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Functionalized Copolymers of Isobutylene with Vinyl Phenol: Synthesis, Characterization, and Property

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Abstract The random copolymers of isobutylene (IB) with polar comonomers of 4-acetoxystyrene (ACS) or 4-*tert*-butoxystyrene (TBO), P(IB-*co*-ACS) and P(IB-*co*-TBO), could be successfully synthesized *via* cationic copolymerization with $FeCl_3$-based initiating system. The kinetics of the cationic copolymerization process was *in situ* investigated by inserting a diamond probe into the reaction system by ATR-FTIR spectroscopy. The chemical structure and incorporation content of polar comonomers in the copolymers were characterized by GPC with RI/UV dual detectors and ^{1}H-NMR spectroscopy. The corresponding functionalized random copolymers of IB with vinyl phenol P(IB-*co*-POH) carrying phenolic hydroxyl side groups could be further prepared *via* the complete hydrolysis of acetoxyl side groups in P(IB-*co*-ACS) or *tert*-butoxyl side groups in P(IB-*co*-TBO) copolymers. The functionalized P(IB-*co*-POH) copolymers became hydrophilic with water contact angle (WCA) of *ca*. 80° for the self-assembly in hot water, compared to the hydrophobic polyisobutylene with WCA of *ca*. 110°. The functionalized P(IB-*co*-POH) copolymers also displayed an excellent self-healing property due to the interaction of intermolecular hydrogen bonding and formation of three dimentional supramolecular networks from phenolic hydroxyl side groups. Furthermore, P(IB-*co*-POH) copolymers also provided a good matrix for the homogeneous dispersion for silica nanoparticles due to the formation of hydrogen bonding between copolymer chains and silica nanoparticles.

Keywords Cationic polymerization; Isobutylene; Copolymers; Polar monomer; Functionalized polyisobutylenes

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INTRODUCTION

Polyisobutylene (PIB) is an important constituent of numerous industrial polyolefins because of its desirable properties, for instance, excellent impermeability to air and water, chemical stability, and thermostability.[1] However, it is still limited in some applications due to the lack of polar chemical functionalities for the fact that PIB has non-polar chemical structure containing only saturated C—C and C—H bonds. In order to improve the surface properties, printing properties, rheology of polyisobutylene, and its compatibility with other polymer materials, introduction of polar moieties into the polymer chains to construct functionalized isobutylene-based copolymers has become an essential research direction.

There are usually some methods for preparing the functionalized polyisobutylenes with polar moieties in the polymer chains. A common method is to introduce the functional groups at the head of PIB chains by using functional initiators in the initiation step or at the end of PIB chains by adding functional reagents to terminate the growing PIB chains during cationic polymerization of isobutylene (IB).[2−16] On the other hand, a convenient synthetic strategy by direct copolymerization of IB with polar monomers for the synthesis of functionalized isobutylene-based copolymers has also been developed in recent years.[17,18] The strong electrophilicity of both the Lewis acid coinitiator and cationic active centers might easily interact with polar groups containing elements with strong electronegativity such as nitrogen, phosphorus, and oxygen in these copolymerization systems. Binder and coworker introduced polar styrene monomers containing pyridine, collidine, thymine, or triazole moieties into polyisobutylene by living cationic copolymerization using TMP-Cl/$TiCl_4$ as an initiating system.[19] The copolymerization of IB with styrene monomers containing pyridine, collidine, or thymine moieties proceeded with incorporating 2 mol% comonomers into the copolymer chains. Then, the synthesis and melt rheology of supramolecular polyisobutylenes bearing statistically distributed hydrogen-bonding moieties were reported for the self-healing materials due to the formation of hydrogen bonding supramolecular networks.[20−28] Poly(*p*-hydroxystyrene-*b*-isobutylene-*b*-*p*-hydroxystyrene) triblock copolymer was synthesized *via* living cationic sequential block copolymerization of isobutylene with 4-*tert*-butoxystyrene using $TiCl_4$ as a coinitiator for isobutylene polymerization and $SnBr_4$ as a coinitiator for 4-*tert*-butoxystyrene polymerization.[29] Poly(hydroxystyrene-*b*-isobutylene-*b*-hydroxystyrene) triblock copolymer was synthesized by combination of living sequential block copolymerization of iso-

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butylene coinitiated by $TiCl_4$ and *p*-(*tert*-butyldimethylsiloxy)styrene coinitiated by titanium(IV) isopropoxide utilizing the capping-tuning technique with deprotection in the presence of tetrabutylammonium fluoride. Then, the acetylated derivative was further synthesized by quantitative acetylation.[30] Poly(hydroxystyrene-*b*-isobutylene-*b*-hydroxystyrene) and its acetylated derivative were used for the controlled delivery of paclitaxel from stent coatings.[30]

In order to prepare the novel functionalized isobutylene-based copolymers with phenolic hydroxyl side groups, a convenient and effective synthetic method has been developed in this study. The direct copolymerizations of isobutylene with polar monomers of 4-acetoxystyrene (ACS) or 4-*tert*-butoxystyrene (TBO) were firstly carried out with the $FeCl_3$-based initiating system to synthesize the statistically distributed copolymers of isobutylene with ACS or TBO, *i.e.*, P(IB-*co*-ACS) and P(IB-*co*-TBO). Then, the hydrolysis of the above two kinds of copolymers containing acetoxy or *tert*-butoxy side groups was conducted under different reaction conditions to achieve the desired isobutylene-based copolymers of P(IB-*co*-POH) with phenolic hydroxyl groups. The functionalized P(IB-*co*-POH) copolymers became hydrophilic with water contact angle (WCA) of *ca.* 80° for the self-assembly in hot water, which is largely different from the behavior of hydrophobic polyisobutylene. P(IB-*co*-POH) copolymers also displayed an excellent self-healing property due to the interaction of intermolecular hydrogen bonding and formation of three dimentional supramolecular networks from phenolic hydroxyl side groups. Further, the P(IB-*co*-POH) copolymers provided a good matrix of the homogeneous dispersion of silica nanoparticles due to the formation of hydrogen bonding between copolymer chains and silica nanoparticles.

EXPERIMENTAL

Materials

Dichloromethane (DCM, A.R., Beijing Yili Fine Chemicals) and *n*-hexane (*n*-Hex, A.R., Beijing Yili Fine Chemicals) were dried before use by distilling over calcium hydride (CaH_2, A.R., Tianjin Jingke Company). Tetrahydrofuran (THF, A.R., Beijing Chemical Company) was dried before use by distilling over sodium wire with diphenylmethanone as an indicator until the system became bright blue. 2-Chloro-2-methylpropane (*t*-BuCl, purity: 99%, Aladdin), isobutylene (IB, purity: 99.9%, Beijing Yanshan Petroleum Chemical Corp.), 4-acetoxystyrene (ACS, purity: 98%, Acros), 4-*tert*-butoxystyrene (TBO, purity: 99%, Aldrich), anhydrous ferric chloride ($FeCl_3$, purity: 99%, Acros, packaging under nitrogen), sodium methylate (CH_3ONa, purity: 98%, Macklin), sulfuric acid (H_2SO_4, Beijing Chemical Company), ethanol (A.R., Beijing Yili Fine Chemicals), and isopropanol (*i*-PrOH, A.R., Beijing Chemical Company) were used as received. The average size of silica nanoparticles (SiO_2-383, Yingchuang Technology Company, China) was around 20 nm.

General Procedure for the Copolymerization of IB with TBO or ACS

Copolymerization was carried out in a three-necked round-bottom Schlenk bottle under a dry nitrogen atmosphere at –80 °C according to our previous work.[31−34] Specific reaction conditions were listed in the figure captions. A typical polymerization procedure is described as follows: *n*-Hex, DCM, and IB were added sequentially to a round-bottomed flask, and the mixture was stirred. Then, 20 mL portions were air-tightly transferred to reaction flask *via* a 20 mL volumetric pipette and cooled at −80 °C for more than 30 min. The comonomer and *t*-BuCl were added as a solution in DCM to the above reaction mixture for pre-cooling. The copolymerization was initiated by adding the solution of $FeCl_3$ and *i*-PrOH in DCM and quenched by pre-cooled ethanol at specified time. The copolymer was washed with ethanol and *n*-Hex for several times and dried at 40 °C under high vacuum until a constant weight. The conversion was determined gravimetrically.

General Procedure for the Hydrolysis Reaction of P(IB-*co*-ACS) and P(IB-*co*-TBO)

The hydrolysis of P(IB-*co*-ACS) was carried out in stirred THF by treatment with CH_3ONa under stirring at various temperatures for different time according to the references.[35,36] In a representative hydrolysis process, 0.3 g of P(IB-*co*-ACS) containing about 0.03 mmol of acetyl groups was dissolved in 30 mL of THF in a flask equipped with a condenser, and 0.16 g of CH_3ONa was added in the above reaction system. The reaction was allowed to proceed at 60 °C under nitrogen for different time.

For the hydrolysis of P(IB-*co*-TBO), the typical sample was dissolved in stirred THF and *n*-Hex mixed solvent (6:4, *V*:*V*) under the nitrogen atmosphere at 60 °C using 1 mL of sulfuric acid over the *tert*-butoxy groups for 24 h according to the references.[37−39] The hydrolysis solutions were precipitated and washed with deionized water for three times until the pH was neutral, then dried in a vacuum oven until a constant weight.

Characterizations

Gel permeation chromatography (GPC)

Number-average molecular weight (M_n) and molecular weight distribution (MWD, M_w/M_n) of copolymers were determined by GPC using a Waters 1515 isocratic HPLC pump connected to 4 Waters Styragel HT2, HT3, HT4, and HT6 columns, a Waters 2414 refractive index detector, and a Waters 2489 ultraviolet visible light detector at 30 °C. The copolymers (10 mg) of P(IB-*co*-ACS) or P(IB-*co*-TBO) were dissolved in 5 mL of THF, which also served as the mobile phase at a flow rate of 1.0 $mL\cdot min^{-1}$. The column was calibrated against the standard polystyrene samples.

Proton nuclear magnetic resonance spectroscopy (^{1}H-NMR)

^{1}H-NMR (400 MHz) spectra of the isobutylene-based copolymers were recorded on a Bruker 400 MHz spectrometer using 5 mm o.d. tubes with samples (12 mg) of P(IB-*co*-ACS), P(IB-*co*-TBO), or P(IB-*co*-POH) in 0.5 mL of deuterated chloroform ($CDCl_3$) containing tetramethylsilane (TMS) as an internal reference at 25 °C. MestReNova was used for interpretation of the ^{1}H-NMR spectra. The chemical shifts are given in ppm. The incorporation contents of polar comonomer in the isobutylene-based copolymers of P(IB-*co*-ACS) and P(IB-*co*-TBO), expressed as C_{ACS} and C_{TBO}, were

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calculated according to Eqs. (1) and (2):

$$C_{\mathrm{ACS}} = \frac{\frac{A_{2.27}}{3}}{\frac{A_{2.27}}{3}+\frac{A_{1.41}}{2}} \tag{1}$$

$$C_{\mathrm{TBO}} = \frac{\frac{A_{7.02-7.04}}{2}}{\frac{A_{7.02-7.04}}{2}+\frac{A_{1.41}}{2}} \tag{2}$$

where $A_{2.27}$ corresponds to the integration for $-C\underline{H}_3$ in acetoxy groups and $A_{1.41}$ corresponds to the integration for $-C\underline{H}_2-$ in isobutylene units. $A_{7.02-7.04}$ corresponds to the integration for protons in the phenyl groups in TBO units.

The conversion of polar comonomers, expressed as R_c, was determined according to Eq. (3):

$$R_{\mathrm{c}} = \frac{C \times Y}{F} \tag{3}$$

where C corresponds to the incorporation content of polar comonomer in the copolymers, Y corresponds to the yield of copolymer, and F corresponds to the molar ratio of polar comonomers in feed.

Fourier transform infrared spectrometry (FTIR)

The samples (12 mg) of P(IB-*co*-ACS) and their hydrolysis products P(IB-*co*-POH) were dissolved in 1 mL of THF and coated directly on KBr pellets. All the formed polymer films were vacuum-dried and thin enough to be within the absorbance range (800−3600 $\mathrm{cm^{-1}}$) where the Beer-Lambert law is obeyed. All infrared spectra were collected at a resolution of 4 $\mathrm{cm^{-1}}$ on a Nicolet 6700 FTIR spectrometer at 25 °C.

Attenuated total reflection Fourier transform infrared spectrometry (ATR-FTIR) data were treated by Nicolet OMNIC Series software during reagent addition and subsequent copolymerization of IB with ACS on the Nicolet 6700 FTIR spectrometer equipped with an Axiom DMD-270X-LT diamond-composite insertion probe. The ATR-FTIR data were comprised of spectra collected from four scans, over the spectral ranges of 600−1800 $\mathrm{cm^{-1}}$, with 4 $\mathrm{cm^{-1}}$ solution.

Water contact angle (WCA)

WCA measurements were carried out using the sessile drop method on a goniometer (JC2000D2M, China) equipped with image analysis software at 25 °C. The obtained copolymers of P(IB-*co*-ACS), P(IB-*co*-TBO), and P(IB-*co*-POH) were dissolved in *n*-Hex with concentration of 10 $\mathrm{g\cdot L^{-1}}$. The copolymer solution was dropped on a glass slide to form a smooth film and then the film was dried in vacuum at room temperature for 24 h. A drop of water was placed on the surface of the totally smooth horizontal film. The values at 5 different positions on the entire surface of the film were recorded for each sample and the average of the water contact angle was obtained to ensure the reproducibility.

Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS)

The samples of P(IB-*co*-POH) were dissolved in THF to form polymer solution with concentration of 5 $\mathrm{g\cdot L^{-1}}$ and coated directly on wafer. The element composition and distribution on film surface were detected on SEM (JEOL-7600 OXFORD) and EDS operating at 15 kV after sputtering the samples with a layer of gold.

Dynamic thermomechanical analysis (DMA)

Viscoelasticity of the P(IB-*co*-POH) copolymer thick sheet having a size of 1 cm × 1 cm was measured under an air atmosphere at 20 °C. The fixed strain was 0.01% of the initial state and the frequency range was set from 0.01 Hz to 100 Hz.

Phase contrast microscopy (PCM)

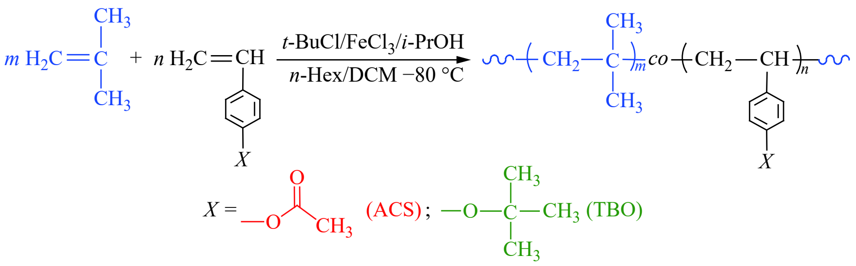
Typically, 5 mg of silica NPs was added to the P(IB-*co*-POH) copolymer solution containing 10 mg of polymer in 5 mL of *n*-Hex. The suspension was stirred for 20 min and dropped on a glass slide. Dispersion of silica nanoparticles in the P(IB-*co*-POH) copolymer solution was observed at room temperature. In order to characterize the self-healing property of the P(IB-*co*-POH) materials, P(IB-*co*-POH) solution was dropped on a glass slide and dried in vacuum at room temperature for 24 h. Then, a cross scratch was drawn on the film surface by a knife. The sample was placed at room temperature and the self-healing process of the cross scratch was observed on-line through Olympus U-OPA JAPAN BX51.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Functionalized Isobutylene-based Copolymers of P(IB-*co*-ACS) and P(IB-*co*-TBO)

The cationic copolymerizations of isobutylene with ACS or TBO were carried out using *t*-BuCl/$\mathrm{FeCl_3}$/*i*PrOH as an initiating system to synthesize the random copolymers of P(IB-*co*-ACS) and P(IB-*co*-TBO). Scheme 1 shows the synthetic route to these two kinds of functionalized copolymers. The experimental conditions for the copolymerization and data of the resulting copolymers are summarized in Table 1. GPC traces of the resulting copolymers with RI/UV dual detectors are shown in Fig. 1. All the P(IB-*co*-ACS) and P(IB-*co*-TBO) copolymers exhibit unimodal molecular weight distributions with polydispersity of 1.47−1.81. The RI detector is responsible for all structural units, while UV detector is only sensitive to carbonyl moiety (280 nm) or phenyl group (254 nm) in the copolymer chains. The GPC trace of P(IB-*co*-ACS) detected by RI coincides with that by UV at 280 nm, indicating that ACS chemical units were incorporated into the P(IB-*co*-ACS) copolymer chains. Similarly, the TBO chemical units are confirmed to be incorporated into the P(IB-*co*-TBO) copolymer chains due to the match of the GPC traces detected by RI and UV at 254 nm dual detectors. It can also be seen from the GPC traces by RI/UV dual detectors that the composition distributions of ACS and TBO moieties are individually uniform along P(IB-*co*-ACS) and P(IB-*co*-TBO) copolymer chains. The above GPC profiles indicate the successful synthesis of P(IB-*co*-ACS) and P(IB-*co*-TBO) copolymers. The number-average molecular weight (M_n) could reach around 25 $\mathrm{kg\cdot mol^{-1}}$ when the content of ACS in monomer feed was 1.5 mol%. The molecular weight distribution became slightly narrower with increasing comonomer content in monomer feed.

It can be observed from Table 1 that the copolymer yields could reach *ca*. 90% when ACS in feed ≤ 1.0% ([$\mathrm{FeCl_3}$] =



Scheme 1 Synthesis of P(IB-*co*-ACS) and P(IB-*co*-TBO) copolymers *via* cationic copolymerization of isobutylene with polar styrene derivates

Table 1 Cationic copolymerization of IB with polar comonomers with *t*-BuCl/FeCl3/*i*PrOH initiating system [a]

Entry	Description	Comonomer	Comonomer in feed (F) (mol%)	Copolymer yield (Y) (%)	M_n [d] (kg·mol^{-1})	M_w/M_n	Incorporation of copolymer (C) [e] (mol%)	Conversion of comonomer (R_c) [f] (%)
1 [b]	P(IB-*co*-ACS-23k-1.6-030)	ACS	0.5	90.9	22.9	1.63	0.41	74.5
2 [b]	P(IB-*co*-ACS-24k-1.8-066)	ACS	1.0	89.4	23.6	1.78	0.66	59.0
3 [b]	P(IB-*co*-ACS-26k-1.5-039)	ACS	1.5	59.0	25.8	1.47	0.39	15.3
4 [b]	P(IB-*co*-ACS-8k-1.4-028)	ACS	2.0	22.5	8.0	1.49	0.28	3.2
5 [c]	P(IB-*co*-TBO-15k-1.8-079)	TBO	1.0	94.2	14.6	1.81	0.79	74.4
6 [c]	P(IB-*co*-TBO-20k-2.0-042)	TBO	2.0	86.7	19.7	1.80	0.42	18.2
7 [c]	P(IB-*co*-TBO-16k-1.7-054)	TBO	3.0	83.0	15.6	1.74	0.54	14.9
8 [c]	P(IB-*co*-TBO-13k-1.5-038)	TBO	5.0	21.1	12.6	1.48	0.38	1.6

[a] Conditions: [IB] = 1 mol·L^{-1}, *n*-Hex/DCM = 60:40 (V:V), −80 °C, [*t*-BuCl] = 5.6 mmol·L^{-1}, [*i*-PrOH]/[FeCl3] = 1; [b] [FeCl3] = 0.066 mol·L^{-1}; [c] [FeCl3] = 0.088 mol·L^{-1}; [d] M_n determined by GPC; [e] Incorporation of ACS or TBO determined by ^{1}H-NMR; [f] Conversion of comonomers calculated by Eq. (3)

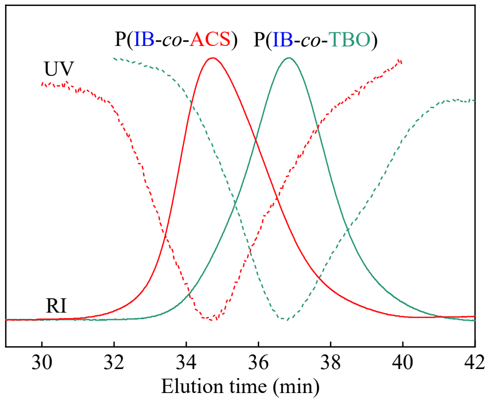


Fig. 1 Representative GPC traces of (a) P(IB-*co*-ACS) (M_n = 25.8 kg·mol^{-1}; M_w/M_n = 1.47; ACS = 0.39 mol%) and (b) P(IB-*co*-TBO) (M_n = 12.6 kg·mol^{-1}; M_w/M_n = 1.48; TBO = 0.38 mol%) by RI/UV dual detectors

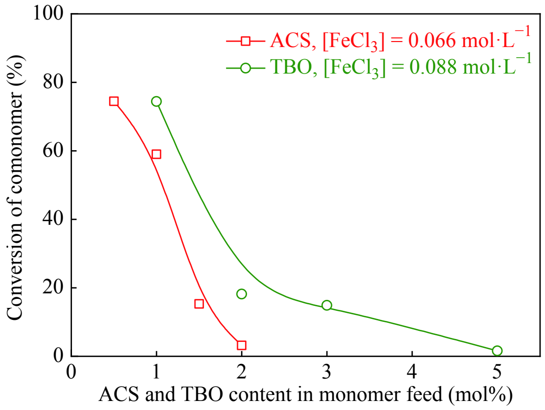


Fig. 2 Effect of ACS and TBO content in monomer feed on conversion of comonomer

0.066 mol·L^{-1}) or more than 83% when TBO ≤ 3.0% ([FeCl$_3$] = 0.088 mol·L^{-1}). The effect of ACS or TBO content in monomer feed on the conversion of comonomers in the cationic copolymerizations of IB with ACS or TBO is shown in Fig. 2. It can be found that the conversion of ACS reached 74.5% when its content in monomer feed was set at 0.5 mol% and the conversion of TBO reached 74.4% when its content in monomer feed was set at 1.0 mol%. The conversion of comonomers (ACS or TBO) decreased gradually with increasing their contents in monomer feeds.

The representative ^{1}H-NMR spectrum of P(IB-*co*-ACS) is shown in Fig. 3(A). It reveals that the P(IB-*co*-ACS) copolymer was successfully synthesized due to the appearance of characteristic resonance at δ_c = 2.27 ppm for —CH$_3$ of acetoxy side groups. The copolymer composition of the polar monomers was determined on the basis of ^{1}H-NMR characterization according to Eqs. (1) and (2). Similarly, the successful synthesis of P(IB-*co*-TBO) was also confirmed by

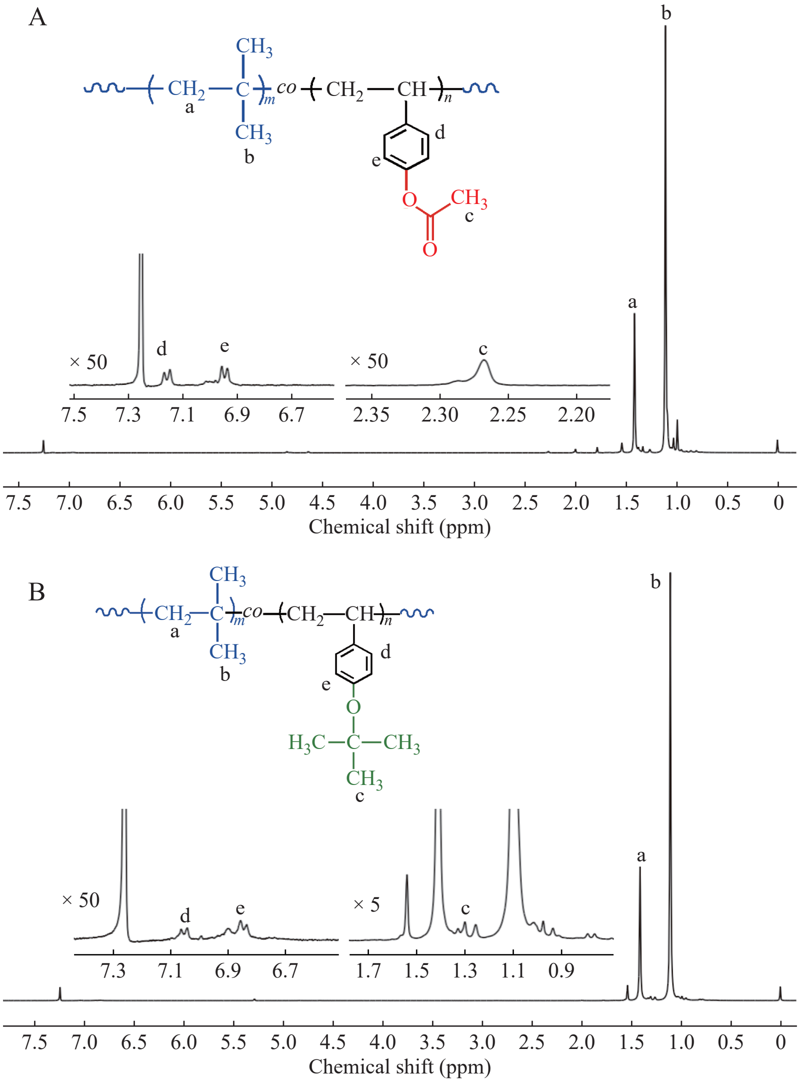


Fig. 3 Representative ^{1}H-NMR spectra of (A) P(IB-*co*-ACS) (M_n = 8.0 kg·mol^{-1}; M_w/M_n = 1.49; ACS = 0.28 mol%) and (B) P(IB-*co*-TBO) (M_n = 14.6 kg·mol^{-1}; M_w/M_n = 1.81; TBO = 0.79 mol%)

^{1}H-NMR characterization shown in Fig. 3(B) for the appearance of characteristic signal at δ_c = 1.31 ppm belonging to $-CH_3$ of *tert*-butoxy side groups.

The kinetic investigation on copolymerization of IB and ACS was compared with IB polymerization under the same polymerization conditions by *in situ* ATR-FTIR. The waterfall plots based on the characteristic absorption at 887 cm^{-1} for IB in the polymerization process is given in Fig. 4(a). It can be observed that IB was consumed in propagation to form the corresponding polymer since the intensity of characteristic band for the $=CH_2$ wag of IB at 887 cm^{-1} gradually weakened during the polymerization process. The apparent propagation rate constant (k_p^A) of IB polymerization could be determined from the slope of linearity between ln([M]$_0$/[M]) and time through the origin. It can be observed from Fig. 4(b) that k_p^A (0.00304 s^{-1}) of polymerization of IB was larger than that (0.00122 s^{-1}) of the copolymerization of IB with ACS at −80 °C; the rate of copolymerization was lower due to the existence of polar moieties containing oxygen atoms in the comonomers.

Synthesis and Characterization of P(IB-*co*-POH) Incorporated with Vinyl Phenol Structural Units *via* Hydrolysis of P(IB-*co*-ACS) and P(IB-*co*-TBO)

The novel functionalized copolymers of isobutylene with *p*-hydroxyl substituted styrene or vinyl phenol, P(IB-*co*-POH), with phenolic hydroxyl side groups along copolymer chains were further synthesized through the hydrolysis reaction of P(IB-*co*-ACS) or P(IB-*co*-TBO) copolymers. The detailed synthetic routes of P(IB-*co*-POH) from P(IB-*co*-ACS) or P(IB-*co*-TBO) copolymers are shown in Scheme 2. The hydrolysis of P(IB-*co*-ACS) was carried out in THF by using CH_3ONa as a catalyst at 60 °C for different time. The complete hydrolysis of acetoxy groups could be achieved under the base-catalyzed conditions which is similar to the results in references.[35,36] The FTIR spectra of P(IB-*co*-ACS) and its hydrolysed products, P(IB-*co*-ACS-*co*-POH) obtained for 6 h and P(IB-*co*-POH) obtained for 12 h are shown in Fig. 5. After the hydrolysis reaction for 12 h, the acetyl groups could be completely removed from acetoxy side groups, which led to the formation of phenolic hydroxyl side groups.

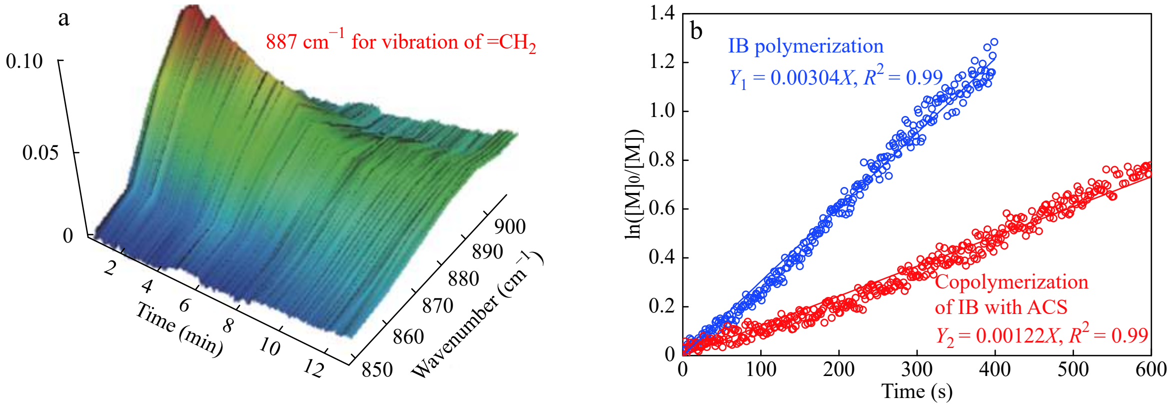
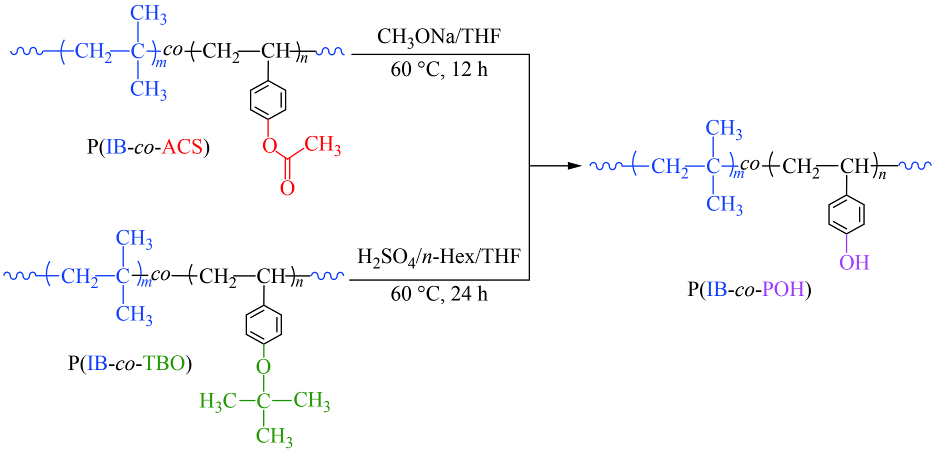


Fig. 4 (a) *In situ* FTIR waterfall plots for the $=CH_2$ wag at 887 cm^{-1} for IB polymerization; (b) Kinetic plots for IB polymerization and copolymerization of IB with ACS. Conditions: [IB] = 1 $mol\cdot L^{-1}$, [*t*-BuCl] = 14 $mmol\cdot L^{-1}$, [$FeCl_3$] = 0.060 $mol\cdot L^{-1}$, [*i*-PrOH] = 0.072 $mol\cdot L^{-1}$, *n*-Hex/DCM = 60:40 (*V*:*V*), −80 °C.



Scheme 2 Synthesis of P(IB-*co*-POH) from P(IB-*co*-ACS) and P(IB-*co*-TBO) by hydrolysis

It can be seen from the FTIR spectra in Fig. 5 that the obvious stretching vibration band of carbonyl at 1769 cm^{-1} could no longer be seen after the reaction. The chemical structure of P(IB-*co*-POH) derived from P(IB-*co*-ACS) can be further confirmed by ^{1}H-NMR (Fig. 6a). The resonance of methyl in the acetoxy groups in P(IB-*co*-ACS) at δ_c = 2.27 ppm disappeared after the hydrolysis process and the degree of hydrolysis reached nearly 100% according to ^{1}H-NMR characterization. Based on the above observation, the complete hydrolysis of P(IB-*co*-ACS) could be achieved using excess CH_3ONa as a catalyst in THF and the corresponding functionalized P(IB-*co*-POH) random copolymer could be successfully prepared.

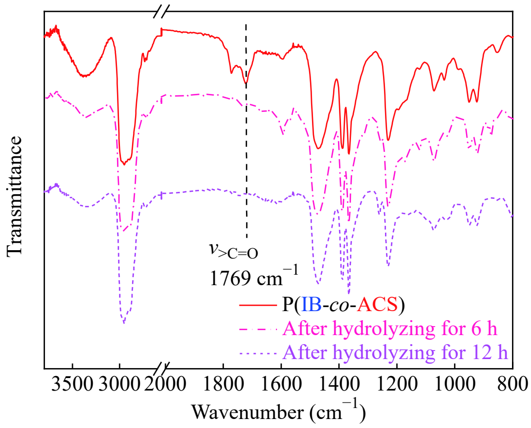


Fig. 5 FTIR spectra of P(IB-*co*-ACS) (M_n = 23.6 $kg\cdot mol^{-1}$; M_w/M_n = 1.78; ACS = 0.66 mol%) and its hydrolysized product P(IB-*co*-ACS-*co*-POH) for 6 h and P(IB-*co*-POH) for 12 h

Likewise, the *tert*-butoxy groups can be easily converted into hydroxy through the acidic hydrolysis reaction. The mixed solvent of THF and *n*-Hex (6:4, *V*:*V*) was used in the hydrolysis of P(IB-*co*-TBO) in the presence of sulfuric acid. Complete hydrolysis of P(IB-*co*-TBO) could be achieved to obtain P(IB-*co*-POH) at 60 °C for 24 h. The chemical structure of P(IB-*co*-POH) hydrolyzed from P(IB-*co*-TBO) was also confirmed by ^{1}H-NMR characterization (Fig. 6b). The resonance at δ_c = 1.31 ppm for the three identical methyl groups in the *tert*-butoxy group disappeared after hydrolysis reaction. Similarly, all the *tert*-butoxy groups in the side groups could be completely removed by the acid-catalyzed hydrolysis to produce the desired P(IB-*co*-POH) copolymers.

In order to further verify the successful synthesis of the copolymers of isobutylene with vinyl phenol having various copolymer molecular weights and compositions, the functionalized P(IB-*co*-POH) copolymer solution in *n*-Hex was

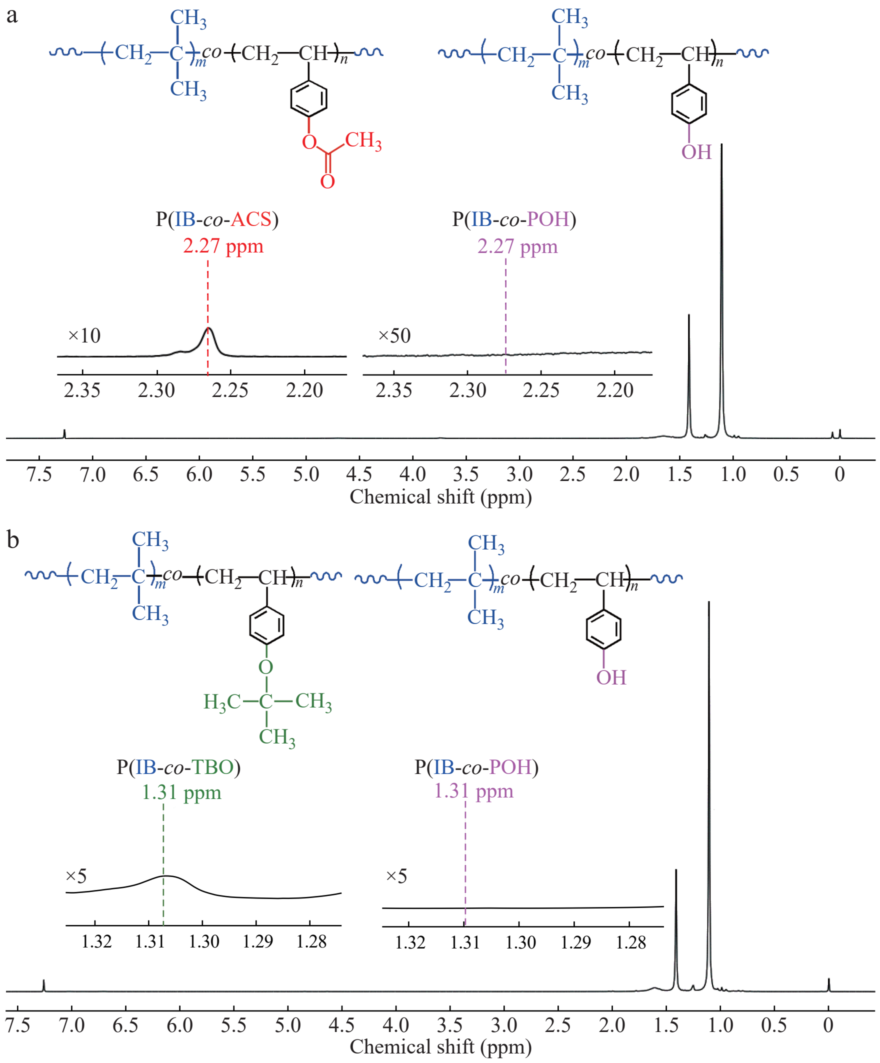


Fig. 6 ^{1}H-NMR spectra of (a) P(IB-*co*-POH) from P(IB-*co*-ACS) (M_n = 25.8 kg·mol^{-1}; M_w/M_n = 1.47; ACS = 0.39 mol%) and (b) P(IB-*co*-POH) from P(IB-*co*-TBO) (M_n = 14.6 kg·mol^{-1}; M_w/M_n = 1.81; TBO = 0.79 mol%)

mixed with silica nanoparticles. P(IB-*co*-POH) copolymer (10 mg) was dissolved in 5 mL of *n*-Hex and 5 mg of nanosilica (*ca*. 20 nm) was added under stirring. The mixed suspension of nanosilica in the P(IB-*co*-POH) copolymer solution was droped on a glass slide to check the dispersion status of nanosilica particles in the P(IB-*co*-POH) copolymer solution by PCM. The photos of suspension and PCM images of the different suspension samples are shown in Fig. 7. The inorganic silica nanoparticles normally precipitate from *n*-Hex solvent or from the PIB solution in *n*-Hex. Importantly, the silica nanoparticles (*ca*. 20 nm) agglomerated to form silica particles with diameter less than 800 nm, which could be homogeneously suspended in the P(IB-*co*-POH) copolymer solution. The schematic diagram of the suspension system is shown in Scheme 3. This dispersion of silica nanoparticles in P(IB-*co*-POH) copolymer solution is different from the serious precipitation of inorganic silica nanoparticles in PIB solution since phenolic hydroxyl side groups in P(IB-*co*-POH) copolymer chains interact with hydroxyl groups on the surface of the nanosilica particles.

Hydrophobicity/hydrophilicity Transition on the Surfaces of P(IB-*co*-POH) Copolymer Films

All the PIB samples, P(IB-*co*-ACS) with a small amount of acetoxy side groups, P(IB-*co*-TBO) copolymers with a small amount of *tert*-butoxy side groups, and P(IB-*co*-POH) having a small amount of phenolic hydroxyl side groups, are hydrophobic polymeric materials with WCA of around 110°, since the functional groups were covered by a large number of hydrophobic PIB segments. The water contact angles on the surfaces of PIB and the hydrolyzed products were characterized for comparison, as shown in Fig. 8 (original series). In order to induce the hydroxyl side groups of P(IB-*co*-POH) copolymer to move outside to the film surfaces *via* interaction and self-assembly, the copolymer films coated on glass surfaces were inserted into hot water (50 °C) for 5 h under stirring. Interestingly, the water contact angles on the film surfaces of P(IB-*co*-POH) copolymers with various contents of the vinyl phenol structural units remarkably decreased from *ca*. 110° to *ca*. 80° afterwards, as shown in Fig. 8. As comparison, the water contact angle of PIB almost

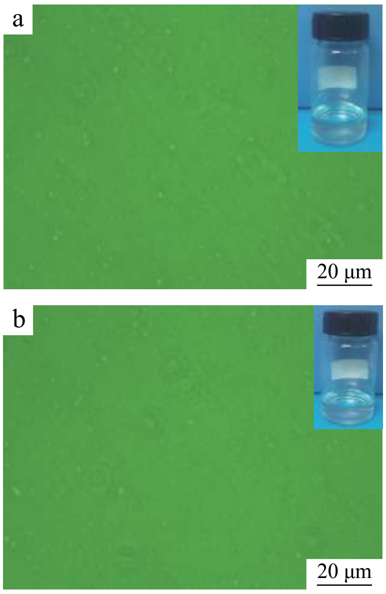
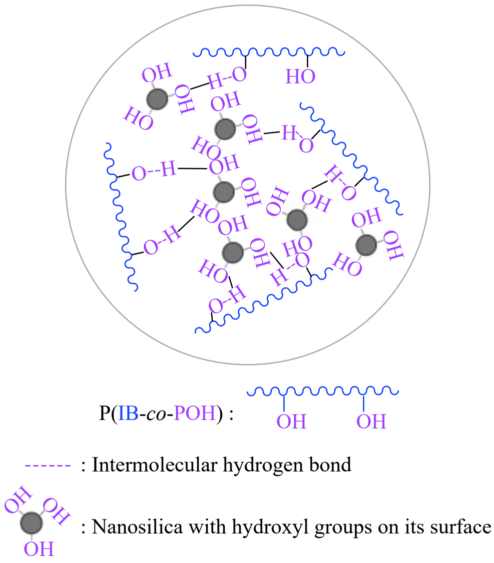


Fig. 7 PCM images of (a) P(IB-*co*-POH) from P(IB-*co*-ACS) (M_n = 23.6 kg·mol^{-1}; M_w/M_n = 1.78; ACS = 0.66 mol%) and (b) P(IB-*co*-POH) from P(IB-*co*-TBO) (M_n = 14.6 kg·mol^{-1}; M_w/M_n = 1.81; TBO = 0.79 mol%) with silica nanoparticles



Scheme 3 Illustration of the uniform dispersion of nanosilica particles in P(IB-*co*-POH) copolymer solution

kept unchanged after the same treating process and under the same conditions.

In order to further verify that hydrophilic chemical units containing phenolic hydroxyl side groups moved to the surface of copolymer film, the surface of P(IB-*co*-POH) copolymer films was characterized by SEM and EDS. The SEM and EDS images are shown in Fig. 9. It can be observed that the oxygen element from vinyl phenol structural units was homogeneously distributed on the surface of the original P(IB-*co*-POH) copolymer with its content determined to be 1.1%. Interestingly, the oxygen element from vinyl phenol structural units was homogeneously distributed on the surface of P(IB-*co*-POH) copolymer after treated in hot water and the content of oxygen element was determined to be 3.4%. Comparatively, the oxygen content on the film surface was greatly increased by the induction treatment in hot water, indicating that hydrophilic units containing phenolic hydroxyl groups could move to the surface of the P(IB-*co*-POH) copolymer films. The possible mechanism that the phenolic hydroxyl side groups moved and self-assembled onto the surfaces of P(IB-*co*-POH) copolymer films is also given in Fig. 9.

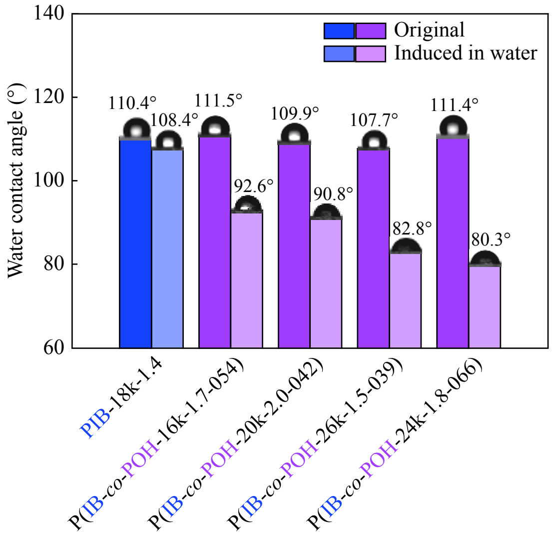


Fig. 8 Water contact angles of PIB and P(IB-*co*-POH) copolymers before and after induction in hot water (50 °C) for 5 h

Self-healing Property of P(IB-*co*-POH)

The polymer solutions of PIB and P(IB-*co*-POH) were separately dropped on the glass slides and dried in vacuum for 24 h. A cross scratch was drawn on the surface of polymer film with a knife. As shown in Fig. 10, the edge of crack in PIB (M_n = 18.0 kg·mol^{-1}; M_w/M_n = 1.39) film hardly self-healed at 25 °C even after 120 min. Very interestingly, the crack on the surface of P(IB-*co*-POH) from P(IB-*co*-ACS) (M_n = 24.8 kg·mol^{-1}; M_w/M_n = 1.88; ACS = 0.13 mol%) partially self-healed after 20 min and then completely self-healed after another 40 min. The similar self-healing phenomenon at room temperature was also observed on the film surface of P(IB-*co*-POH) from P(IB-*co*-TBO) (M_n = 19.7 kg·mol^{-1}; M_w/M_n = 1.80; TBO = 0.42 mol%). It can be seen from Fig. 10 that the rate of self-healing became higher with increasing the incorporation content of vinyl phenol chemical units along PIB chains. Intermolecular hydrogen bonding could be formed in P(IB-*co*-POH) due to the presence of phenolic hydroxyl side groups in the macromolecular chains. After the film surface was cut in the macroscopic state, hydrogen bonding supramolecular networks in P(IB-*co*-POH) copolymers would accelerate the self-healing process of the polymer materials.

In order to confirm the formation of hydrogen bonding supramolecular network in the P(IB-*co*-POH) copolymers, frequency sweep measurements were performed on the above P(IB-*co*-POH) copolymers by DMA at 25 °C. The obvious crossover of G' and G'' is displayed in Fig. 11. The approx-

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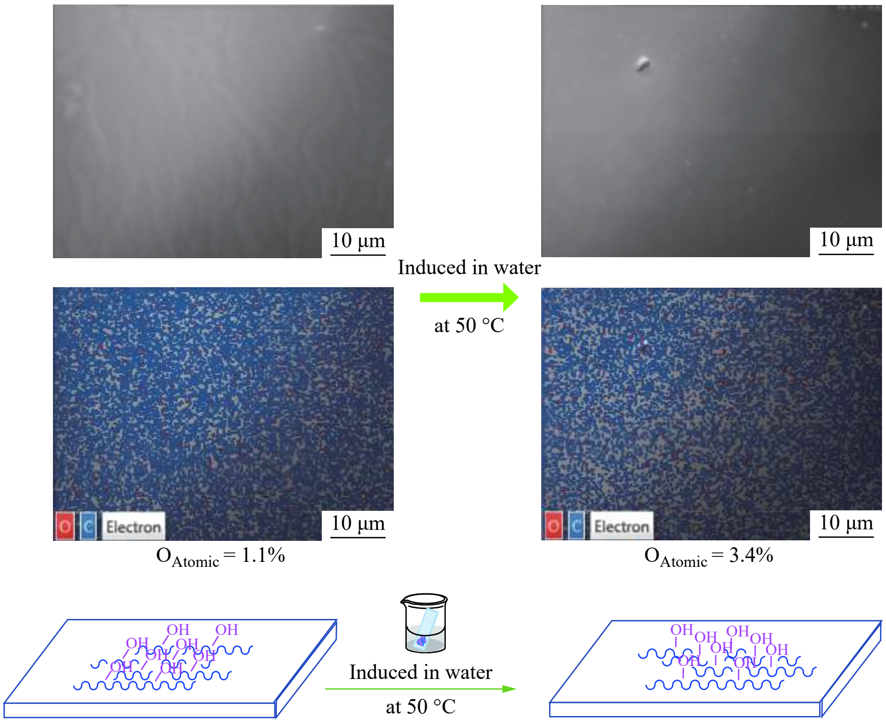

Fig. 9 Top, SEM images; Bottom, surface element of oxygen composition and distribution of P(IB-*co*-POH) from P(IB-*co*-ACS) (M_n = 23.6 kg·mol^{-1}; M_w/M_n = 1.78; ACS = 0.66 mol%) before and after induction in 50 °C water for 5 h

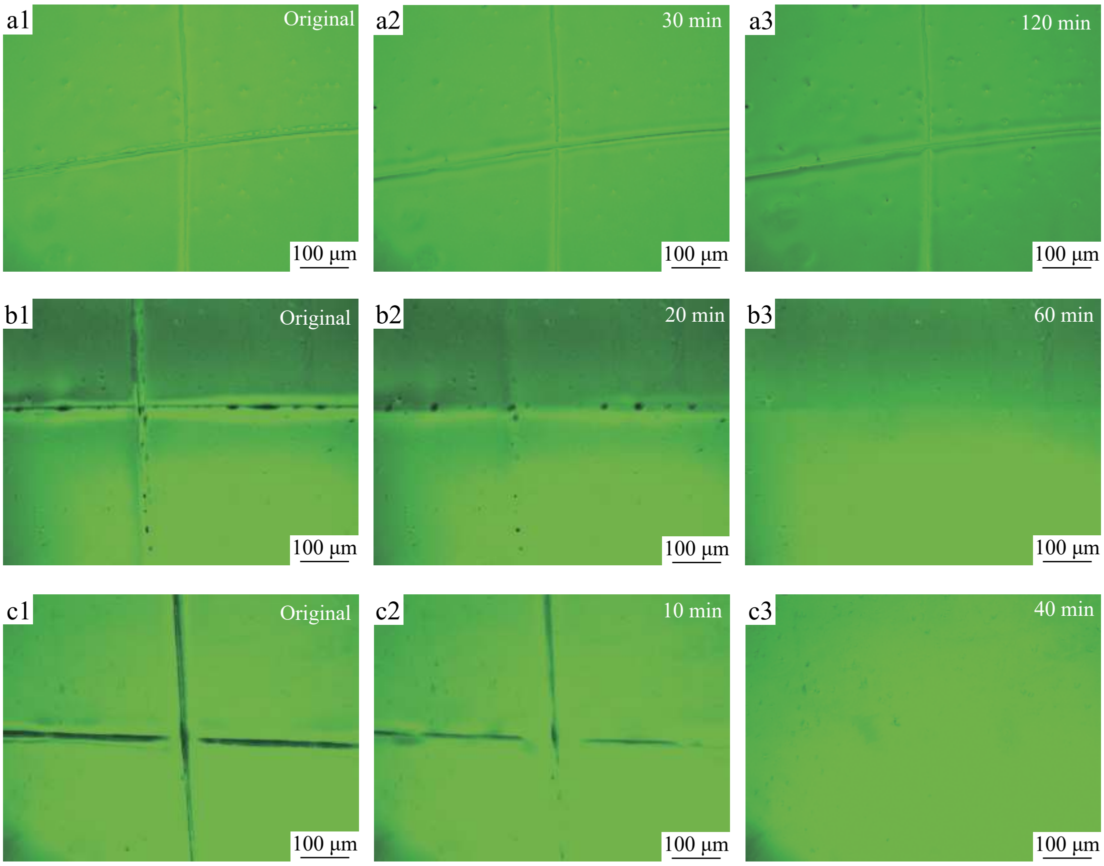

Fig. 10 Self-healing process of (a1−a3) PIB (M_n = 18.0 kg·mol^{-1}; M_w/M_n = 1.39), (b1−b3) P(IB-*co*-POH) from P(IB-*co*-ACS) (M_n = 24.8 kg·mol^{-1}; M_w/M_n = 1.88; ACS = 0.13 mol%), and (c1−c3) P(IB-*co*-POH) from P(IB-*co*-TBO) (M_n = 19.7 kg·mol^{-1}; M_w/M_n = 1.80; TBO = 0.42 mol%) at 25 °C

imate lifetime around 4.2 or 2.9 s was calculated *via* the crossover time, which is dependent on the dissociation of hydrogen-bonded clusters according to the theory of supramolecular aggregation by Kramer and Hawker.[40] This bond lifetime lies in the intermediate range (0.001–60 s), well situated in the known time range observed for supramolecular materials that display responsiveness and self-healing under certain conditions.[41] It means that the formation of hydrogen bonding supramolecular network in the P(IB-*co*-POH) copolymers could explain the self-healing behavior of the copolymer materials.

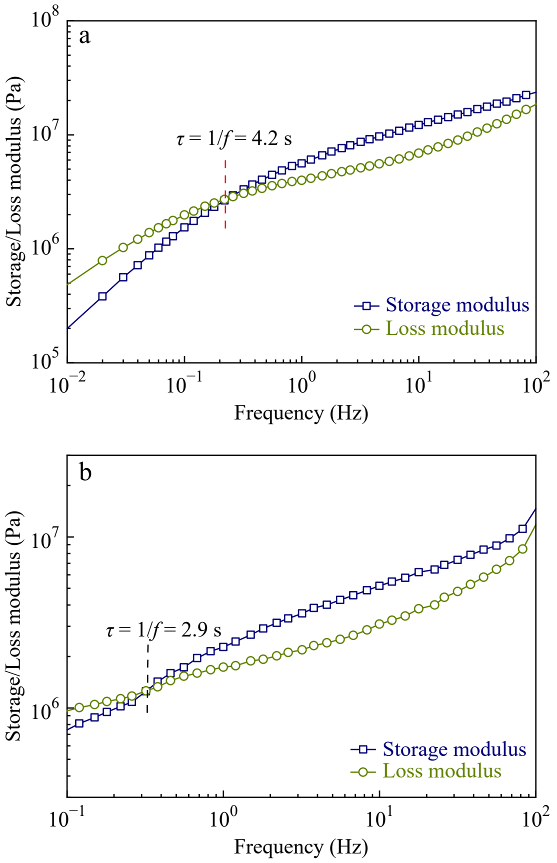

Fig. 11 Frequency sweep measurement of (a) P(IB-*co*-POH) from P(IB-*co*-ACS) (M_n = 24.8 kg·mol^{-1}; M_w/M_n = 1.88; ACS = 0.13 mol%) and (b) P(IB-*co*-POH) from P(IB-*co*-TBO) (M_n = 19.7 kg·mol^{-1}; M_w/M_n = 1.80; TBO = 0.42 mol%) at 25 °C

CONCLUSIONS

The isobutylene-based random copolymers of P(IB-*co*-ACS) with a small amount of acetoxy side groups and P(IB-*co*-TBO) with a small amount of *tert*-butoxy side groups were successfully synthesized *via* direct cationic copolymerization using *t*-BuCl/$FeCl_3$/*i*PrOH as an initiating system. The copolymer yields could reach *ca*. 90% when ACS in feed ≤ 1.0% or more than 83% when TBO ≤ 3.0%. The conversion of comonomer reached around 74% when its content in monomer feed was 0.5 mol% for ACS and 1.0 mol% for TBO. The conversion of comonomer decreased gradually with increasing its content in monomer feed and the monomer reactivity of TBO was higher than that of ACS. Kinetic investigation on the cationic copolymerization process of IB with ACS by *in situ* FTIR indicates that copolymerization was slow down in the presence of a small amount of ACS. Furthermore, P(IB-*co*-POH) with phenolic hydroxyl groups was obtained through the highly effective hydrolysis of acetoxy and *tert*-butoxy moieties under acidic or basic conditions. The inorganic silica particles with several —OH groups on their surfaces and diameter less than 800 nm could be homogeneously suspended in the P(IB-*co*-POH) copolymer solution and no precipitation of inorganic silica particles occurred in the system.

The water contact angles on the film surfaces of P(IB-*co*-POH) copolymers with various contents of vinyl phenol structural units decreased from *ca*. 110° to *ca*. 80° for the shift of —OH side groups to the film surface and self-assembly after inserting the copolymer films in hot water (50 °C) for 5 h. The P(IB-*co*-POH) copolymers exhibited an excellent self-healing property at room temperature, which is attributed to the formation of hydrogen bonding supramolecular network in the copolymers.

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