed down the molecular chain mobility, which hinder the crystal lateral growth. The above results help us to gain a deeper understanding for the function of phosphate groups in the formation of “naturally occurring network” and guide the molecular design of next generation polyisoprene rubber.

Keywords Phosphate groups; Strain-induced crystallization; Naturally occurring network; Natural rubber

INTRODUCTION

Natural rubber (NR) is widely applied in daily life and industry due to its outstanding comprehensive properties.[1] However, due to the constraints of geographical location and climatic conditions, the supply-demand relationship of NR in some regions is seriously unbalanced. Under this circumstance, synthetic cis-1,4 polyisoprene rubber (PIP) is considered to be the most promising alternative to NR because of its similar molecular chain structure. Previous scholars have devoted a lot of work to mimic the structure and function of NR by PIP. Unfortunately, the comprehensive properties of PIP were still inferior to NR. As widely recognized, it is attributed to the nonrubber components of NR.[3] Previous studies have revealed that the α-terminal and ω-terminal of NR are connected to phospholipids and proteins, respectively, forming a “naturally occurring network”. This natural network has a strong enhancement effect on the strain-induced crystallization (SIC) behavior and greatly improves the mechanical properties.[3−5] It is ideal that the similar natural work could be built in synthetic polyisoprene rubber and mimic the structure and function of NR. However, the influences of these nonrubber components on synthetic polyisoprene rubber have not been fully revealed yet.

Since the beginning of the 20th century, scholars have done a lot of research to elucidate the extraordinary SIC mechanism of NR.[6−9] Solid evidence manifested that the “naturally occurring network” promotes the SIC behavior and enhances the tensile strength and modulus of NR.[10,11] Huang et al. compared the SIC behavior of NR, deproteinized natural rubber (DPNR) and transesterified DPNR (TEDPNR). It was found that the α-terminal of NR makes entanglements as permanent entanglements. These permanent entanglements can be used as physical cross-linking points to accelerate SIC behavior and increase mechanical properties of NR.[12] It is assumed that if we can successfully mimic the phosphate groups at α-terminal of NR by PIP, not only the function of phosphate groups in NR could be confirmed, but also the structure-property relationship of nonrubber components in synthetic rubber could be built up. This kind of investigation is very critical for synthesizing biomimetic polyisoprene rubber with outstanding comprehensive properties. Previously, the synthetic methodology has been developed by our group to introduce nonrubber components into PIP. For example, Tang et al. synthesized a terminally functionalized polyisoprene rubber to mimic the physical cross-linking network formed by the ω-terminal of NR.[13] Li et al. synthesized a model compound to explore the branching structures formed by the α-terminal of NR.[14] However, it is not yet investigated about...
the function of phosphate groups on vulcanized rubbers, in which covalent bonds will maintain the network integrity and phosphate aggregates become weaker crosslinkers.

In this work, a vulcanized model compound (V-PIP-P) with relatively high molecular weight was prepared to explore the function of phosphate groups in the formation of "naturally occurring network" and its effect on the SIC behavior. Through analyzing the test results, it was found that these phosphate groups formed polar aggregates in non-polar polyisoprene rubber matrix, thus constructing additional dynamic cross-linking network, which increased the cross-linking density and improved mechanical properties. Meanwhile, the formation of phosphate groups aggregates also brought smaller onset strain of SIC for V-PIP-P compared to V-PIP. The phosphate groups also reduced the rubber molecule chains mobility, which hinder the crystal lateral growth, so that the crystallinity and crystallization rate were reduced. This work is expected to reveal the function of phosphate groups in NR, which plays a critical role for us to design biomimetic synthetic rubbers with excellent performance.

EXPERIMENTAL

Sample Preparation

The detailed synthetic routes and characterization data of polymer are included in the electronic supplementary information (ESI). All the manipulations were performed under a dry nitrogen atmosphere.

Preparation of Cross-linked V-PIP and V-PIP-P

A mixture of 5 g of PIP and 50 mg of dicumyl peroxide (DCP) was dissolved in THF. The mixed sample was dried in a vacuum oven at 40 °C. Finally, the dried mixed sample was Vulcanized at 160 °C and 10 MPa for 30 min to generate the covalent cross-linking sample (V-PIP). The V-PIP-P sample was prepared using the same operation.

Characterization

\(^{1}H\)-NMR spectra were collected on a nuclear magnetic resonance spectrometer (Bruker ASCEND 400) at room temperature in deuterated chloroform solution with TMS as reference.

GPC measurements were performed on HPLC-8320 against polystyrene standard. The samples were dissolved in THF and filtered through 0.45 μm membrane filter.

FTIR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer with a heating device and the scan range is 400–4000 cm\(^{-1}\). The FTIR spectra were normalized with the band of 2965 cm\(^{-1}\).

DSC tests were performed on a Q200 (TA Instruments). Samples with weight about 4–6 mg were heated from −80 °C to 100 °C at a ramping rate of 10 °C min\(^{-1}\). The heat flow was recorded.

TEM images were acquired on a G2F20S-TWIN instrument at the accelerating voltage of 100 kV. Low-temperature ultrathin sections were carried on a Leica EMUC6/FC6 ultramicrotome.

AFM images were acquired on a SPI4000 AFM instrument of Seiko using silicon tips (NSG10) with a spring constant of 3 N m\(^{-1}\) at a resonance frequency of 228.9 kHz. All measurements were carried out in the tapping (AC) mode. The samples were drop-coated from solution (0.1 mg·mL\(^{-1}\)) using silicon substrates.

Equilibrium swelling experiments were performed to determine the cross-linking density of the model compound by the Flory-Rhener equation:\[^{13}\]

\[
\ln(1 - \phi_L) - \phi_L - \chi_L \phi_L^2 = n V_0 \left[ \phi_L^{1/3} - \frac{1}{2} \phi_L \right], \quad M_C = \rho/n
\]  
(1)

where \(\phi_L\) is the volume fraction of the model compound in the swelling polymer network, \(\chi_L\) is the Huggins-Flory-solvent-polymer interaction parameter (0.393 for our system), \(V_0\) is the molar volume of the solvent (106.5 mL·mol\(^{-1}\) for toluene), \(M_C\) is the average mass of the network chain, \(\rho\) is the density of polymer (0.92 g·mL\(^{-1}\) for our system) and \(n\) is the cross-linking density of the model compound.

Rheology measurements were performed on the HAAKE PXR800 rheometer. We performed frequency sweeps from 100 Hz to 0.01 Hz at 25 °C and fixed strain of 1%. We performed strain sweeps from 0.01% to 100% at 25 °C and a fixed frequency of 1 Hz. The sample has a diameter of 20 mm and a thickness of 0.5 mm.

Vulcanization curves of V-PIP and V-PIP-P were recorded on the MCR302 rheometer. Time sweep tests (30 min) were performed at 160 °C with a fixed frequency of 1 Hz and a fixed strain of 0.5%. The samples have a diameter of 8 mm and a thickness of 0.5 mm.

DMA measurements were performed on the DMA Q800 instrument. The stress relaxation tests were performed on stress-relaxation mode. First of all, the samples were stretched to a strain of 100%, and then the strain was kept to measure the change of relaxation stress within 60 min.

Tensile measurements were performed on a universal testing machine (Instron-5567) at 25 °C and with the stretching rate of 100 mm·min\(^{-1}\). The cyclic tensile tests were also performed at 25 °C and with the stretching rate of 100 mm·min\(^{-1}\). The samples were stretched to a strain of 100%, 200%, 300%, and each sample repeated cycle three times under the corresponding strains. We also performed a uniaxial tensile test at 25 °C and with the stretching rate of 12 mm·min\(^{-1}\).

WAXD experiments for the samples were performed at the beamline BL16B1 in Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of the X-rays was 0.124 nm. The WAXD patterns were collected with a MAR-CCD detector. The collection time of each WAXD pattern was 20 s. For the uniaxial tensile test, the stretching rate was 12 mm·min\(^{-1}\). The Fit2D software was used to process the WAXD patterns for further analysis.

RESULTS AND DISCUSSION

Chemical Structure Characterization of the Synthetic Compounds

Based on the previous experience, the rare-earth catalytic system (Nd(VA)\(_2\)/Al(i-Bu)\(_3\)) was applied to synthesize the model compounds in this work. This catalytic system can achieve a high cis content and a high ratio of incorporation polar monomer simultaneously. The synthetic route to each compound is shown in Scheme 1. The molecular weights of PIP and PIP-OH are 4.96×10\(^2\) and 4.47×10\(^2\) g·mol\(^{-1}\), respectively. Other molecular weight information is summarized in Table S1 (in ESI). The \(^{1}H\)-NMR spectra of PIP, PIP-OH, PIP-DSC and PIP-P...
are shown in Figs. S1−S4 (in ESI). Compared to PIP, a new signal appeared at 3.63 ppm (CH$_2$OH) in PIP-OH, indicating successful incorporation of IP-OH monomers into the rubber chains. By integrating the two signals at 3.63 and 5.12 ppm, it is calculated that 58 IP-OH monomers are inserted into each chain. By comparing the NMR spectra of PIP-OH, PIP-DSC and PIP-P, the grafting ratios of DSC groups and phosphate groups were calculated to be 100% and 96%, respectively. PIP and PIP-P have almost the same glass transition temperature ($T_g$), maintaining at around −65 °C. The detailed information is shown in Fig. S5 (in ESI) and Table S2 (in ESI). The model compound (V-PIP-P) was prepared by vulcanizing the PIP-P.

Cross-linking Density of the Model Compounds

The crosslinking process of V-PIP and V-PIP-P was monitored on a rheometer to determine the vulcanized time at 160 °C. As shown in Fig. S6 (in ESI), the storage modulus of two samples increases gradually and then levels off. The constant storage modulus indicates the formation of crosslinking network. The time periods required for the storage modulus to reach a plateau are used to determine the crosslinking time at 160 °C, which are both almost 15 min. Therefore, in order to ensure that both samples are fully vulcanized, the vulcanized time was set to be 30 min.

The cross-linking densities of V-PIP-P and V-PIP were tested through the equilibrium swelling experiments$^{[14]}$ (toluene as the solvent) and the data are summarized in Table 1. According to the vulcanization curve, the amount of DCP and vulcanization time of both samples are the same. However, it is found that the increase in storage modulus ($G'$) of V-PIP-P is 27.5 kPa, which is less than that of V-PIP (33.2 kPa). It is speculated that the aggregates formed by phosphate groups will affect the vulcanization effect, resulting in a less increase in $G'$ of V-PIP-P. Even so, the measured cross-linking density of V-PIP-P is much higher than that of V-PIP. Due to the polar nature of phosphate groups grafted on rubber chains, these phosphate groups formed aggregates in non-polar polyisoprene rubber matrix. When swelled with toluene, these polar phosphate group aggregates are insoluble and cannot be disaggregated by solvents, which are equivalent to cross-linking points, leading to an increase in the cross-linking density.

In order to verify our hypothesis about the cross-linking density, TEM experiment was conducted to explore the aggregation behavior of phosphate groups in the model compound. The TEM images of V-PIP and V-PIP-P are shown in Fig. 1. It was found that V-PIP sample formed homogeneous structure, while V-PIP-P sample formed apparent island phases structure. The morphology of thin film samples was further investigated by atomic force microscopy (AFM), as shown in Fig. S7 (in ESI). Spherical aggregates were formed in polyisoprene samples, while a continuous network structure was found in the V-PIP-P sample, demonstrating the crosslinking effect of the phosphate groups.

| Sample | $\varphi_r$ (%) | $M_c$ (g·mol$^{-1}$) | Cross-linking density (mol·cm$^{-3}$) |
|--------|----------------|------------------|-----------------------------|
| V-PIP  | 12.7           | 1.72×10$^4$      | 3.34×10$^{-5}$              |
| V-PIP-P| 16.4           | 9.98×10$^3$      | 9.22×10$^{-5}$              |

Table 1 The cross-linking density of V-PIP and V-PIP-P.

**Scheme 1** The synthetic routes to PIP and PIP-P.

**Fig. 1** TEM images of model compounds (a) V-PIP, (b) V-PIP-P.
Rheological Behavior of the Model Compounds

Since the linear viscoelastic response of the polymer materials is very sensitive to the change of network structure, rheological experiments were conducted to explore the network structure changes of model compounds. We performed frequency sweeps under small strain to explore the frequency dependence of storage modulus ($G'$) and loss modulus ($G''$), so that the network structure of model compounds can be described quantitatively. Meanwhile, strain sweeps were also performed to not only reflect the response of polymer structure to external stimulus, but also determine the linear viscoelastic regions of the model compounds.

Through the analysis of $G'$ and $G''$, the influence of phosphate group aggregates on the network structure can be revealed. As shown in Fig. 2(a), the $G'$ of V-PIP and V-PIP-P is higher than $G''$. And $G'$ does not change significantly with frequency changes, which is the typical characteristics of permanently cross-linking polymer. Meanwhile, it is found that the $G'$ of V-PIP-P is higher than that of V-PIP and the $G''$ is slightly lower than V-PIP. Combining the test results of TEM experiment, we speculated that these phosphate group aggregates of V-PIP-P are equivalent to cross-linking points, increasing the cross-linking density, resulting in an increase in $G'$. As the frequency increases, the enhanced cross-linking density will reduce the segmental motion, thereby reducing the $G''$. In addition, strain sweeps were also performed, as shown in Fig. 2(b). The $G'$ of V-PIP keeps constant until the strain of 20%, followed by a decline which could be ascribed to the disentanglement of molecular chains. In contrast, the $G'$ of V-PIP-P starts to decrease at strain as small as 1%, followed by a sharp decline at strain of 30%, which included both disruption of weak interactions (e.g. hydrogen bonds) and disentanglement of the molecular chains. The dissociation of phosphate group aggregates will lead to the decrease of cross-linking points, resulting in more obvious decrease of $G'$ for V-PIP-P sample.

Mechanical Properties of the Model Compounds

In order to investigate the function of phosphate groups on mechanical properties, the uniaxial tensile tests were conducted. The stress-strain curves and corresponding mechanical performance parameters are shown in Fig. 3(a) and Table 2. When the strain rate is 100 mm/min⁻¹, the V-PIP sample exhibits a tensile strength of 4.28 MPa and a Young’s modulus of 2.27 MPa. In comparison, the tensile modulus and Young’s modulus of V-PIP-P are 6.61 and 3.35 MPa, respectively. This phenomenon indicates that the phosphate group aggregates form an additional network structure, increasing the cross-linking density of V-PIP-P, resulting in an increase in Young’s modulus (2.27 MPa→3.35 MPa). Meanwhile, from the perspective of composite materials, these phosphate group aggregates also act like nano-fillers. The strong interfacial interaction of phosphate group aggregates and rubber chains will reduce the rubber molecule chains mobility and influence the network structure of model compounds. Therefore, the elongation at break of V-PIP-P is decreased (691%→454%). Moreover, this strong interfacial interaction can effectively transfer the load, resulting in an increase in tensile modulus (4.28 MPa→6.61 MPa).

Since the strain rate of the WAXD experiments was 12 mm/min⁻¹, the uniaxial tensile tests with a strain rate of 12 mm/min⁻¹ were also performed. Compared with the strain rate of 100 mm/min⁻¹, it was found that the elongation at break of both samples increased slightly (691%→791% for V-PIP and 454%→503% for V-PIP-P), the tensile strength decreased slightly (4.28 MPa→3.76 MPa for V-PIP and 6.61 MPa→6.38 MPa for V-PIP-P) and the Young’s modulus decreased slightly (2.27 MPa→1.55 MPa for V-PIP and 3.35 MPa→3.03 MPa for V-PIP-P). This phenomenon can be attributed to the transient entanglements of rubber chains. At higher strain rate, a part of these transient entanglements can act as cross-linking points, resulting in an increase in the tensile strength and Young’s modulus.

In order to better visualize the function mechanism of phosphate groups aggregates, the reduced stress ($f^*$) was plotted against the reciprocal of extension ratio ($\lambda$) using the well-known Mooney equation:

$$f^* = \sigma/(\lambda - \lambda^{-2}) = 2C_1 + 2C_2\lambda^{-1} = G_e + G_c f(\lambda)$$

(2)

where $\sigma$ is stress and $\lambda$ is the elongation ratio, $G_e$ is the elastic modulus resulting from the contribution of relatively permanent cross-linking points, $G_c$ is the modulus from contribution of the entanglements, $G_e$ and $G_c$ can be determined respectively from the y-axis intercept and the slope of the fitting line. The deformation range chosen for the linear fit is 0.4 < $\lambda^{-1}$ < 0.7 to avoid the influence of SIC and finite extensibility at large strain.

As shown in Fig. 3(b), at small $\lambda$ ($\lambda^{-1}$ > 0.3), the $f^*$ of V-PIP is
Nearly invariable and its uniaxial deformation can be well described by the rubber elasticity model. As the rubber chains are further stretching ($\lambda^{-1}<0.3$), the $f^*$ exhibits an obvious up-turn, which is attributed to the SIC behavior of rubber samples during stretching. The fitting parameters $G_e$ and $G_c$ are presented in Fig. 3(c). It is worthy to note that the $G_e$ of V-PIP-P is much higher than V-PIP and $G_c$ is much smaller than V-PIP. It is speculated that these phosphate groups formed polar aggregates in non-polar polyisoprene rubber matrix, serving as an additional dynamic cross-linking sites, which increases the $G_e$. Meanwhile, phosphate group aggregate also prohibited disentanglement, thus turning the transient entanglements into permanent entanglements, which also further increases the $G_c$ and decreases the $G_e$.

By comparing the fitting parameters of V-PIP-P at different strain rates, we found that the $G_c$ at low strain rate become much smaller. At the low strain rate, the breakage of weak H-bond would lead to the decreases of $G_e$. However, the fitting parameters of V-PIP at different strain rates did not change significantly, which is reasonable for V-PIP without weak bonds or other polar components.

In order to further investigate the role of the network structure formed by the phosphate group aggregates on mechanical properties, we performed the cyclic tensile tests under the strain of 100%, 200%, and 300%. As shown in Fig. 4(a), the low hysteresis was observed for V-PIP in the cyclic tensile tests as expected, which is reasonable for a vulcanized rubber without any fillers or weak bonds. In contrast, the V-PIP-P sample presents a significant hysteresis phenomenon in the cyclic tensile tests (Fig. 4b), which indicates the energy dissipation during the cyclic tensile tests. FTIR tests showed that hydrogen bonds existed between phosphate group aggregates. The full FTIR spectra of unvulcanized PIP and PIP-P are shown in Fig. S8 (in ESI). The normalized FTIR spectra are shown in Fig. 5; with increasing temperature, the $\mathrm{C}=\mathrm{O}$ characteristic band of the amide group shifts from 1663 cm$^{-1}$ to 1659 cm$^{-1}$ (Fig. 5a) and the $\mathrm{P}—\mathrm{O}$ characteristic band of the phosphate groups shifts from 1711 cm$^{-1}$ to 1715 cm$^{-1}$ (Fig. 5b), which are associated with gradual breakage of hydrogen bonds.[28,29] This temperature-dependent band shifting provides strong evidence for the formation of hydrogen bonds. Meanwhile, it is speculated that the phosphate group aggregates also construct additional dynamic cross-linking network. The rupture of these phosphate group aggregates will further dissipate energy during the stretching cycle tests. Therefore, compared with V-PIP, V-PIP-P has a larger hysteresis and residual strain in the first cycle. All the above test results proved that the phosphate group aggregates form a dynamic cross-linking network in the V-PIP-P.

To further illustrate the energy dissipation of phosphate group aggregates, we performed a stress relaxation analysis. The samples were stretched to a strain of 100%, and then the strain was kept to measure the change of relaxation stress within 60 min. The stress relaxation curves are shown in Fig. 6. It is found that V-PIP-P sample has a higher relaxation rate than V-PIP because of the dissociation of dynamic cross-linking network formed by phosphate group aggregates and the rupture of hydrogen bonds. It was found that the relaxation stress of V-PIP and V-PIP-P almost did not change with time after a significant decrease period, which is due to the stable covalent cross-linking network under loading.[30]

![Stress-strain curves](image1)

**Fig. 3** (a) Stress-strain curves of V-PIP and V-PIP-P at the strain rates of 100 and 12 mm·min$^{-1}$. (b) Mooney-Rivlin plots of V-PIP and V-PIP-P at the strain rates of 100 and 12 mm·min$^{-1}$. (c) The fitting parameters of $G_e$ and $G_c$.

**Table 2** Mechanical properties parameters of V-PIP and V-PIP-P at different strain rates.

| Samples       | Young's modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) |
|---------------|-----------------------|------------------------|-------------------------|
| V-PIP-12      | 3.55                  | 3.76                   | 791                     |
| V-PIP-P-12    | 3.03                  | 6.38                   | 503                     |
| V-PIP-100     | 2.27                  | 4.28                   | 691                     |
| V-PIP-P-100   | 3.35                  | 6.61                   | 454                     |

https://doi.org/10.1007/s10118-021-2497-z
Comparison of Crystallization Behavior of Model Compounds

The superior SIC ability of NR is now recognized as the main origin of its excellent comprehensive properties, which is caused by the "naturally occurring network". Therefore, it is essential to investigate the influence of network structure on the SIC behavior.\[31−35\]

The typical WAXD patterns of V-PIP and V-PIP-P at different strains are shown in Fig. 7. It is noted that the SIC phenomenon occurred much earlier for V-PIP-P than V-PIP, showing a smaller onset strain of 3.8. Previous studies have shown that the SIC mechanism of NR is short chain-induced crystallization, and the onset strain is associated with the inhomogeneous degree of network structure. It indicates that the phosphate group aggregates contribute to the inhomogeneous crosslinking in the rubber matrix.\[36−39\]

Quantitative analysis of WAXD patterns was carried out to understand the SIC behaviors of V-PIP and V-PIP-P. The Fit2D software was used to process the WAXD patterns for further analysis. The curves after successfully fitting are shown in Fig. 8. The crystallinity ($X_c$) can be calculated by the following equation:

$$X_c = \frac{\sum A_c}{\sum A_a + \sum A_c}$$  \hspace{1cm} (3)

where $\sum A_a$ and $\sum A_c$ represent the regions of amorphous and crystalline, respectively. The evolution of the crystalline peak of V-PIP and V-PIP-P during stretching is shown in Fig. 9. It is found that the crystalline peak becomes more obvious as the strain increases, which indicates that the crystallinity ($X_c$) of the samples gradually increases with the increase of strain. Meanwhile, we found that the crystallinity of V-PIP-P is lower than V-PIP. In order to explore the reason, we conducted a further study.

The crystallinity index as a function of strain during stretching is shown in Fig. 10. It was found that the V-PIP-P has lower onset strain of SIC, lower crystallinity and crystallization rate than those of V-PIP. Combining the results of tensile tests and stress relaxation tests, these phosphate group aggregates contribute to the inhomogeneous crosslinking in the rubber matrix.
form an additional dynamic cross-linking network, resulting in the inhomogeneous crosslinking in the rubber matrix. Under stretching, these high network density regions of V-PIP-P lead to the early orientation of rubber chains, promote the nucleation, and eventually accelerate the SIC behavior, so that the onset strain of SIC shifts to lower strain. Meanwhile, these phosphate group aggregates also reduce the molecule chain mobility, which hinders the crystal lateral growth. Therefore, the crystallinity and crystallization rate of V-PIP-P are lower than those of V-PIP.\textsuperscript{[15,40−42]}

Schematic Network Structure Model of the Model Compounds

On the basis of above results, we propose a hypothetical model to elucidate the function of phosphate groups in the formation of “naturally occurring network” and give further explanations to the SIC behavior. As shown in Fig. 11(b), these phosphate groups formed polar aggregates in non-polar polyisoprene rubber matrix, which are equivalent to cross-linking sites, thus forming an additional dynamic cross-linking network. In the initial stretching process, these phosphate group aggregates will promote amorphous chains align into crystalline, resulting in the formation of highly stretched segments and accelerating the SIC behavior. These crystallites embedded into the amorphous phase and formed additional physical cross-linking network, resulting in the superior mechanical properties

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Fig. 7  WAXD patterns of (a) V-PIP and (b) V-PIP-P at different strains.

Fig. 8  WAXD fitting curves of V-PIP at the strain of 7. Crystalline peaks and amorphous areas are indicated by arrows.

Fig. 9  Evolution of the integrated 1D WAXD profiles of (a) V-PIP and (b) V-PIP-P during stretching.

Fig. 10  Crystalline evolution of V-PIP and V-PIP-P samples with strains.
of V-PIP. Compared with Fig. 11(a), when further stretching is applied, these phosphate group aggregates also reduce the molecule chain mobility, which hinder the crystal lateral growth, so that the crystallinity and crystallization rate were reduced.

![Fig. 11](https://example.com/fig11.png)

**Fig. 11** Schematic models of (a) V-PIP and (b) V-PIP-P under smaller and larger strain.

**CONCLUSIONS**

In this work, we successfully synthesized a model compound (V-PIP-P) to explore the function of phosphate groups in the formation of “naturally occurring network”. It can further investigate the influence of phosphate groups on SIC behavior. These phosphate groups formed polar aggregates in non-polar polyisoprene rubber matrix, serving as additional dynamic cross-linking sites, which increases the cross-linking density and improves mechanical properties. These phosphate groups form a high network density region, leading to the early orientation of rubber chains and promoting the nucleation, so that the onset strain of SIC shifts to lower strain. However, these phosphate group aggregates also reduced the rubber molecule chains mobility, which hinder the crystal lateral growth, so that the crystallinity and crystallization rate of V-PIP-P are lower than those of V-PIP. The above test results help us to gain a deeper understanding for the function of phosphate groups in the formation of “naturally occurring network” and its influence on SIC behavior. In summary, the present work is expected to reveal the function of phosphate groups in NR, which plays a critical role for us to design biomimetic synthetic rubbers with excellent performance.

**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/s10118-021-2497-z.

**ACKNOWLEDGMENTS**

This work was financially supported by the National Natural Science Foundation of China (Nos. 51973126 and 51333003). The authors gratefully acknowledge the Shanghai Synchrotron Radiation Facility (SSRF).

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