

Polyisoprene Bearing Dual Functionalized Mini-blocky Chain-ends Prepared from Neodymium-mediated Coordinative Chain Transfer Polymerizations

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Abstract Through neodymium-mediated coordinative chain transfer copolymerization (CCTcoP), polyisoprenes bearing dual hydroxylated mini-blocky chain-ends were prepared via a three-step strategy. Kinetic studies revealed that, the polymerization demonstrated typical features of CCTcoP across the whole polymerization process, *i.e.*, quasi-living polymerization characteristic, tunable molecular weights, narrow molecular weight distributions, and atom economies. Comparing to previously reported CCTP homopolymerization systems, the presence of oxygen-containing Ip_{OAl} polar comonomer slowed down chain transfer rates obviously, rendering slightly higher molecular weights of the resultant Plps and smaller N_p (number of polymer chains per Nd atom) values. Moreover, to mimic the structure of natural rubber, the hydroxyl end groups can be facilely modified into phosphonate, amide, and UPy, whose structures were further confirmed by NMR spectra. Incorporation these functionalities could greatly improve the hydrophilic properties of the polymers, as revealed from the significantly reduced static water contact angles.

Keywords Functional polyisoprene; Neodymium; Coordinative chain transfer polymerization; Synthetic rubber

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INTRODUCTION

Among all types of synthetic rubbers, *cis*-1,4-polyisoprene (*cis*-1,4-PIp) shows the highest resembling microstructure and thereby elastomeric properties to natural rubber (NR), and has been long regarded as an indispensable alternative that can be directly prepared from selective isoprene polymerizations.^[1,2] Nevertheless, due to the lack of α,ω -biterminal non-rubber substances, which are usually in the forms of polar proteins, phospholipids, higher fatty acid, *etc.*, such synthetic *cis*-1,4-PIps often performed inferior comprehensive properties, such as raw rubber strength, anti-fatigue and tensile properties of the vulcanized rubber, and so on. To overcome these shortages, scientists have been recently devoted to incorporate different functional groups to the main chain of PIp to mimic NR.^[3–11] For instance, Cui *et al.* incorporated methoxyl and pyridine functionalities to the *cis*-1,4-PIp chain via random

copolymerization of isoprene with polar diene derivatives, and the resultant copolymer products were able to demonstrate much improved hydrophilic properties.^[12–14] Gong *et al.* copolymerized isoprene with various amounts of hydroxylmyrecene comonomer, and with the aid of hydroxyl groups in the resultant *cis*-1,4-PIps, greatly improved filler-polymer interfacial interactions and much higher tensile strength were obviously observed.^[15] In contrast to these in-chain randomly functionalized PIps, terminally functionalized counterparts are more preferable, because only in this way, the long stereoregular *cis*-1,4-sequence can be retained without damaging the strain-induced crystallization (SIC) performances. In 2018, Xu *et al.* reported the synthesis of α,ω -tetrapeptide functionalized PIps, the obtained products not only demonstrated good SIC behaviors, giving desired higher mechanical strength, but also revealed good compatibility and therefore an good dispersion of inorganic fillers.^[16–18] Nevertheless, such synthetic strategies employed a traditional neodymium-based Ziegler-Natta type catalytic system, which usually gave ill-defined active species and ill-controlled behaviors due to the coordination of heteroatoms to Nd atoms. Our group has been long devoted to large-scale industrialization of Nd-mediated isoprene polymerization to

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access high-performance Plp synthetic rubbers that can parallel NR. To address the above-mentioned traditional issues that accompanied in Nd-based system, including ill-defined active species, ill-controlled performances, broader polydispersities, low atom-economy of Nd metal, etc., we put forward a new synthetic methodology called coordinative chain transfer polymerization (CCTP).^[19–25] In such a system, the excessive chain transfer agents (CTAs), that are usually in the forms of aluminium alkyls, could bridge with Nd-based precatalyst through alkyls to dissociate Nd-based cluster and subsequently give single-site active species. Moreover, the growing polydienyl chains are able to reversibly transferred to the excessive CTAs through transmetalation reactions, and such processes are so rapid, versus propagation ($K_{ex} \gg K_p$), that the polydienyl chains appear to grow simultaneously on CTAs, which eventually results in well-controlled behaviors, including precisely designed molecular weights and extremely narrow dispersities.^[26–29] Moreover, multiple chains (up to 10) are able to be generated per Nd atom, demonstrating high atom-economy in contrast to traditional Ziegler-Natta catalytic systems. Ever since the launch of CCTP in diene polymerization field, most research interests are paid to homopolymerization, yet very rare reports on coordinative chain transfer copolymerization (CCTcoP) are documented, let alone CCTcoP of polar comonomers. In our recent research, we found that the Nd-based CCTP systems revealed good tolerance to heteroatoms, which gave good catalytic activities as well as well-controlled polymerization behaviors.^[30] As a continuation of such work, Nd-promoted CCTcoP of isoprene with hydroxyl-containing diene derivatives to prepare Plps bearing dual hydroxylated mini-blocky chain-ends (*abbr.* $Plp_{(OH)_2}$) are disclosed herein, and details will be given in the following.

EXPERIMENTAL

Materials

Nd(vers)₃ was commercial products and diluted to 0.05 mol/L by hexane. Diisobutylaluminum hydride (DIBAH, $Al(i-Bu)_2H$), dichlorodimethylsilane (Me_2SiCl_2) were the commercial product of Akzo Nobel and diluted with hexane into 1.0 and 0.2 mol/L solution, respectively. Isoprene was purchased from Fluka and refluxed over CaH_2 for 2 h and distilled before use. Toluene was dried by heating to reflux over sodium/diphenylketyl until the solution turned into atropurpureus and then distilled prior to use. 1,6-hexyldiisocyanate (HDI), diphenyl chlorophosphate (DCPP) were purchased from J&K (Beijing, China) and used as received without further purification. 2-Amino-4-hydroxy-6-methylpyrimidine (Upy) and 2(6-isocyanatohexylamino-carbonylamino)-6-methyl-4[1H] pyrimidinone (Upy-NCO) were synthesized according to the literature procedures.^[31,32]

General Procedure for the CCTcoP Processes

All the manipulations were performed under an atmosphere of dry nitrogen. A detailed polymerization procedure is described as a typical example. Nd(vers)₃, IP, $Al(i-Bu)_2H$, and Me_2SiCl_2 in toluene solution at a designed ratio were injected into the ampule sequentially and then aged at 50 °C for 30 min before use. Then IP_{OAI} was added and polymerized for another 30 min at 50 °C. A toluene solution of isoprene (1.5 mol/L, 20 mL) was placed in an oxygen and moisture-free bottle capped with a

rubber septum. After the monomer solution was heated to a desired temperature, the preformed catalyst solution was added. The polymerization was carried out at 50 °C for 4 h and then IP_{OAI} was added into the ampule, and kept for another 1 h. Polymerization was quenched by adding 2.0 mL of acidified ethanol containing 2,6-di-*tert*-butyl-4-methylphenol (1 wt%) as a stabilizer. The polymer was repeatedly washed with ethanol, and then dried under vacuum at 40 °C to constant weight. The polymer yield was determined by gravimetry.

Preparation of Plps Bearing Dual Hydroxylated Mini-blocky Chain-ends ($Plp_{(OH)_2}$)

Modification of $Plp_{(OH)_2}$ by HDI

Into a 25 mL of THF solution of 0.2 g of $Plp_{(OH)_2}$ (3.5 mol% of —OH) were added 1,6-hexyldiisocyanate (0.17 g, 1 mmol) and DBTDL (2 drops). The reaction mixture was stirred at room temperature for 10 h. To this mixture was added 10 mL of H_2O and 10 mL of ethanol, and the organic layer was separated. The aqueous layer was washed for three times with THF. The organic layers were combined and dried over anhydrous $MgSO_4$. After THF was removed, the polymer was isolated and dried at 40 °C under vacuum for 24 h.

Modification of $Plp_{(OH)_2}$ by DPCC

To a 100 mL flask containing 0.2 g of $Plp_{(OH)_2}$ (3.5 mol% of —OH) in 25 mL of THF, diphenyl chlorophosphate (0.32 g, 1.2 mmol) and triethylamine (0.12 g, 1.2 mmol) were added sequentially. The reaction mixture was stirred at room temperature for 10 h, and then 10 mL of H_2O and 10 mL of ethanol were added to the reaction mixture, the organic layer was separated. The aqueous layer was washed for three times with THF. All the organic layers were combined and dried over anhydrous $MgSO_4$. After removal of solvent using a rotary evaporator, the polymer was isolated and dried at 40 °C under vacuum for 24 h.

Modification of $Plp_{(OH)_2}$ by UPy-NCO

To a 100 mL flask containing 0.2 g of $Plp_{(OH)_2}$ (3.5 mol% of —OH) in 25 mL of THF, Upy-NCO (0.3 g, 1.0 mmol) and DBTDL (2 drops) were added. The reaction mixture was stirred at room temperature for 10 h. THF (20 mL), silica (0.3 g, 200–300 meshes) and 1 drop of DBTDL were added into the reaction mixture and further stirred for 1 h. After filtration, the filtrate was concentrated by rotary evaporation, and then the polymer was isolated by precipitation into ethanol and dried at 40 °C under vacuum for 24 h.

Characterization

The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymers were measured at 40 °C using gel permeation chromatography (GPC) equipped with a Waters 515 HPLC pump, four columns (HMW 7 THF, HMW 6E THF $\times$ 2, HMW 2 THF), and a Waters 2414 refractive index detector. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0 mL/min. Sample solutions were filtered through a 0.45 μm microfilter before injection. The values of M_n and M_w/M_n were calculated using polystyrene (PS) calibration. The NMR spectra of samples were recorded on BRUKER AVANCE NEO 400 MHz spectrometer using $CDCl_3$ as solvent at ambient temperature and tetramethylsilane (TMS) as an internal standard. The static contact angle of the film was assessed by contact angle goniometer (OSA 100, LAUDA, Germany) at 20 °C

with deionized water.

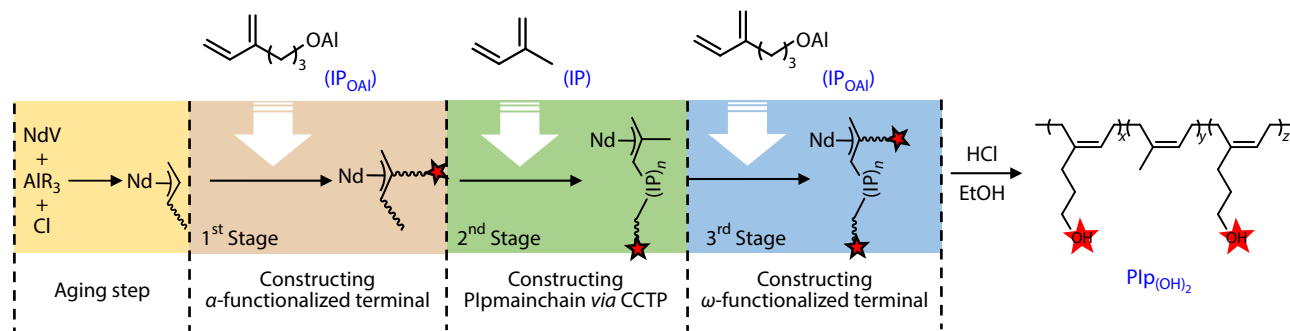
RESULTS AND DISCUSSION

CCTcoP Behaviors of Ip and Ip_{OAI}

Constructing α -functionalized terminal is the crucial firststep to prepare Plps bearing dual functionalized chain-ends. For classical Nd-promoted diene polymerizations, chain initiation occurs during the aging step, in which diene monomers insert into the Nd—C bonds that are freshly formed from the alkylation reaction of neodymium precatalyst with alkylaluminium cocatalysts. Therefore, in order to achieve α -functionalized Plp chains, functional groups are best to be incorporated right after such an aging step, because otherwise the Lewis acidic active species would be severely deactivated by the heteroatoms in the incorporated functional groups. Traditional common-used polar comonomers, such as acrylates, alkenols, cyclic esters, etc., do not suite for Nd-mediated diene polymerizations, because they adopt completely different polymerization mechanisms. Therefore, conjugated diene based polar derivatives, that also propagates *via* Nd-allyl moieties as in Ip monomer, are preferably targeted. Based on such a considerations, we commenced the study by evaluation the copolymerization performance of Ip and three different polar comonomers, including 1-(4-methoxy)phenyl-1,3-butadiene,^[33] 2-(4-methoxy)phenyl-1,3-butadiene,^[12] and 2-(ω -hydroxypropyl)-1,3-butadiene (Ip_{OH}),^[16] and only Ip_{OH} was found to be successfully incorporated the mainchain, although dramatically decreased polymer yield was accompanied. Therefore, Ip_{OH} was selected to construct the α -functionalized terminal. Moreover, to minimize the poisoning of hydroxyl group on the Nd active species, Ip_{OH} was expected to pre-treated with alkylaluminium cocatalyst to achieve Ip_{OAI} before being polymerized. In our previous reports, we disclosed an efficient Nd-promoted CCTP system of Nd(vers)₃/Al(*i*-Bu)₂H/Me₂SiCl₂ for diene

polymerization,^[20,21,23] in which Al(*i*-Bu)₂H performed much higher chain transfer rates than other alkylaluminium compounds, and therefore could allow for faster and reversible polydiene transferring with neodymium centre. To minimize the possible detrimental effect of Ip_{OH} and simultaneously guarantee the chain transfer efficiency, Al(*i*-Bu)₂H was chosen to protect the hydroxyl group in Ip_{OH} in the present research, and the system of Nd(vers)₃/Al(*i*-Bu)₂H/Me₂SiCl₂ was employed to conduct the CCTcoP investigations.

Scheme 1 illustrates the “three-step” strategy for constructing Plp_{(OH)₂} chains *via* Nd-mediated CCTcoP strategy, *i.e.*, after the formation of Nd-allyl active species during aging step, a few equivalents of Ip_{OAI} were firstly added into the reaction mixture to incorporate the α -functionalized terminal. Because Ip_{OAI} also inserted into the active species *via* a π -allyl intermediate, it showed little influence on latter isoprene insertions, which proceeded through a CCTP manner to manipulate the molecular weights and polydispersities. And in the end, a few more equivalents of Ip_{OAI} were added again into the polymerization system to introduce the ω -functional end-caps. Table 1 summarizes the CCTcoP results of Ip and Ip_{OAI} at various [Ip+Ip_{OAI}]/[Nd] ratios (200–800) at a condition of [Ip_{OAI}]/[Ip+Ip_{OAI}] = 0.2% in the 1st and 3rd stage, respectively, through which it was demonstrated that incorporation polar Ip_{OAI} comonomer brought very little influence on the polymer yields, and all the polymer yields were higher than 93%. Moreover, when increasing the [Ip+Ip_{OAI}]/[Nd] ratios, a good linear relationship between number-averaged molecular weights (M_n s) of the resultant Plps and [Ip+Ip_{OAI}]/[Nd] ratios was observed (Fig. 1). For instance, gradual increasing the [Ip+Ip_{OAI}]/[Nd] ratio from 200 to 300, 500, 600 and 800, the M_n s increased from 0.43×10^4 Dalton to 0.64×10^4 Dalton, 1.19×10^4 Dalton, 1.42×10^4 Dalton and eventually almost quadrupled to 2.05×10^4 Dalton at a ratio of [Ip+Ip_{OAI}]/[Nd] = 800. Additionally, all the GPC curves of the resultant Plps were



Scheme 1 Illustrative strategy for construction Plp_{(OH)₂} chain *via* Nd-mediated CCTcoP strategy.

Table 1 CCTcoP studies of Ip and Ip_{OAI} at different [Ip+Ip_{OAI}]/[Nd] ratios.^a

Run	[Ip+Ip _{OAI}]/[Nd]	Yield ^b (%)	M_n^c ($\times 10^4$)	M_w^c ($\times 10^4$)	PDI ^c	<i>Cis</i> -1,4- ^d	3,4- ^d	N_p^e
1	200	100	0.43	0.58	1.35	95.33	4.67	3.2
2	300	100	0.64	1.13	1.76	95.85	4.15	3.2
3	500	100	1.19	1.97	1.65	96.17	3.83	2.9
4	600	95.56	1.42	2.79	1.95	95.95	4.05	2.7
5	800	93.04	2.05	4.73	2.30	96.44	3.56	2.7

^a Polymerization conditions: catalytic system of Nd(vers)₃/Al(*i*-Bu)₂H/Me₂SiCl₂, Al(*i*-Bu)₂H/Nd=20, Cl/Nd=3, [Ip_{OAI}]/[Ip+Ip_{OAI}]=0.2% in the 1st and 3rd stage respectively, in toluene, 50 °C for 5 h; ^b Polymer yields were calculated based on Ip monomer only; ^c Determined by (GPC) using polystyrene standards;

^d Determined by NMR; ^e The number of polymer chains produced by per Nd atom.

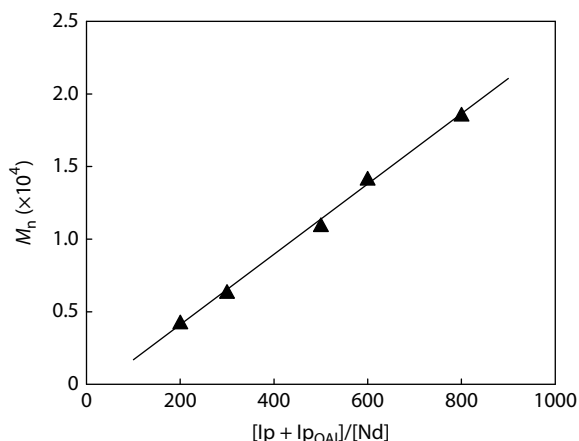


Fig. 1 Linear relationship between M_n s and $[Ip+Ip_{OAI}]/[Nd]$ ratios.

unimodal and the polydispersities kept narrow (<2.0) (Fig. 2), implying again that the presence of Ip_{OAI} showed little poisoning influence on the concentration of Nd-based active species, because otherwise obvious deviation from the linearity or very broad molecular weight distributions would be observed. At the ratio of $[Ip+Ip_{OAI}]/[Nd]=800$, the molecular weight distribution of the obtained PIP increased slightly to 2.30, which might be ascribed to the slight increased viscosities in such a reaction medium because of the increased molecular weights, that hampered fast and reversible polyisoprenyl chain transfers.

A detailed kinetic study was subsequently carried out at a ratio of $[Ip+Ip_{OAI}]/[Nd]=500$ by using the same catalytic system. As shown in Fig. 3, molecular weights M_n s of the obtained PIPs increase linearly against polymer yields across the whole polymerization period, while simultaneously keep very narrow molecular weight distributions ($PDI < 1.6$) (Fig. 3). GPC curves of the produced PIPs shifted to higher molecular weight regions with polymerization time prolonging, and maintained unimodal shape during the whole course of the polymerization (Fig. 4). All these results suggested the quasi-living nature of the active species, which was a representative characteristic of CCTP system. The semilogarithmic plot of $-\ln(1-x)$ (x is the yield) versus time was also linear, giving

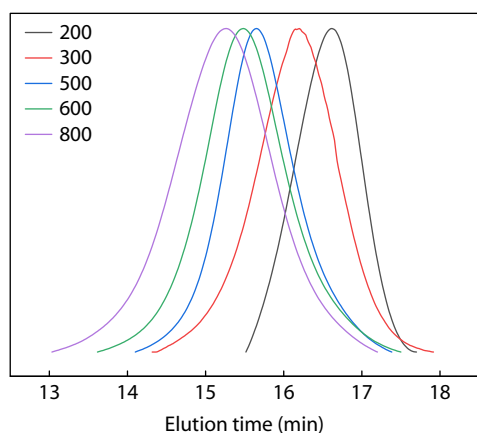


Fig. 2 GPC curves of the PIPs obtained from Table 1.

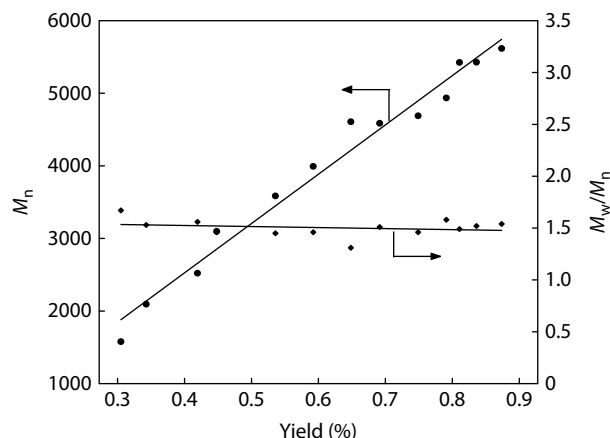


Fig. 3 Plots of M_n and M_w/M_n against polymer yields for the kinetic study.

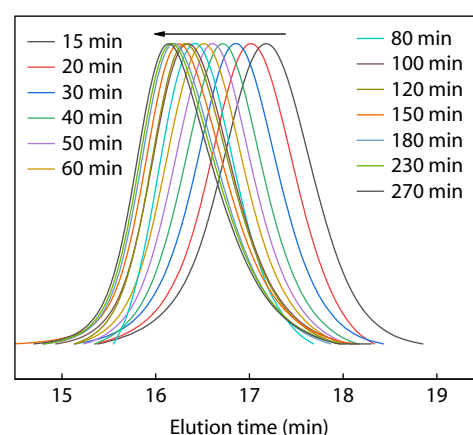


Fig. 4 GPC curves of the PIPs obtained from kinetic study.

an apparent first-order rate constant k_{app} of 0.0088 ($R^2=0.9928$) (Fig. 5), implying the concentration of the active species maintained constant during the whole polymerization process. All of these results shed light on that the CCTCoP process of Ip and Ip_{OAI} to achieve $PIP_{(OH)_2}$ proceeded in a well-controlled manner, and the molecular weights as well as polydispersities could be precisely regulated as anticipated.

Besides well-controlled polymerization behaviors, another important characteristic of the CCTP is that multiple chains could be generated per Nd atom to give high atom-economies. In our previous reports, we had demonstrated that, for the catalytic system of $Nd(vers)_3/Al(i-Bu)_2H/Me_2SiCl_2$ for dienes homopolymerizations, 6–10 chains were able to be generated per Nd atom.^[20,21] For the present research on CCTCoP of IP and Ip_{OAI} , however, only *ca.* 3 chains per Nd atom was obtained (Table 1), which was obviously lower than diene homopolymerization systems. These results could be explained by the coordination of alkoxy group to the Lewis acidic Nd metal centre, which caused significantly changed micro-environments around the Nd atom that slowed down chain transfer rates. From the viewpoint of mechanism, chain transfer occurred through a transmetalation process, in which the four-member hetero-bimetallic Nd/Al ring served as the intermediate, any factors caused steric or electronic changes could in-

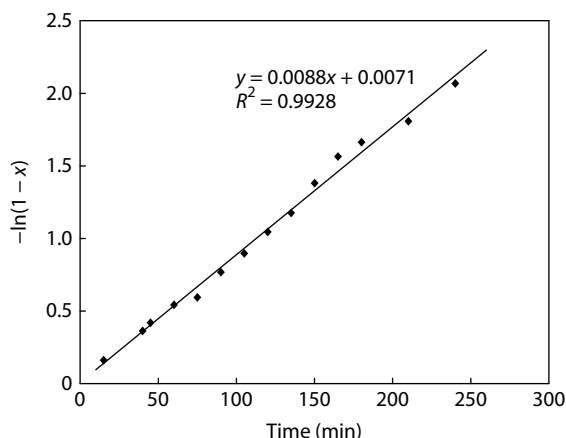


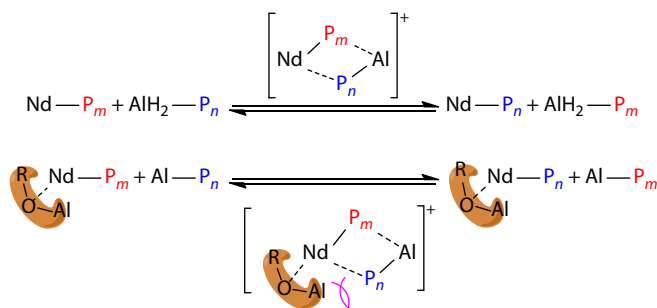
Fig. 5 The relationship of $-\ln(1-x)$ versus polymerization time.

fluence the formation of such four-membered ring and then impact on chain transfer rates. For the present CCTcoP of IP and Ip_{OAI} , due to the presence of Lewis basic oxygen atoms in Ip_{OAI} , they could coordinate to the Nd center, causing significantly increased steric crowdedness around the metal centre. Such an increased bulky nature was unfavorable for the approaching of chain transfer agent of alkylaluminium compounds due to mutual steric repulsion reasons (Scheme 2), and therefore, chain transfer reactions were prohibited.

Besides, we also tried to regulate the Ip_{OH} incorporation content in the obtained $\text{Plp}_{(\text{OH})_2}$ through varying the $[\text{Ip}_{\text{OAI}}]/[\text{Ip}+\text{Ip}_{\text{OAI}}]$ feeding ratios in the 1st and 3rd stages of the polymerisation. As the results shown in Table 2, when increas-

ing the Ip_{OAI} feeding percentages from 0.01% to as high as 5%, the catalytic system can still maintain high catalytic activities, giving quantitative conversions of the Ip monomers in all cases, which suggested again that the presence of polar Ip_{OAI} comonomer brought little negative influences on the activities of the active species under such a condition. Besides, with an increasing Ip_{OAI} feeding percentage, a gradually increased Ip_{OH} contents, with a maximum value of 6.30%, in the obtained polymer were witnessed, as revealed from the increased resonance intensities of the methylene group CH_2OH at 3.63 ppm in the ^1H -NMR spectra (Fig. 6). Introducing more Ip_{OAI} percentages showed also big influences on the molecular weights as well as polydispersities of the resultant Plps. Due to the coordination of oxygen atoms to the Nd active species that slowed down chain transfer reaction rates (Scheme 2), an approximately increasing trend of the molecular weights from 0.77×10^4 Dalton to 1.48×10^4 Dalton were observed. Partially because of the same reason, gradually broadening polydispersities from 1.60 to 4.39 were also accompanied (Fig. 7). Besides this, the stronger interactions among mutual hydroxyl groups (hydrogen bond) from different Plp chains, or between the hydroxyl groups with the gels in the GPC column also contributed to the broadened polydispersities.

Fig. 8 shows the ^{13}C -NMR and DEPT135 spectra of the obtained $\text{Plp}_{(\text{OH})_2}$ products, from which the *cis*-1,4- inserted Ip_{OH} monomers could be clearly detected by the resonance signals at 137.65 ppm (C2), 122.69 ppm (C3), 61.86 ppm (C7), 39.14 ppm (C5), 32.08 ppm (C6), 30.05 ppm (C1), 29.38 ppm (C4). The 3,4-inserted Ip_{OH} monomer could be excluded,



Scheme 2 Influence of alkoxyl group on chain transfer reactions.

Table 2 CCTcoP studies of Ip and Ip_{OAI} at different Ip_{OAI} concentrations. ^a

Run	Ip_{OAI} feed ^b (mol%)	Yield ^c (%)	M_n ^d ($\times 10^4$)	M_w ^d ($\times 10^4$)	PDI ^d	<i>Cis</i> -1,4- ^e	3,4- ^e	χ ^f (%)
1	0	100	0.77	1.24	1.60	95.70	4.30	—
2	0.01	100	1.03	1.95	1.89	96.05	3.95	^g
3	0.05	100	1.11	1.76	1.59	96.07	3.93	^g
4	0.1	100	1.05	1.84	1.75	96.09	3.91	0.18
5	0.2	100	1.19	1.97	1.65	96.17	3.83	0.34
6	0.5	100	1.14	1.97	1.71	96.05	3.95	0.84
7	1.0	100	1.48	5.51	3.72	96.44	3.56	1.43
8	5.0	100	1.35	5.92	4.39	95.99	4.01	6.30

^a Polymerization conditions: catalytic system of $\text{Nd}(\text{vers})_3/\text{Al}(i\text{-Bu})_2\text{H}/\text{Me}_2\text{SiCl}_2$, $\text{Al}(i\text{-Bu})_2\text{H}/\text{Nd}=20$, $\text{Cl}/\text{Nd}=3$, $[\text{Ip}+\text{Ip}_{\text{OAI}}]/[\text{Nd}]=500$, in toluene, 50 °C for 5 h; ^b $[\text{Ip}_{\text{OAI}}]/[\text{Ip}+\text{Ip}_{\text{OAI}}]$ ratio in the 1st and 3rd stages respectively; ^c Polymer yields were calculated based on Ip monomer only; ^d Determined by (GPC) using polystyrene standards; ^e Determined by NMR; ^f Total incorporation percentage of Ip_{OH} ; ^g Incorporation percentages cannot be calculated precisely because of the small peaks of methylene group.

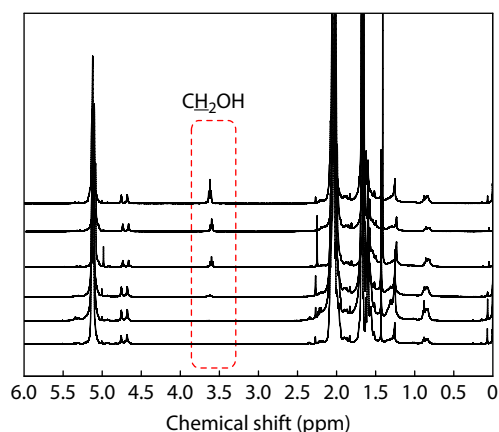


Fig. 6 ^1H -NMR spectra of $\text{Plp}(\text{OH})_2$.

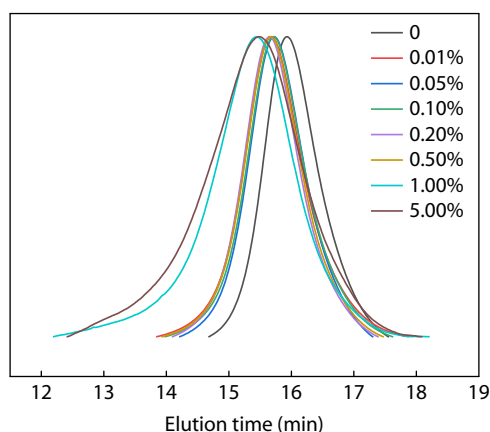


Fig. 7 GPC curves of the Plps obtained from Table 2.

which shows difference to previous reports.^[15] Connectivity of the two types of monomers can be found at 134.69 ppm ($9'$), 123.57 ppm ($\text{C}10'$), 61.79 ppm ($\text{C}7'$), 38.97 ppm ($\text{C}5'$), 31.35 ppm ($\text{C}6'$), 31.05 ppm ($\text{C}8'$), 30.26 ppm ($\text{C}1'$), 28.30 ppm ($\text{C}4'$), 25.74 ppm ($\text{C}11'$), 21.70 ppm ($\text{C}12'$) that were ascribed to IP and Ip_{OH} monomers respectively. The ^{13}C -NMR spectrum also confirmed the predominant *cis*-1,4- structure of IP monomers, because only trace amount of *trans*-1,4- units could be detected (134.33 and 123.88 ppm).

The presence of abundant reactive hydroxyl groups in the Plp chain-ends allowed us for further modifying the chain ends. Herein, we introduced three different types of functionalities, *i.e.* phosphonate, amide and 2-ureido-4[1*H*]pyrimidinone (UPy), to mimic the polar chain-end moieties of phospholipid, hydrogen bonding structure, proteins respectively in the chain-ends of natural rubber. All the modifications were carried out under mild conditions. Reacting hydroxyl groups with diphenyl chlorophosphate (DPCP) in the presence of triethyl amine could convert the $-\text{CH}_2\text{OH}$ group to $-\text{CH}_2\text{OP}(=\text{O})(\text{OPh})_2$ quantitatively, that could be verified from ^1H -NMR spectrum that the methylene $-\text{CH}_2-$ resonance peak shifted from original 3.63 ppm to a lower field of 4.15 ppm. Treating hydroxyl groups with HDI and UPy-NCO by using dibutyltin dilaurate (DBTDL) as catalyst also gave the corresponding products quantitatively, as revealed from their corresponding ^1H -NMR spectra in Fig. 9. DPCP, HDI, UPy-NCO modified Plps also brought significant improvement on their hydrophilic natures, as revealed from significantly decreased static water contact angles (WCA) from 109.9° to 96.4°, 99.1° and 86.4°, respectively (Fig. 10).

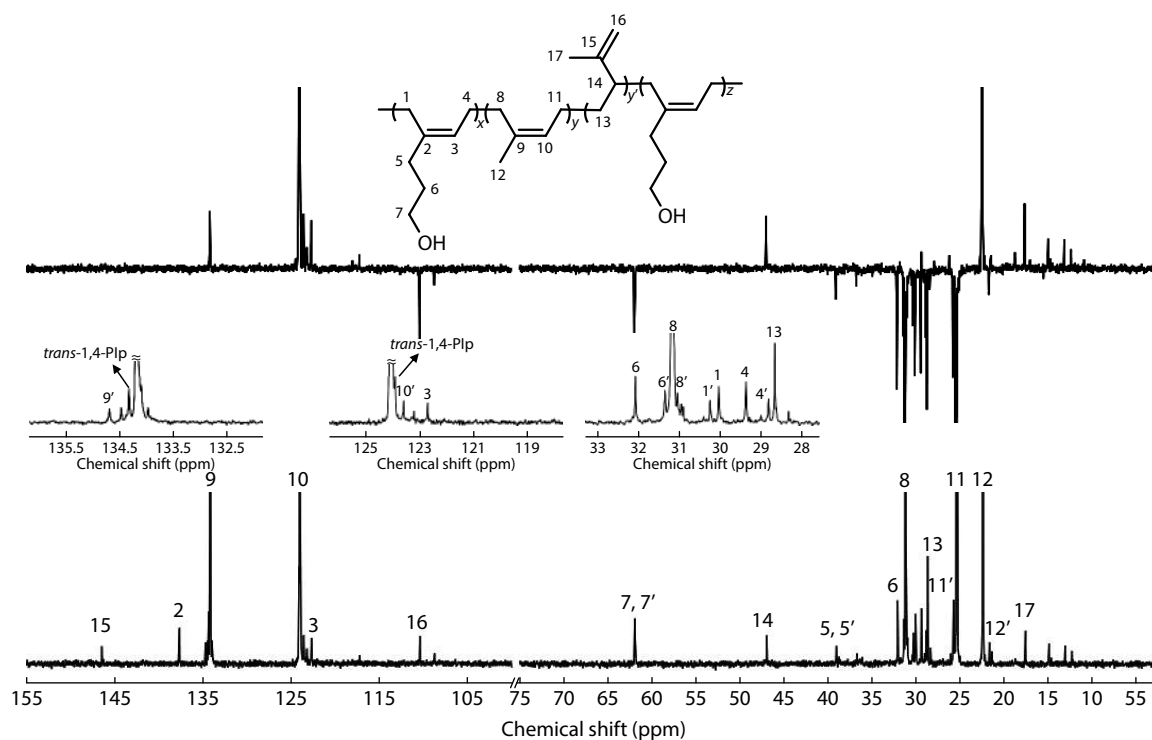


Fig. 8 ^{13}C -NMR and DEPT135 spectra of $\text{Plp}(\text{OH})_2$.

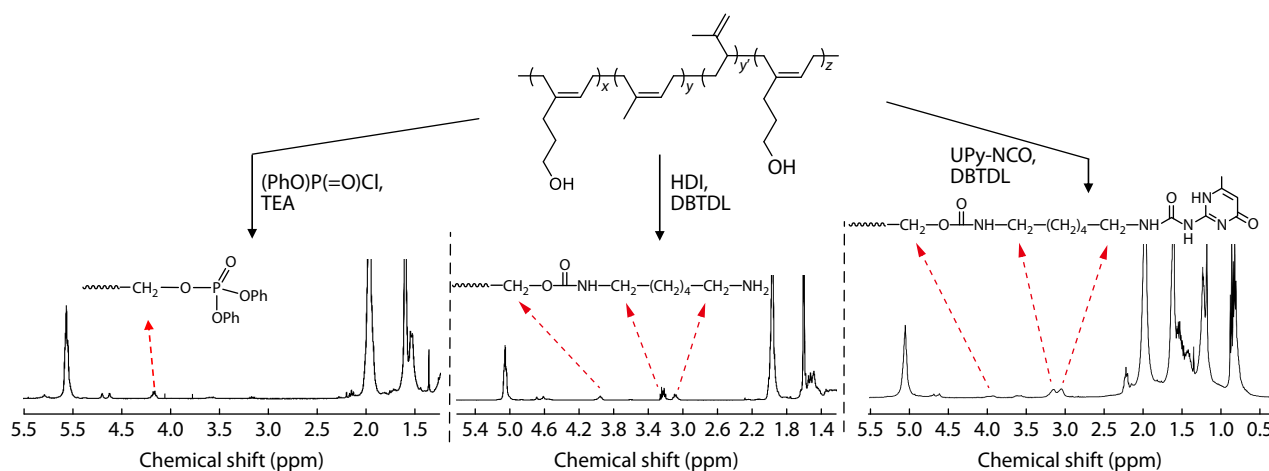


Fig. 9 ^1H -NMR spectra of modified $\text{PIp}_{(\text{OH})_2}$ by DPCP, HDI and UPy-NCO.

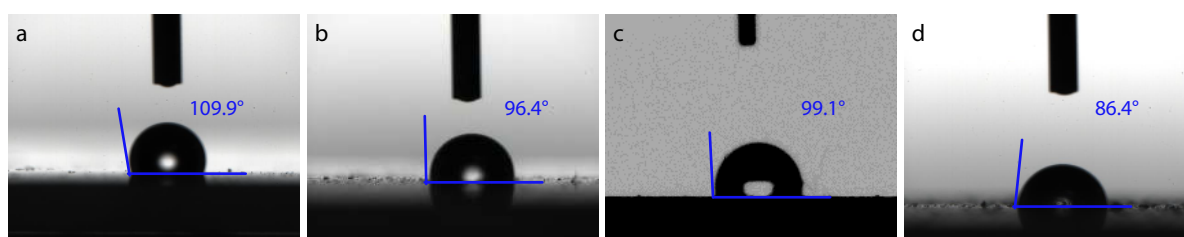


Fig. 10 Static water contact angles for (a) PIp_{OH} and the corresponding modification products by (b) DPCP, (c) UPy-NCO and (d) HDI.

CONCLUSIONS

In this study, we disclosed a well-controlled strategy, *i.e.* coordinative chain transfer copolymerization (CCTcoP), for preparing PIPs bearing dual hydroxylated mini-blocky chain-ends ($\text{PIp}_{(\text{OH})_2}$) in three steps. By using $\text{Nd}(\text{vers})_3/\text{Al}(i\text{-Bu})_2\text{H}/\text{Me}_2\text{SiCl}_2$ catalytic system and $\text{Al}(i\text{-Bu})_2\text{H}$ as chain transfer agent, the whole polymerization process revealed well-controlled manner, *i.e.* precisely regulated molecular weights and narrow polydispersities. Detailed kinetic studies demonstrated that molecular weights M_n s of the obtained PIPs increased linearly against polymer yields and simultaneously keeping very narrow molecular weight distributions ($\text{PDI} < 1.6$). Moreover, semilogarithmic plot of $-\ln(1-x)$ (x is the yield) versus time was also linear, implying a quasi-living nature of such catalytic system. Besides, multiple chains (*ca.* 3.0) could be generated per Nd atom, suggesting an atom-economic property, although the values are smaller than homopolymerization systems. Varying the IP_{OAl} polar comonomer contents imposed little negative influence on the catalytic activities, and PIPs bearing different amounts of hydroxyl chain ends were successfully obtained. Nevertheless, such comonomer affected the chain transfer rates due to their coordination to the active species, which slow down chain transfers and then resulted in higher molecular weights and slightly broader molecular weight distributions. The end-capped reactive hydroxyl groups could be further converted to other functionalities under mild conditions, such as phosphonate, amide, UPy. And such post-modifications could improve the hydrophilic properties of the polymers significantly, which was desired for scientists from the viewpoint of improving the compatibility between polymer substrates and

polar inorganic fillers.

NOTES

The authors declare no competing financial interest.

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