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Highly *cis*-1,4-selective coordination polymerization of polar 2-(4-methoxyphenyl)-1,3-butadiene and copolymerization with isoprene using *β*-diketiminato yttrium bis(alkyl) complex

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The unprecedented highly *cis*-1,4 selective (> 99%) coordination–insertion polymerization of the polar monomer 2-(4-methoxyphenyl)-1,3-butadiene (2-MOPB) had been achieved by using the *β*-diketiminato yttrium bis(alkyl) complex to afford a hydrophilic plastic polymer P(2-MOPB) with a water contact angle of 87.7° and a glass transition temperature of 34.2 °C. The copolymerization of polar 2-MOPB and nonpolar isoprene had also been successfully realized for the first time to produce a kind of modified high *cis*-1,4 polyisoprene with a wide range of 2-MOPB contents (8.2%～88.5%). The composition was adjusted by regulating the monomer fed ratios according to the copolymerization kinetics. Hydrogenation of P(2-MOPB) provided an unusual alternating copolymer poly(4-methoxystyrene-*alt*-ethylene) that couldn't be obtained in any other manners.

Introduction

Polyhydrocarbons (polyolefins, polystyrene and polydienes) have been widely applied in modern human life because of their excellent chemical and physical properties in combination with low cost, superior processability and good recyclability. Nonetheless, consisting solely carbon and hydrogen two elements and lacking of polar groups, polyhydrocarbons exhibit poor surface properties, low adhesive property as well as affinity for dyes, *etc*.[1], which encounter serious compatible problems when mixing with other polymers to make blends, or with additives to make composites. With respect of the conjugated dienes based polymers, the synthetic rubbers, these problems are even serious since they must be charged with inorganic fillers such as carbon black and/or silica when used as tires and mechanical engineering goods in order to improve the modulus, tear resistance, abrasion resistance, tensile strength, and dynamic and static toughness properties.[2] However, the hydrophilic silica and the hydrophobic polydienes are completely incompatible and it is very hard to modify the inorganic fillers, therefore, scientists have devoted to change the surface properties of the hydrocarbon polydienes through copolymerization with polar monomers for decades.[3] Although significant progresses have been achieved for modification of polyolefins through copolymerization of ethylene or propylene with polar olefinic monomers,[1] modification of polydienes has been far from success via the copolymerization route, because synthesis of substituted diene monomers is difficult, and their regio- and stereo-selective control polymerization in high efficiency without cross linking and cyclization side reactions, has still been a challenging project.[4] So far, a few 2-substituted-1,3-butadiene derivatives bearing silicon-,[5] cyano-,[4,6] ester-[7] and amino[8] groups have been synthesized and polymerized through anionic and free radical polymerizations with low regio- and stereo-selectivity.[4-8] Although various highly specific selective coordination polymerization of the non-substituted conjugated dienes has achieved great successes to afford high performance rubbers or plastics,[9] it losses power on the polymerization of 2-substituted-1,3-butadienes, in particular, on those bearing polar functional groups. Because the Lewis acidic transition metal based coordination catalysts employed in the polymerization process prefer complexing with the Lewis-basic heteroatoms O, N, and X (halides) of the functional monomers to the reactive C=C double bonds, resulting in deactivation of the active sites.[1] Therefore, synthesizing conjugated dienes containing polar functional groups and exploring a suitable catalyst to realize their control polymerization have been a long-standing and challenging project in the research field of polymer science.

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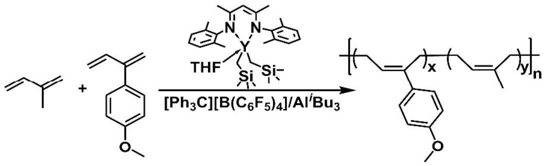
Table 1. Copolymerization of 2-MOPB with IP using BDI-Y(CH_2SiMe_3)$_2$(THF)/Al^{i}Bu$_3$/[Ph_3C][$B(C_6F_5)_4$]^a



entry	[2-MOPB] /[IP]/[Y]	T_p (°C)	t (h)	Yield (%)	2-MOPB/IP in copolymer (mol %)	*cis*-1,4(%) in P(2-MOPB)	*cis*-1,4(%) in PIP	M_n^{c} × 10^{-4}	M_w/M_n^{c}	T_g^{d} (°C)
1	200: 0: 1	25	3	97.8	100	>99^e	-	2.56	1.6	34.2
2	200: 0: 1	40	2	98.4	100	98.3^e	-	1.75	1.6	33.8
3	200: 0: 1	60	1.5	98.6	100	97.5^e	-	1.48	1.7	33.5
4	100:1200:1	25	6	>99	8.2/91.8	98.9	96.8	12.6	1.8	-62.9
5	100: 900: 1	25	6	98.6	10.2/89.8	98.9	96.5	9.05	1.7	-63.6/-23.5
6	100: 600: 1	25	6	97.3	13.8/86.2	98.7	96.3	6.96	1.9	-63.7/-12.9
7	200: 600: 1	25	6	96.2	22.2/77.8	98.6	96.2	6.12	2.0	-62.6/6.7
8	200: 300: 1	25	6	94.1	39.1/60.9	98.7	96.0	4.41	1.8	-63.9/20.1
9	200: 200: 1	25	6	93.3	59.9/40.1	98.5	96.0	4.18	1.6	21.9
10	600: 200: 1	25	6	91.7	76.3/23.7	98.3	95.8	5.72	1.8	25.2
11	900: 100: 1	25	6	87.9	88.5/11.5	98.2	95.7	8.41	2.1	32.9

[a] Conditions: BDI-Y 10 μmol, [Ph_3C][$B(C_6F_5)_4$] 10 μmol, Al^{i}Bu$_3$ 100 μmol, toluene 2mL/5mL (homo-/copolymerization). [b] Determined by ^{1}H and ^{13}C NMR spectroscopy in $CDCl_3$. [c] Determined by GPC in THF at 40 °C against polystyrene standard. [d] Measured by DSC. [e] The *cis*-1,4 content of P(2-MOPB).

Herein, we report an unprecedented highly *cis*-1,4 selective coordination polymerization of methoxy phenyl substituted 1,3-conjugated butadiene (MOPB) by the group 3 yttrium precursor bearing the *β*-diketiminato ligand to afford new plastic P(2-MOPB)s. Moreover, the copolymerization of 2-MOPB with isoprene is also successful to yield random copolymers P(2-MOPB-*co*-IP)s of various compositions and sequence distributions. The resultant copolymers incorporating the polar plastic segments in the rubbery macromolecular chains could be viewed as an alternative of the polar group modified poly(butadiene-*co*-styrene) rubber prepared by anionic catalyst (nowadays, they are the main component of the "green tyres"), anticipated to result in desirable dispersion of silica in rubbery materials to provide good aging, abrasion, ozone and oil resistances.[2] The thus copolymers can't be accessed by any present methods, as far as we are aware.

Results and discussion

Synthesis and Homopolymerization of 2-(4-Methoxyphenyl)-1,3-Butadiene 2-MOPB was synthesized through the dehydration of 2-(4-methoxyphenyl)but-3-en-2-ol by using pyridinium *p*-toluenesulfonate as dehydrant under mild conditions in a moderate yield (46%), which was a better synthon than dehydration of 2-phenyl-1,3-butadiene (2-PB) with aniline hydrobromide as dehydrant that takes place at a higher temperature for a longer time.[10] 2-MOPB was purified by the flash column chromatography followed by vacuum distillations over CaH_2 for 24 hours. Delighted

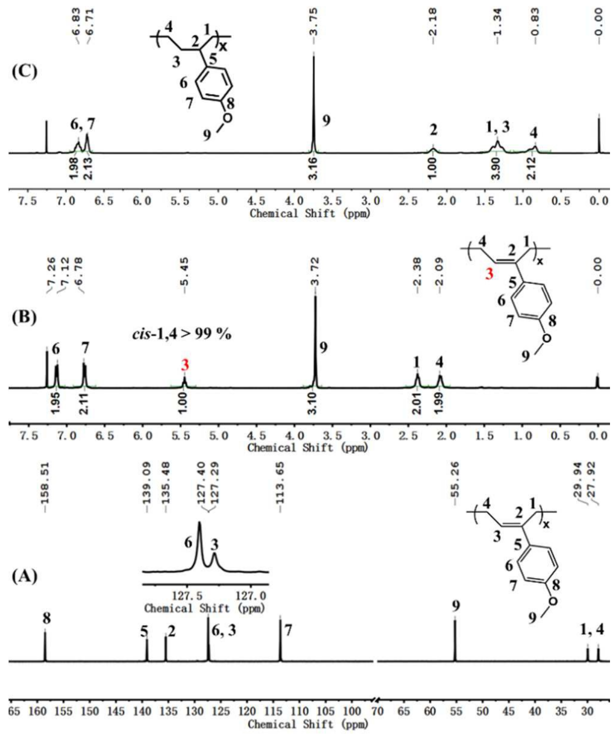


Fig. 1 ^{1}H and ^{13}C NMR spectra of P(2-MOPB) and P(MOSt-*alt*-E).

to us this polar monomer could be polymerized fluently with the ternary catalytic system BDI-Y(CH_2SiMe_3)$_2$(THF)/Al^{i}Bu$_3$/[Ph_3C][B(C_6F_5)$_4$] (BDI: $CH_3C=N(C_6H_3$-2,6-Me_2)CHCN(C_6H_3-2,6-Me_2)CH_3) under mild conditions as shown in Table 1 (entries 1-3), although much slower than the polymerization of its isoprene (IP) analogue.[11] A 97.8% monomer conversion was achieved in 3 h, which increased to 98.6% within 1.5 h when the polymerization was conducted at 60 °C. In contrast, the selectivity dropped slightly at high temperatures (*cis*-1,4-content: 98.3% (40 °C), 97.5% (60 °C)), which might be ascribed to the switching of the transition state of *anti*-allyl geometry to the more thermal stable *syn*-allyl geometry, leading to a slight increase of the *trans*-1,4 enchainment. The minor decline of the molecular weight (M_n: 1.75×10^4 (40 °C), 1.48×10^4 (60 °C)) at the elevated temperatures was probably due to the presence of the chain-transfer reaction. ^{1}H and ^{13}C NMR spectra of a resultant P(2-MOPB) sample (Table 1, entry 1) were shown in Fig. 1B and 1A. The assignments were established by means of 2D-NMR techniques (^{1}H-^{1}H-COSY, DEPT,HSQC and HMBC, Figures S2-5). The signal at δ 5.45 ppm is ascribed to the internal olefinic proton H_3 and the resonances for the terminal vinyl protons are absent, suggesting an over 99% *cis*-1,4 regularity for P(2-MOPB) (Fig. 1B). Correspondingly, the ^{13}C NMR spectrum gives two singlets at δ 135.48 and 127.29 ppm assigned to the olefinic carbons C_2 and C_3 (Fig. 1A). This represents the first example of highly specific selective coordination-insertion polymerization of polar group substituted diene monomers, since to date, the polar group substituted diene monomers have been reported to be polymerized by anionic or radical polymerizations to give irregular products.[4-8] Noteworthy is that the resulting highly *cis*-1,4 regulated P(2-MOPB) has a striking property discrimination from its PIP counterpart. The latter is a typical rubber with a lower T_g (-63.7 °C), but P(2-MOPB) is recognized as a plastics possessing a relatively higher T_g of 34.2 °C (Figure S6A), which may be arising from the large rigid methoxy phenyl substituent at C_2 of 2-MOPB.

It is well known that alternating hydrocarbon copolymers are of important vale in both academy and industry, nonetheless, difficult to access via simply copolymerizing two hydrocarbon monomers since they bear too similar electronics to satisfy the strict preconditions for the competitive polymerization ratios: $r_1 \approx 0$ and $r_2 \approx 0$. Fortunately, hydrogenation of the highly 1,4-regulated polydienes can provide alternating copolymers such as poly(ethylene-*alt*-propylene)[14] and poly(ethylene-*alt*-styrene)[15]. In the present work, we obtained a new alternating copolymer poly(4-methoxystyrene-*alt*-ethylene) (P(MOSt-*alt*-E)) (E = etylene, MOSt = methoxystyrene,) via hydrogenating P(2-MOPB). The ^{1}H NMR spectrum of P(MOSt-*alt*-E) is shown in Fig. 1C, the signal olefinic H_3 of P(2-MOPB) disappeared in Fig. 1B, and the resonances at δ 2.17 and 1.34 ppm are assignable to the newly generated saturate methylene and methine groups. In the mean time, the signals arising from H_6, H_1 and H_4 of P(2-MOPB) shift markedly upfield. All these results suggested that the hydrogenation was successful and complete to give the unprecedented alternating copolymer of P(MOSt-*alt*-E) with a T_g of 35.8 °C (Figure S6B) comparable to its precursor P(2-MOPB).

Copolymerization of 2-(4-Methoxyphenyl)-1,3-Butadiene with Isoprene Up to now, synthesis of high-molecular-weight copolymers with tuneable incorporation of the functional groups and consecutive insertions of polar monomers occurring via coordination-insertion copolymerization is still in its infancy.[12] The unique regularity and thermal property of P(2-MOPB) intrigued us to explore its copolymerization behaviour with IP, anticipated to pave a way of improving dispersion of silica in rubber compounds and wear property of *cis*-1,4-PIP.[2] The copolymerization of 2-MOPB and IP was carried out in toluene at 25 °C with the ternary catalyst system BDI-Y(CH_2SiMe_3)$_2$(THF)/Al^{i}Bu$_3$/[Ph_3C][B(C_6F_5)$_4$]. To our surprise, the copolymerization went on fluently albeit with a lower activity than the homopolymerization of 2-MOPB. As reported previously, the copolymerization of a polar monomer with nonpolar monomer usually results in deactivation of the catalytic active species owing to the formation of the stable chelate between the polar group with the metal center, or a mixture of the homopolymers. The resultant copolymers had high molecular weights close to the theoretic values and narrow molecular weight distributions, indicative of the single-sited nature of the catalytic system and the controllable polymerization fashion, in particular, the formation of copolymers rather than the mixture of both homopolymers (Table 1 entries 4-11). Noted that the copolymerization was extremely sensitive to 2-MOPB. Addition of a small amount of 2-MOPB (2-MOPB-to-IP molar ratio = 100:1200) dramatically slowed down the copolymerization rate to achieve 98.6% conversion in 6 h as compared with homopolymerization of 2-MOPB in 3 h and of IP in 10 min. The presence of the polar group prohibited the reactive C=C double bond from coordinating to the active metal center by complexing with it, obviously, such complexing was not strong enough to terminate propagation of the macromolecular chains. Therefore with increasing the 2-MOPB loading, the polymerization activity didn't decreased further even at a higher than 90% mole fraction. Inspection of ^{13}CNMR spectrum of the obtained copolymers revealed the excellent *cis*-1,4 regularity for both IP and 2-MOPB sequences as shown in Fig. 2. The signals at δ 158.52, 139.40, 127.39 and 113.65 ppm of the aryl carbons of 2-MOPB appear nearly the similar resonances to those in homopolymer P(2-MOPB) as compared with Fig. 1A, while the signals at δ 30.01 and 27.30 ppm corresponding to the main chain carbons C_1 and C_4 shift slightly downfield maybe arising from the influence of the

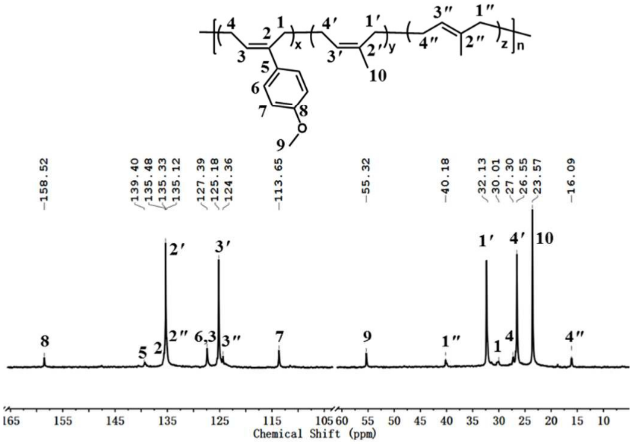


Fig. 2 ^{13}C NMR spectrum of P(2-MOPB-*co*-IP).(Table 1, entry 4)

Fig. 3 Various microstructures of P(2-MOPB-*co*-IP)s with different content of 2-MOPB (A: 8.2%; B: 10.2-39.1%; C: 59.9-88.5%)

neighbouring IP-units. The peaks at δ 32.13, 135.33, 125.18 and 26.55 ppm are attributed to C_1–C_4 carbons in the *cis*-PIP-units.With the increase of [2-MOPB]/[IP] feed ratio, we can clearly find that the signals corresponding to PIP-units weaken but the signals attributed to P(2-MOPB)-segments strengthen gradually (Figure S8). In particular, when the monomer feed ratio was 1:1, 2-MOPB content was higher than that of IP in the obtained copolymer, corroborative of the rate of 2-MOPB being higher than that of IP(Table 1, entry 9).

Composition and Properties of P(2-MOPB-*co*-IP) The reactivity ratios r_M (k_{MM}/k_{MI}) and r_I (k_{II}/k_{IM}) (M = 2-MOPB, I = IP) were evaluated using Fineman–Ross equation (Figure S10). A plot of F(f-1)/f as ordinate and (F^2/f) as abscissa (F = [2-MOPB]/[IP] fed of monomers, f = [2-MOPB]/[IP] found of monomers in the copolymer) is a straight line. The slope is $r_M = 2.32$ and the intercept is minus $r_I = 0.05$, correlating to the reactivity ratio of 2-MOPB and IP, respectively, which suggests 2-MOPB prefers homopolymerization to its copolymerization with IP. Based on the above kinetics results, by varying the monomer feed ratio [2-MOPB]/[IP], the composition of the copolymer could be adjusted. When the feed ratio was very low ([2-MOPB]/[IP] =100: 1200), the single 2-MOPB or short 2-MOPB-sequence distribute randomly along the long PIP sequences (Fig. 3A). So the resultant copolymer show a single T_g of -62.9 °C close to that of homo PIP (Fig. 4, curve A). The length of consecutive 2-MOPB units increase gradually with increasing the monomer feed ratio from 100:900 to 200:300, resulting in a random composition in the initial stage and the single PIP component in the final stage during the copolymerization (Fig. 3B). Thus, all these copolymers show two T_gs, one is around -63 °C but the other escalates from -23.5 °C to 20.1 °C, in consistence with the lengths of the randomly distributed P(2-MOPB) sequences (Fig. 4B to 4E). Further increasing the feed ratios to 200: 200, 600: 200 and 900: 100, the continuous P(2-MOPB) units are interrupted by the single IP or short IP sequences (Fig. 3C). The larger the ratio is, the longer the P(2-MOPB) sequence is, and the higher the T_g is, which is nearly equal to that of homo-P(2-MOPB) (Table 1, entry 11).[13]

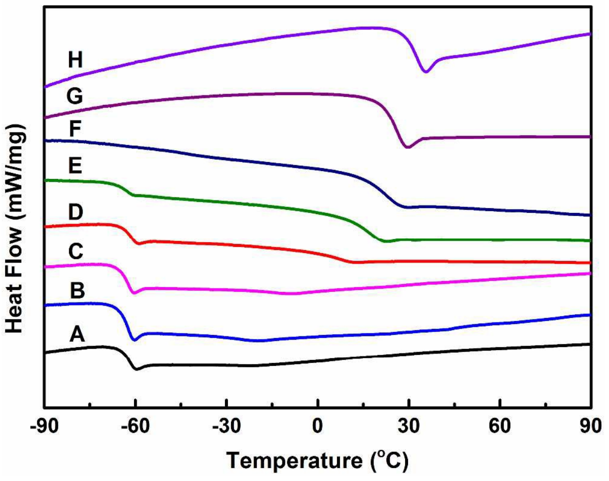


Fig. 4 Thermograms of P(2-MOPB-*co*-IP)s. (A-H corresponding to entries 4-11 in Table 1).

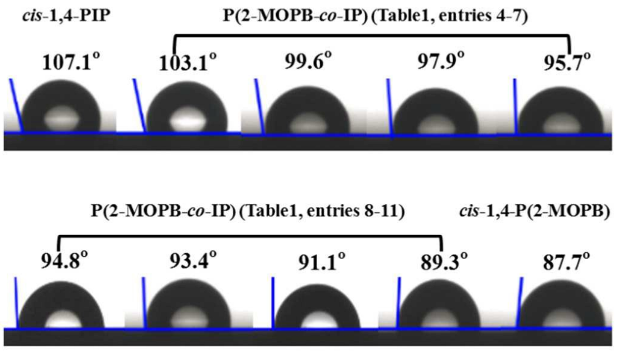
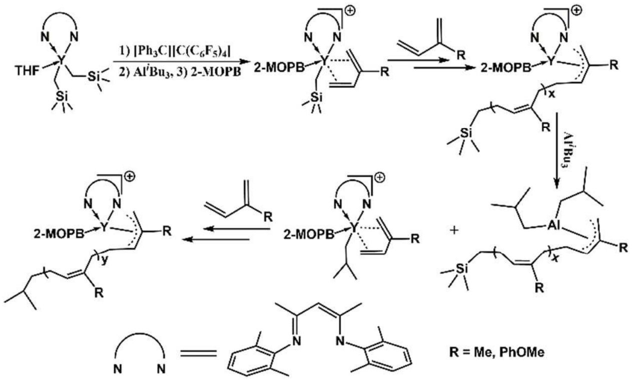


Fig. 5 WCAs of PIP, P(2-MOPB) and P(2-MOPB-*co*-IP)s.

Incorporation of the polar 2-MOPB units into a PIP chains aroused the change of the surface property such as the static water contact angle (WCA), which was measured by using the sessile drop method. The results showed that the WCA of P(2-MOPB-*co*-IP) declines from 103.1° to 89.3° with increasing the content of 2-MOPB from 8.2% to 88.5% (Fig. 5), which is lower than 107.1° for PIP, indicative of improved surface property.

Probable (co)polymerization mechanism In order to obtain the information about the active species, the activation of yttrium complex with $[Ph_3C][B(C_6F_5)_4]$ was monitored by NMR spectroscopic techniques in $C_6D_4Cl_2$. Both ^1H and ^{13}C NMR spectra displayed that one CH_2SiMe_3 moiety in BDI-Y was abstracted and a new cationic yttrium monoalkyl species $[(BDI)Y(CH_2SiMe_3)(THF)]^+[B(C_6F_5)_4]^-$ was formed, which could initiate the polymerization of 2-MOPB. From the ^1H NMR spectrum (Figure S11) of oligomer P(2-MOPB) catalyzed by the binary system BDI-Y /$[Ph_3C][B(C_6F_5)_4]$, we could find the signals at δ 0.82 ppm and δ 0.02 ppm corresponding to the resonance of $–CH_2Si(CH_3)_3$ respectively, meaning that the ionic compound of $[(BDI)Y(CH_2SiMe_3)(THF)]^+[B(C_6F_5)_4]^-$ is the active species. However, when Al^iBu_3 was added to the binary catalytic system, we could discover the isobutyl signals in the ^1H NMR spectrum (Figure S12) of oligomer P(2-MOPB), suggesting that Al^iBu_3 resulted in chain transfer.



Scheme 1 Probable mechanism for copolymerization of isoprene and 2-MOPB.

Based on these results, the probable reaction pathway for the copolymerization of isoprene and 2-MOPB could be proposed (Scheme 1): under the activation of $[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ and addition of the monomer 2-MOPB, a monomer-containing (oxygen coordination) monoalkyl cationic species $[(BDI)Y(CH_2SiMe_3)(2\text{-}MOPB)]^+[B(C_6F_5)_4]^-$was formed. 2-MOPB or IP monomer *cis*-η^4 coordinated to the yttrium center, inserted into Y-CH_2SiMe_3 bond, and propagated to cationic yttrium poly(2-MOPB-*co*-IP). In the meantime, the yttrium-polymer chain could exchange with isobutyl moiety in Al^iBu_3 to form a new active species $[BDI\text{-}Y(2\text{-}MOPB)CH_2CH(Me)_2]^+$, which further initiated the copolymerization of IP and 2-MOPB to produce the isobutyl capped copolymers.

Conclusions

We have demonstrated a simple strategy to synthesize a polar butadiene derivative, 2-MOPB, which, under the catalysis of the *β*-diketiminato yttrium cationic catalyst, could polymerize to a new highly *cis*-1,4 regulated (> 99%) polydiene with a T_g of 34.2 °C. In addition, its copolymerization with nonpolar IP has been achieved successfully for the first time albeit in a low activity than those of the both homopolymerizations, suggesting the presence of interaction of the polar group with the active species. The resultant copolymers P(2-MOPB-*co*-IP)s have highly *cis*-1,4 regulated microstructures with variable 2-MOPB insertion ratios by adjusting its fed amount. Introduction of polar monomer sequences into PIP backbone indeed improved its surface property by lowing the WCA from 107.1° for PIP to 87.7 ° for P(2-MOPB). This work sheds a new light on modifying polydiene rubbers by introducing the polar functional group into *cis*-PIP chain by the means of coordination polymerization.

Experimental

General experimental procedures All manipulations were performed under a dried and oxygen-free argon atmosphere using standard high vacuum Schlenk techniques or in an Mbraun glovebox. All solvents were purified from Mbraun SPS system. Al^iBu_3 (1.0 M in hexane), n-butyllithium (1.6 M in hexane) and vinyl magnesium bromide (1.0 M in THF) were purchased from Aldrich. 4'-methoxyacetophenone and pyridinium *p*-toluenesulfonate were purchased from the National Medicine Co. (China) and were used without further purification. $[Ph_3C][B(C_6F_5)_4]$[16] and BDI–$Y(CH_2SiMe_3)_2(THF)$[11] (BDI: $CH_3C{=}N(C_6H_3\text{-}2,6\text{-}Me_2)CHCN(C_6H_3\text{-}2,6\text{-}Me_2)CH_3$) were prepared according to the literatures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 and 500. The number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polymer samples were measured by means of gel permeation chromatography (GPC) on a TOSOHHLC-8220 GPC apparatus (Column: SuperHZM-Hx3) at 40 °C using THF as the eluent (the flowing rate is 0.35 mL/min) against polystyrene standards. Differential scanning calorimetry (DSC) analyses were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere. The static contact angle of the film was assessed by sessile drop angle measurement using a contact angle goniometer (DSA 100, Kruss GmbH, Hamburg, Germany) at 20 °C. At least five measurements were carried out for a single sample and the values obtained were averaged. The testing liquids used were deionized water.

Preparation of 2-(4-Methoxyphenyl)-1,3-Butadiene To a stirred solution of vinylmagnesium bromide (240 mL, 1.0 M solution in THF, 240 mmol, 1.2 equiv) in THF (100 mL), a solution of 4'-methoxyacetophenone (30.0 g, 200 mmol) in THF (100 mL) was added dropwise over 30 min at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at the same temperature for 2 h and then quenched with a saturated NH_4Cl aqueous (300 mL) and extracted with ethyl acetate (300 mL). The extract was washed with saturated brine (200 mL), dried over Na_2SO_4 and concentrated to afford 2-(4-methoxyphenyl)but-3-en-2-ol.

Under a nitrogen atmosphere, a solution of 2-(4-methoxyphenyl)but-3-en-2-ol (8.91 g, 50 mmol) and pyridinium *p*-toluenesulfonate (62.83 mg, 0.25 mmol, 0.005 equiv) in toluene (100 mL) was heated at 80 °C for 4 h. The reaction mixture was washed with saturated $NaHCO_3$ aqueous and saturated brine. The organic layer was dried over Na_2SO_4 and evaporated to give diene as a pale-yellow oil in a yield of 46%: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.27 (d, J = 7.5 Hz, 2H, Ar–H), 6.89(d, J = 7.1 Hz, 2H, Ar–H), 6.63 (dd, J = 17.9, 10.3 Hz, 1H, CH=CH_2), 5.25 (d, J = 8.9 Hz, 2H, C=CH_2), 5.20 (d, J = 11.2 Hz, 2H, CH=CH_2). 3.82 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 159.24 (C–OCH_3), 147.78 (C=CH_2), 138.51 (Ar–C), 132.27 (CH=CH_2), 129.43 (Ar–C), 117.05 (C=CH_2), 116.05 (CH=CH$_2$), 113.66 (Ar–C), 55.36 (OCH$_3$).

Preparation of Poly{2-(4-Methoxyphenyl)-1,3-Butadiene} A typical polymerization procedure (Table1, entry 1) was described as follows. Under a nitrogen atmosphere, 2-MOPB (0.32 g, 2 mmol) was added into a 10 mL flask. Then, 10 equiv Al^iBu_3 (0.2 mL, 0.5 mol/L), a toluene solution (2.0 mL) of complex BDI-$Y(CH_2SiMe_3)_2$ (6.4 mg, 10 μmol) and 1 equiv $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 μmol) were added to the flask. The reaction apparatus was placed in a bath at 25 °C. After the reaction was stirred for 3 h, methanol was injected to terminate the polymerization. The viscous mixture was poured into a large quantity of methanol. The obtained white polymer was filtered and then dried under vacuum at 40 °C to a constant weight.

Preparation of Poly(4-Methoxystyrene-*alt*-Ethylene) Under a nitrogen atmosphere, P(2-MOPB) (0.32 g, 2.0 mmol of double bonds), *p*-toluenesulfonylhydrazide (0.82 g, 4.4 mmol) and 30 mL of *p*-xylene were added to100 mL flask and refluxed for 24 h. After being cooled to room temperature, the clear solution was poured into a large quantity of methanol. The obtained white polymer was filtered and then dried under vacuum at 40 °C to a constant weight.

Preparation of Poly{2-(4-Methoxyphenyl)-1,3-Butadiene-*co*-Isoprene} A typical polymerization procedure (Table1, entry 4) was described as follows. Under a nitrogen atmosphere, 2-MOPB (0.16 g, 1 mmol) and isoprene (0.82 g, 12 mmol) were added into a 10 mL flask. Then, 10 equiv $Al^{i}Bu_3$ (0.20 mL, 0.5 mol/L), a toluene solution (5.0 mL) of complex BDI-$Y(CH_2SiMe_3)_2$ (6.4 mg, 10 μmol) and 1 equiv $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg,10 μmol) were added to the flask. The reaction apparatus was placed in a 25 °C bath. After the reaction was stirred for 6 h, methanol was injected to terminate the polymerization. The viscous mixture was poured into a large quantity of methanol. The obtained white polymer was filtered and then dried under vacuum at 40 °C to a constant weight.

Synthesis of complex $[(BDI)Y(CH_2SiMe_3)(THF)][B(C_6F_5)_4]$. $[Ph_3C][B(C_6F_5)_4]$ (46.0 mg, 50 μmol) was added to a $C_6D_4Cl_2$ solution (0.5 mL) of $(BDI)Y(CH_2SiMe_3)_2(THF)$ (32.0 mg, 50 μmol). A red solution was afforded, which was added to an NMR tube, sealed, and analyzed in situ by NMR spectroscopy. ^{1}H NMR (400 MHz, C6D4Cl2, δ): 6.84-6.94 (6H, *Ar*), 5.49 (1H, $HC(C(CH_3)NAr)_2$), 3.57 (4H, *THF*), 2.02-2.17 (12H, 2,6-CH_3Ar), 1.61 (6H, CH_3), 1.41 (br, 4H, *THF*), 0.05 (s, 9H, $Si(CH_3)_3$), -0.24 (2H, CH_2SiMe_3). ^{13}C NMR (125 MHz, $C_6D_4Cl_2$, δ): 168.31 (2C, $HC(C(CH_3)NAr)_2$), 150.31, 148.38, 140.12, 138.27, 136.29, 134.75, 133.81, 133.49, 131.57, 130.15, 129.92, 128.99, 127.03 (*Ar*), 99.19 (1C, $HC(C(CH_3)NAr)_2$), 71.51 (2C, *THF*), 45.15 (1C, $CH_2Si(CH_3)_3$), 25.74 (2C, *THF*), 24.07 (2C, $HC(C(CH_3)NAr)_2$), 19.36 (4C, 2,6-$(CH_3)_2C_6H_3$), 3.74 (3C, $Si(CH_3)_3$).

Preparation of oligomer P(2-MOPB)-1. Under a nitrogen atmosphere, 2-MOPB (0.32 g, 2 mmol) was added into a 10 mL flask. Then, a toluene solution (3.0 mL) of complex BDI-$Y(CH_2SiMe_3)_2$ (32.0 mg, 50 μmol) and 1 equiv $[Ph_3C][B(C_6F_5)_4]$ (46.0 mg,50 μmol) were added to the flask. The reaction apparatus was placed in a bath at 25 °C. After the reaction was stirred for 3 h, methanol was injected to terminate the polymerization. The viscous mixture was poured into a large quantity of methanol. The obtained white polymer was filtered and then dried under vacuum at 40 °C to a constant weight. The yield is 92%. The M_n 8440 caculated by ^{1}H NMR is slight higher than the M_n 6400 measured by GPC.

Preparation of oligomer P(2-MOPB)-2. Under a nitrogen atmosphere, 2-MOPB (0.32 g, 2 mmol) was added into a 10 mL flask. Then, 10 equiv $Al^{i}Bu_3$ (1. 0 mL, 0.5 mol/L), a toluene solution (3.0 mL) of complex BDI-$Y(CH_2SiMe_3)_2$ (32.0 mg, 50 μmol) and 1 equiv $[Ph_3C][B(C_6F_5)_4]$ (46.0 mg,50 μmol) were added to the flask. The reaction apparatus was placed in a bath at 25 °C. After the reaction was stirred for 3 h, methanol was injected to terminate the polymerization. The viscous mixture was poured into a large quantity of methanol. The obtained white polymer was filtered and then dried under vacuum at 40 °C to a constant weight. The yield is 95%. The M_n 5150 caculated by ^{1}H NMR is slight higher than the M_n 4080 measured by GPC.

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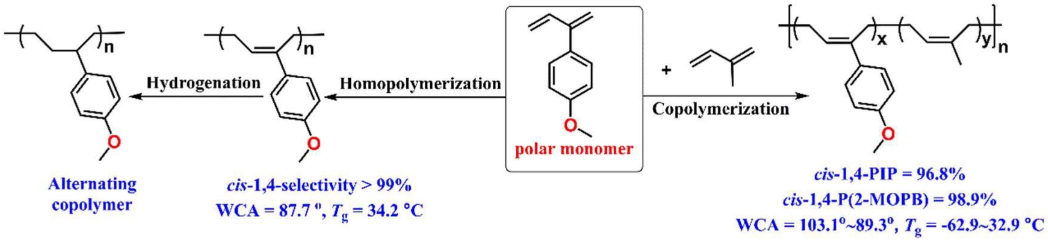
Graphical abstract



A novel polar monomer 2-(4-methoxyphenyl)-1,3-butadiene (2-MOPB) has been synthesized and (co)polymerized by using *β*-diketiminato yttrium bis(alkyl) precursor to afford the highly *cis*-1,4 regulated homopolymer P(2-MOPB) and copolymer P(2-MOPB-*co*-IP) of new plastics and rubber depending on the compositions. A new alternating copolymer P(MOSt-*alt*-E) can be obtained via hydrogenating P(2-MOPB).