

Hydroxyl-terminated Polyethylenes Bearing Functional Side Groups: Facile Synthesis and Their Properties

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Electronic Supplementary Information

Abstract A series of hydroxyl-terminated polyethylenes (HTPE) bearing various functional side groups (e.g. carboxyl, ester and butane groups) were synthesized by the combination of ring-opening metathesis polymerization (ROMP) and visible light photocatalytic thiol-ene reaction. The products are named as α,ω -dihydroxyl-poly[(propionyloxythio)methinetrimethylene] (HTPE_{carboxyl}), α,ω -dihydroxyl-poly[(methylpropionatethio)methinetrimethylene] (HTPE_{ester}) and α,ω -dihydroxyl-poly[(butylthio)methinetrimethylene] (HTPE_{butane}), respectively. The investigation of ROMP indicated that the molecular weight of resultant hydroxyl-terminated polybutadiene (HTPB) can be tailored by varying the feed ratios of monomer to chain transfer agent (CTA). The exploration of the photocatalytic thiol-ene reaction between HTPB precursor and methyl 3-mercaptopropionate revealed that blue light as well as oxygen accelerated the reaction. ¹H-NMR and ¹³C-NMR results verified all the double bonds in HTPB can be modified, and the main chain of resultant polymer can be considered as polyethylene. Subsequently, relationship between the structure of side groups and the thermal properties of functional PEs was studied. And the results suggested that the T_g was in the order of HTPE_{butane} < HTPE_{ester} < HTPE_{carboxyl}. Greater interaction between side groups resulted in higher T_g . Moreover, all the functional PE samples exhibited poor thermostability as compared to HTPB. Finally, the promising applications for functional PEs were explored. HTPE_{carboxyl} can be utilized as a smart material with pH-responsive properties due to its pH-dependent ionization of carboxyl side groups. HTPE_{butane} can be employed as a macro-initiator for building the triblock copolymer due to the presence of active hydroxyl end groups. HTPE_{ester} can serve as a plasticizer for PVC which can enhance the ductility of PVC without obviously sacrificing strength.

Keywords Polyethylene; Ring-opening metathesis polymerization; Thiol-ene reaction; Polybutadiene; Structure-property relationships

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INTRODUCTION

Polyethylene (PE), as one of the most common polymeric materials, has been widespread used in our daily life and industrial fields, such as packaging, bags, bottles, pipes, etc.^[1–4] This wide range of applications results from its outstanding properties, for instance high tolerance to harsh environment and superb mechanical and processing properties.^[5–7] However, although the mechanical properties of PE can be varied by tuning the molecular weight and branching degree, its inherent drawbacks such as poor polarity and lack of functional groups are still unchanged fundamentally, which severely restrict the development and application of PE products.^[8–10] Hence,

synthesis of PE analogous products bearing functional groups and further study of their promising applications are of great significance in both academia and industry.

During the past decades, several strategies have been proposed to endow PE with functional groups. One of the strategies is copolymerization of ethylene with functional monomers.^[11] This strategy faces two challenges. Firstly, the reactivity of ethylene and functional monomers are significantly different, leading to the requirement of harsh copolymerization conditions. Also, functional monomer content in the resultant copolymers is relatively low.^[12] Secondly, polar functional monomers usually give rise to catalyst poisoning, and thus specific catalyst with high tolerance needs to be developed.^[13,14] Homopolymerization of functionalized cyclooctene monomer *via* ring opening metathesis polymerization (ROMP) followed by hydrogenation is another strategy for obtaining PE bearing functional groups.^[15,16] However, in this strategy, the type of functional group is limited as the specif-

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ic cyclooctene monomers containing functional groups are usually difficult to obtain. Otherwise, multi-step reactions are generally required in this strategy.^[17] Post-functionalization offers another pathway for incorporating functional side groups into PE backbone. However, as PE is chemically inert, harsh conditions are generally required in the direct post-functionalization of PE. For instance, as reported by Beyou and co-workers, the optimal reaction temperature for grafting maleic anhydride onto PE backbone is 230 °C.^[18]

In recent years, post-functionalization of polybutadiene by thiol-ene reaction has been recognized as a facile route for synthesizing PE with functional side groups.^[19] Owing to the high chemical activity of double bonds, when all the unsaturated bonds are modified, the backbone of resultant polymer becomes PE. In general, thermal or UV light are employed to initiate thiol-ene reaction.^[20,21] However, all the above conditions are considered to be harsh and uneconomical. Recently, visible light induced thiol-ene reaction has emerged and received extensive attention due to its inherent advantages such as high efficiency and being environment-friendly.^[22] For instance, Boyer *et al.* reported the post-functionalization of polybutadiene with high 1,2-vinyl units content (85%) by visible light photocatalytic thiol-ene reaction and found that all the double bonds could be modified in a short duration.^[23] It is well known that there are three kinds of isomer units in the structure of polybutadiene, including *cis* 1,4-butadiene, *trans* 1,4-butadiene and 1,2-butadiene units.^[24–26] According to the established fact that double bonds in 1,4-butadiene units are 10 times less reactive than the pendant double bonds in 1,2-vinyl units.^[27,28] Thus, to further test whether visible light photocatalytic thiol-ene reaction can be employed as an effective and versatile platform for the synthesis of functional PE, the post-functionalization of hydroxyl-terminated polybutadiene (HTPB) with high 1,4-butadiene units (89%) has also been investigated.^[29] However, to the best of our knowledge, visible light photocatalytic thiol-ene reaction has not been used for the post-functionalization of HTPB with only 1,4-butadiene units. Additionally, compared to tremendous studies focused on the synthetic routes to functional PE, few research has been performed to reveal the relationships between the structure of functional groups and the properties of resultant functional PEs. Moreover, the potential applications for these functional PEs are still needed to be explored.

Based on the above considerations, herein, a series of PE analogous products simultaneously bearing hydroxyl terminated groups and various functional side groups (e.g., carboxyl, ester and butane groups) were synthesized by combining ROMP with visible light photocatalytic thiol-ene reaction. Firstly, HTPB with only 1,4-butadiene unit was synthesized by ROMP using 1,5-cyclooctadiene as monomer and *cis*-2-butene-1,4-diol as chain transfer agent. Then, ¹H-NMR was employed to track the visible light photocatalytic thiol-ene reaction of HTPB precursor, and the reaction conditions were optimized. After well-defined structural characterization, the relationships between the structure of functional side groups and thermal properties of functional PEs were investigated. Finally, the promising applications of these functional PEs were explored.

EXPERIMENTAL

Materials

1,5-Cyclooctadiene (COD, 99%), *cis*-2-butene-1,4-diol (97%), 3-mercaptopropionic acid (98%), Grubbs 2nd generation catalyst and polyvinyl chloride (PVC, K-value 65–68) were all purchased from Aladdin. Photo catalyst Ru(bpy)₃Cl₂ (98%) and *p*-toluidine (99%) were purchased from Adamas. Methyl 3-mercaptopropionate (>99%), 1-butanethiol (>98%) tetrahydrofuran (THF, 99.5%), ε-caprolactone (>99%), silver trifluoroacetate (AgTFA, 99.9%) and bis(2-ethylhexyl)phthalate (DOP, 99%) were all obtained from Adamas and used as received. *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, 98%) was purchased from TCI. Sn(Oct)₂, alcohol, *N*-methyl-2-pyrrolidone (NMP, 99%), toluene and other organic solvents were all obtained from Sinopharm Chemical Reagent Co., Ltd. Toluene was stored with 3 Å molecular sieves.

Synthesis of Hydroxyl-terminated 1,4-Polybutadiene via ROMP

Hydroxyl-terminated 1,4-polybutadiene (HTPB) was synthesized via ROMP by using COD as the monomer and *cis*-2-butene-1,4-diol as the chain transfer agent (CTA). The polymerization was catalyzed by Grubbs 2nd generation catalyst. A typical polymerization process is briefly described as follows. COD, *cis*-2-butene-1,4-diol, Grubbs 2nd generation catalyst and THF were charged into a Schlenk tube respectively. Then, a standard freeze-vacuum-thaw cycle technique was employed to ensure oxygen free of the mixture. After cycled for three times, the Schlenk tube was sealed. The polymerization was conducted at 40 °C for 2 h. Afterwards, the mixture was precipitated into cold methanol. The supernatant was decanted, and the viscous liquid was dried under vacuum at 40 °C to yield HTPB.

Post-functionalization of HTPB via Blue Light Catalytic Thiol-ene Reaction

Three kinds of PEs simultaneously bearing hydroxyl terminated and functional side groups were obtained by post-functionalization of HTPB. Blue light photocatalytic thiol-ene reaction was employed. Synthesis of ester groups functional HTPB (HTPE_{ester}) is described as an example. HTPB (1.36 g, 0.4 mmol, calculated according to ¹H-NMR) was thoroughly dissolved in 8 mL of NMP. Afterwards, Ru(bpy)₃Cl₂ (7.9 mg, 10.6×10⁻³ mmol), *p*-toluidine (69.6 mg, 0.65 mmol) and methyl 3-mercaptopropionate (15.1 g, 125.7 mmol) were added. The reaction was carried out with irradiation of a blue LED bulb (7 W) at room temperature. During the reaction, fresh air was continuously bubbled into the system. After 2 h of reaction, unreacted methyl 3-mercaptopropionate, NMP and catalyst were isolated by dialyzed (MWCO: 1000 g/mol) against alcohol and distilled water sequentially. After dried under vacuum at 40 °C, HTPE_{ester} was obtained as liquid. For optimizing the synthetic conditions and giving more insight into the reaction process, the reaction was traced by ¹H-NMR spectroscopy. Meanwhile, the reactions were also conducted under N₂ atmosphere with irradiation of blue LED and under air atmosphere with irradiation of natural light.

HTPE_{carboxyl} and HTPE_{butane} were synthesized according the procedure as HTPE_{ester}. The differences are that 3-mercaptopropionic acid and 1-butanethiol were used as the raw materials respectively, and the reaction time was prolonged to 10 h.

Preparation of Triblock Copolymer Using HTPe_{butane} as Macro-initiator

HTPe_{butane} was used as a macro-initiator for synthesis of novel triblock copolymer named polycaprolactone-*b*-polyethylene (bearing butane functional side groups)-*b*-polycaprolactone (PCL-*b*-PE_{butane}-*b*-PCL). HTPe_{butane} (200 mg), ϵ -caprolactone (200 mg) and Sn(Oct)₂ (10 mg) were dissolved thoroughly in 5 mL of anhydrous toluene. The mixture was bubbled with N₂ for 20 min, and then sealed off. The polymerization was conducted at 110 °C for 8 h. After polymerization, toluene was removed by rotary evaporation. The crude product was further dissolved in THF, and purified by dialyzing (MWCO: 1000) against alcohol and distilled water sequentially. After dried under vacuum at 40 °C, PCL-*b*-PE_{butane}-*b*-PCL was obtained as a light yellow waxy solid.

Preparation of the PVC Film by Using HTPe_{ester} as a Plasticizer

Pure PVC and plasticized PVC films were prepared by a solution-casting method according to the literature.^[30] For comparison, PVC film plasticized by the most popular plasticizer DOP was also prepared. Briefly, 3 g of PVC powder was dissolved in 50 mL of THF. After the mixture turn to transparent, 1.2 g of plasticizer was added. The mixture was allowed to be stirred at room temperature for at least 12 h, and then poured into a 9 cm-diameter glass petri dishes. After placed at room temperature for 3 days, petri dishes were moved to a vacuum oven. The residual THF was further volatilized under vacuum at 40 °C for 3 days. Finally, PVC films were obtained and subject to further measurements.

Characterizations

¹H-NMR and ¹³C-NMR spectra were all obtained on a Bruker 600 MHz NMR spectrometer (Bruker Corporation, Germany) with TMS as internal standard. CDCl₃ were used as solvent for all the samples except for HTPe_{carboxyl}, which used DMSO-*d*₆ as solvent due to its poor solubility in CDCl₃. The molecular weight and polydispersity for polymers were all obtained on a PL-GPC50 gel permeation chromatography (GPC, Agilent Corporation, USA). THF was used as eluent with a flow rate of 1 mL/min. All the measurements were carried out at 25 °C. MALDI-TOF mass spectrum of HTPB was obtained on a 5800 MALDI-TOF/TOF (AB SCIEX, USA). THF, DCTB and AgTFA were used as solvent, matrix and cationization agent, respectively. The glass transition temperature (*T*_g) of HTPB was determined on a DSC7020 differential scanning calorimeter (DSC, Hitachi, Japan) equipped with liquid nitrogen refrigeration. *T*_gs of HTPe_{ester}, HTPe_{carboxyl}, HTPe_{butane}, PVC films and PCL-*b*-PE_{butane}-*b*-PCL were determined on a DSC-25 DSC (TA Instruments, USA). In order to remove thermal history, all the samples were first heated to 100 °C and held for 10 min. Then, the temperature was cooled down to -80 °C (-120 °C as for HTPB) and held for another 10 min. The scans were performed at a heating rate of 5 °C/min. The thermostabilities of HTPB, HTPe_{ester}, HTPe_{carboxyl} and HTPe_{butane} were all evaluated by a Discover thermogravimetric analyzer (TGA, TA Instruments, USA). The measurements were performed from 25 °C to 600 °C with a heating rate of 20 °C/min under N₂ atmosphere.

The optical transmittance of HTPe_{carboxyl} aqueous solution with different pH values were determined by a Cary60 UV-Vis

spectroscopy (Agilent Corporation, USA) at an emission wavelength of 750 nm. The hydrodynamic diameter, diameter distribution and zeta potentials of the assemblies formed by HTPe_{carboxyl} at different pH values were measured by a NS90 dynamic light scattering (DLS, Malvern, UK). Before the scans, each sample was stabilized at 25 °C for 3 min. The morphology of assemblies formed by HTPe_{carboxyl} at pH=3.5 was observed by a Tecnai G2 F20 transmission electron microscope (TEM, FEI, USA). HTPe_{carboxyl} aqueous solution (10 μ L, 0.5 mg/mL) was dropped onto a copper grids and dried in air for further observation.

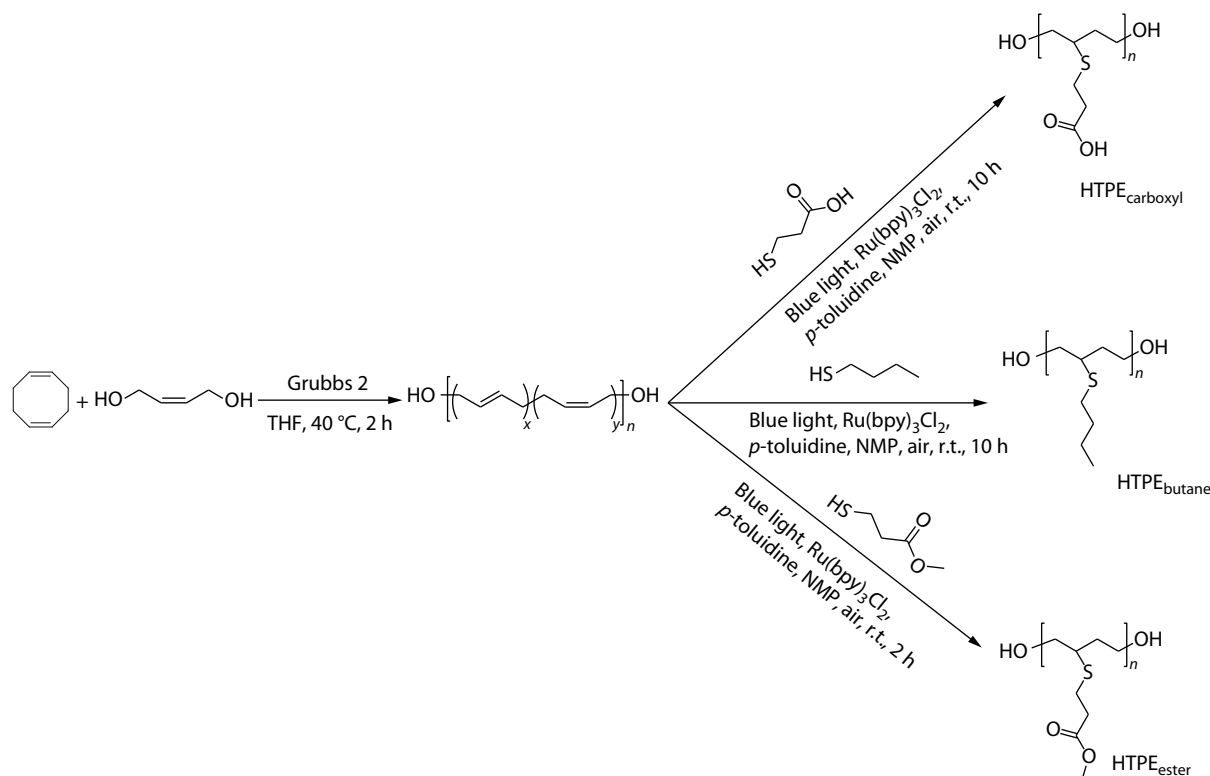
The tensile strength as well as elongation at break of PVC films in the presence and free of plasticizer were tested on an AI-7000-NGD universal testing machine (Goodtechwill Instruments, China) using dumbbell-shaped specimen with a stretching rate of 50 mm/min. The solvent resistance properties of PVC films plasticized with HTPe_{ester} and DOP were tested according to ASTM D 1239-98. PVC films in 25 mm $\times$ 25 mm were immersed into two solvents with different polarities (alcohol and petroleum ether) and soybean oil, respectively. After kept at 25 °C for 48 h, the extracted films were wiped up, washing by distilled water, and dried at 30 °C for 24 h. The solvent resistance properties were evaluated according to the weight loss before and after immersion. EDS of PVC films before and after immersion into petroleum ether were recorded on a SU8100 scanning electron microscope (SEM, Hitachi, Japan).

RESULTS AND DISCUSSION

This work aims to provide a facile strategy for the synthesis of polyethylene derivatives simultaneously bearing terminal hydroxyl and various functional side groups. Also, the relationships between the type of side groups and resultant polymer properties have been explored to further expand their potential applications. The synthetic route proposed in this work involves two main steps, as illustrated in Scheme 1. Firstly, HTPB with only 1,4-butadiene units was synthesized through ROMP. Afterwards, HTPB was used as a precursor, carboxyl, alkyl as well as ester functional side groups were respectively introduced *via* blue light photocatalytic thiol-ene reaction. Notably, although anionic polymerization has been demonstrated to be an inexpensive method for the synthesis of HTPB, herein, ROMP was employed based on the following considerations. Firstly, anionic polymerization inevitably yields 1,2-addition units, which exhibits significantly higher thiol-ene reactivity than the 1,4-addition units. One purpose of this work was to assess whether visible light photocatalytic thiol-ene reaction is a facile and versatile platform for the modification of HTPB. Therefore, HTPB obtained by ROMP and with only 1,4-addition units needs to be investigated. Secondly, synthesis of HTPB *via* anionic polymerization generally requires multi-step reactions and harsh conditions.

Synthesis and Characterization of HTPB

ROMP of COD was conducted at varied feed ratios of monomer to CTA. The detailed polymerization conditions and structural parameters of resultant HTPB are summarized in Table 1. ¹H-NMR spectra of obtained HTPB are depicted in Fig. 1, where all the chemical shifts can be assigned accordingly. Additionally, the molecular weight of HTPB can be calculated as per the ratio



Scheme 1 Synthetic route to HTPB and its functionalized products.

of integral area at $\delta=4.1\text{--}4.2$ ppm (methylene protons linked to hydroxy end groups) and $\delta=5.42\text{--}5.47$ ppm (unsaturated protons in butadiene units), and the results are listed in Table 1. With the increasing feed ratio of COD to CTA, the molecular weight of HTPB increased accordingly. GPC measurements presented in Fig. S1 (in the electronic supplementary information, ESI) and Table 1 are in reasonably good agreement with the analysis of $^1\text{H-NMR}$. MALDI-TOF mass spectrometry shown in Fig. S3 (in ESI) further verified that the end-groups of the obtained polymer were hydroxyl groups. Therefore, all the above analyses confirmed that HTPB with well-defined structure was successfully obtained. Meanwhile, the molecular weight of HTPB can be tailored by changing the feed ratio of COD to CTA. These promising results can primarily be attributed to the controllability of ROMP technology.

Table 1 ROMP conditions and structural parameters of resultant HTPBs.

Entry	[COD]/ [CTA]	Yield (%)	$M_{n,\text{NMR}}^a$ (g/mol)	$M_{n,\text{GPC}}^b$ (g/mol)	PDI ^b	<i>Cis</i> ^c (%)
1	15	52	2900	3900	2.3	74.67
2	23	61	3400	5200	1.9	75.63
3	45	42	5200	5700	3.2	75.99

^a Calculated according to the ratio of integral area at $\delta=4.1\text{--}4.2$ to $\delta=5.42\text{--}5.47$ in $^1\text{H-NMR}$ shown in Fig. S2 (in ESI); ^b Determined by GPC with THF as the eluent; ^c The content of *cis* 1,4-butadiene unit in HTPB backbone was calculated according to the ratio of integral area at $\delta=5.42$ to $\delta=5.47$ in $^1\text{H-NMR}$.

Synthesis and Characterization of HTPB Bearing Various Functional Side Groups

Three kinds of PE analogous products simultaneously bearing hydroxyl terminated and functional side groups (carboxyl,

butane and ester groups) were synthesized by blue light photocatalytic thiol-ene reaction, which is recognized as an efficient and environment-friendly technology. Synthesis of HTPE_{ester} was used as an example to optimize the reaction conditions and provide more insights into the reaction process. The reaction was performed with the irradiation of blue light and bubbling with air. $^1\text{H-NMR}$ was used to track the reaction, and the results are illustrated in Fig. 1. It reveals that as reaction progressed, the proton peaks attributed to double bonds ($\delta=5.42\text{--}5.47$ ppm) weakened gradually and disappeared

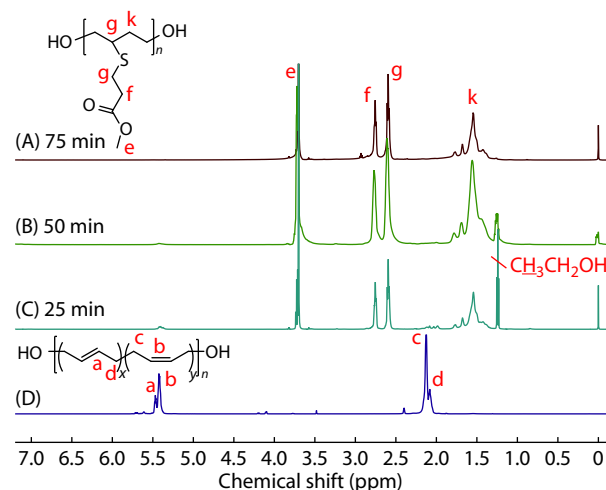


Fig. 1 $^1\text{H-NMR}$ spectra of ester group functionalized products obtained reacting for (A) 75 min, (B) 50 min, (C) 25 min and (D) HTPB precursor.

thoroughly when the reaction was conducted for 75 min. The disappearance of proton peaks at $\delta=5.42\text{--}5.47$ ppm implies the complete modification of double bonds. The exhaust of double bonds can also be evidenced by the ^{13}C -NMR spectra displayed in Fig. S4(d) (in ESI), where the chemical shift for double bond carbon located at $\delta=130$ ppm disappeared completely. When the double bonds in HTPB were consumed completely, the obtained polymer was regarded as hydroxyl-terminated PE bearing ester side groups.

To further optimize the reaction conditions, post-functionalization reactions were also performed under N_2 atmosphere with the irradiation of blue light and under air atmosphere with irradiation of natural light. The degree of modification can be calculated according to the ratio of integral area at $\delta=5.42\text{--}5.47$ ppm (attributed to the double bond protons) to $\delta=2.6$ ppm (attributed to the protons adjacent to S groups), and the results are depicted in Fig. 2, Figs. S5 and S6 (in ESI). It is apparent that the reaction exhibited the highest reactivity when conducted with blue light radiation and under atmosphere. When in an oxygen free system, the reactivity declined. Distinct from traditional thermal or UV light initiation which generally requires an oxygen free system, the thiol-ene functionalization reaction initiated by blue light was accelerated in the presence of oxygen. One of the reasonable explanation is that oxygen has positive contribution towards the regeneration of photocatalyst, just as the reaction mechanism described in Tyson and Boyer's work.^[23,31] Additionally, Fig. 2 implies that the functionalization reaction exhibited the lowest reactivity when exposed to natural light. Therefore, both blue light and oxygen play important roles in the post-functionalization process. The reactivity of isomers in the HTPB backbone such as *cis* 1,4-butadiene units and *trans* 1,4-butadiene units were compared, as shown in Figs. S7 and S8 (in ESI), suggesting that despite the fact that the content of *cis* 1,4-butadiene units is higher than that of *trans* isomers, the former exhibited higher reactivity, and was consumed faster as compared to the latter. Similar trend was also reported in other studies that employed heat as the initiate sources.^[32]

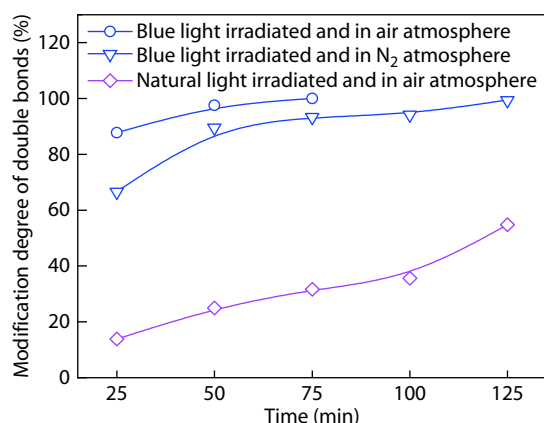


Fig. 2 The variation of modification degree under different reaction conditions.

HTPE_{carboxyl} and HTPE_{butane} were synthesized according to the optimized conditions in synthesizing HTPE_{ester}. To ensure all the double bonds were modified, the reaction time

were prolonged to 10 h. ^1H -NMR spectra of HTPE_{carboxyl} and HTPE_{butane} are presented in Fig. 3, wherein the double bond protons locating at $\delta=5.42\text{--}5.47$ and methylene protons at $\delta=2.13$ completely disappeared. Also, the carboxyl protons at $\delta=12.23$ and alkyl protons at $\delta=1.54, 1.41, 0.92$ could be clearly detected. ^{13}C -NMR spectra displayed in Fig. S4 (in ESI) also confirmed the complete consumption of double bonds. The GPC results for the three functionalized products are summarized in Table S1 (in ESI). M_n of the three samples was relatively close to theoretical values. Therefore, above analyses verifies that HTPE_{carboxyl} and HTPE_{butane} were successfully obtained. In conclusion, combination of ROMP and blue light initiated thiol-ene reaction can be considered as a novel strategy for the facile and effective synthesis of PE with simultaneous hydroxyl terminated and functional side groups. In the following sections, the relationships between side group types and properties of these functionalized products are elucidated, and their promising applications are further explored.

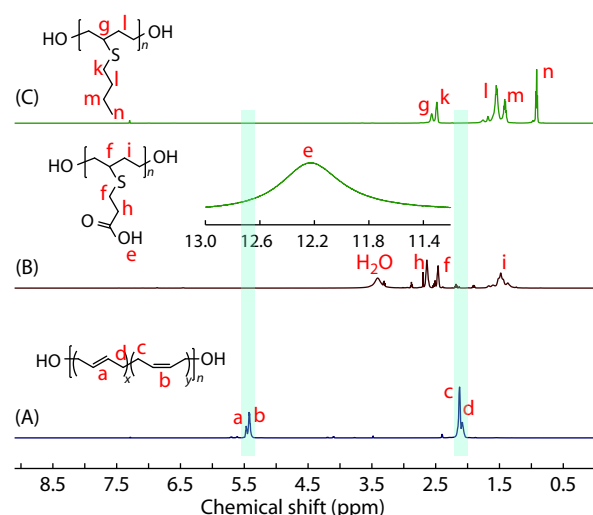


Fig. 3 ^1H -NMR spectra of (A) HTPB, (B) HTPE_{carboxyl} and (C) HTPE_{butane}.

Thermal Properties of HTPB and Functional PEs

Thermal properties of HTPB, HTPE_{carboxyl}, HTPE_{butane} and HTPE_{ester} were comparatively investigated by DSC and TGA, as shown in Fig. 4. Fig. 4(a) indicates that the T_g of HTPB synthesized herein is -103.6°C , which is obviously lower than those reported in previous work.^[33] The reason behind this phenomenon is that HTPB obtained herein possesses higher *cis* 1,4-butadiene unit content than those in previous work.^[34,35] After post-functionalization, the T_g s for all the samples were increased due to the enhancement of interactions between polymer segments. For instance, when carboxyl side groups were incorporated, the intense hydrogen bonds restricted the movement of the segments and T_g was accordingly increased.^[36] The T_g s for all the samples were in the order of HTPB < HTPE_{butane} < HTPE_{ester} < HTPE_{carboxyl}. Fig. 4(b) suggests that after post-functionalization, the thermostabilities were declined. One of the probable explanations is that double bonds in the HTPB backbone with higher bond energy were completely converted to single bonds.

pH-Triggered Self-assembly Behavior of HTPE_{carboxyl}

HTPE_{carboxyl} has abundance of hydrophilic carboxyl side groups and can be ionized based on the ambient pH.^[37] Therefore,

herein, the influence of pH on the properties of HTPE_{carboxyl} aqueous solution was systematically investigated, as shown in Fig. 5. Fig. 5(a) indicates that with decreasing pH the

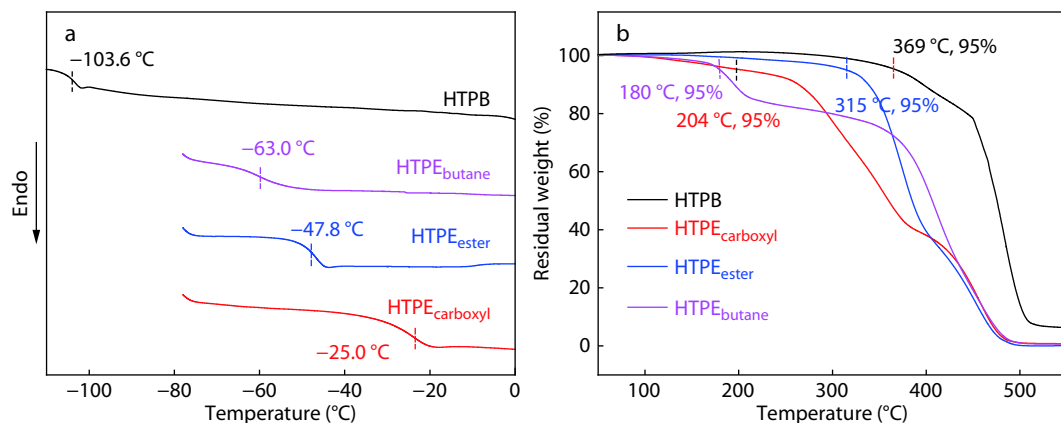


Fig. 4 (a) DSC and (b) TGA curves of HTPB and its post-functionalized products.

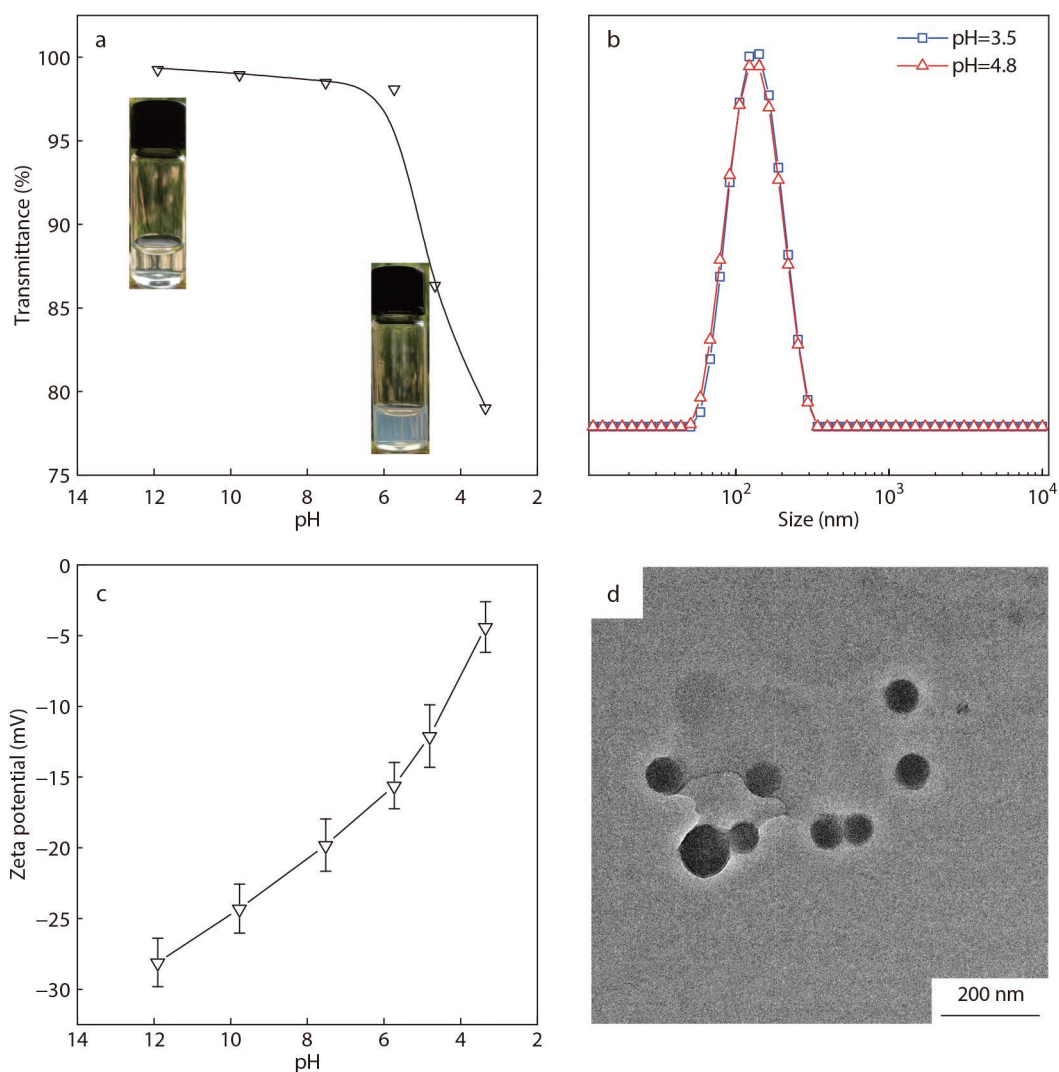


Fig. 5 (a) Transmittance of HTPe_{carboxyl} aqueous solution, (b) DLS traces of assemblies formed by HTPe_{carboxyl} at different pH values, (c) zeta potentials of assemblies at different pH values, (d) TEM image of assemblies formed by HTPe_{carboxyl} at pH 3.5.

transmittance of $\text{HTPE}_{\text{carboxyl}}$ aqueous solution remained almost unchanged initially and decreased sharply when pH value was lowered to 4.8 and 3.5. The solution turned from completely transparent to faint blue, implying that nano-size aggregates were probably formed. DLS traces depicted in Fig. 5(b) verified this inference, wherein aggregates with sizes of 129 nm (pH=4.8) and 121 nm (pH=3.5) could be clearly detected. As is well-known, carboxyl groups can be dramatically ionized and transformed to be more hydrophilic in an alkaline environment. Therefore, in an alkaline environment, $\text{HTPE}_{\text{carboxyl}}$ existed as water-soluble unimer due to the high hydrophilicity of side groups. When pH was lowered to 4.8 (or 3.5), the ionization of carboxyl groups was restricted to an appropriate extent.^[38] In this case, $\text{HTPE}_{\text{carboxyl}}$ can be considered as an amphiphilic homopolymer composed of hydrophobic backbone and hydrophilic side groups, and assemblies in nanoscale were formed accordingly. This speculation was further confirmed using zeta potential measurements. As shown in Fig. 5(c), when the pH increased from 3.5 to 11.9, the zeta potential became more negative due to the enhancement of ionization. The morphology of assemblies was observed by TEM, as shown in Fig. 5(d). TEM images revealed that $\text{HTPE}_{\text{carboxyl}}$ formed well-defined solid spherical micelles at pH 3.5. Therefore, $\text{HTPE}_{\text{carboxyl}}$ possesses potential for use as a smart material with pH-sensitive properties.

Synthesis of Triblock Copolymer Using $\text{HTPE}_{\text{butane}}$ as Macro-initiator

$\text{HTPE}_{\text{butane}}$ synthesized herein possesses two reactive hydroxyl end groups. Therefore, it can be inferred that $\text{HTPE}_{\text{butane}}$ can be used as a polymeric precursor for building the novel block

copolymers. $\text{HTPE}_{\text{butane}}$ was proposed using as a macro-initiator to initiate the ring opening polymerization (ROP) of ϵ -caprolactone. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of the resultant triblock copolymer are presented in Fig. 6(A) and Fig. S9 (in ESI), respectively, which reveal that the chemical shifts of protons and carbons in PCL segments could be clearly detected. Fig. 6(B) displays the DSC curve of $\text{PCL-}b\text{-PE}_{\text{butane}}\text{-}b\text{-PCL}$, wherein two endothermic peaks at -64.7 and 55.8 °C were due to the glass transition of $\text{PE}_{\text{butane}}$ segments and the melting of PCL segments, respectively. Fig. 6(C) exhibits the GPC traces of $\text{PE}_{\text{butane}}$ and $\text{PCL-}b\text{-PE}_{\text{butane}}\text{-}b\text{-PCL}$. In Fig. 6(C), the advancement of elution time for $\text{PCL-}b\text{-PE}_{\text{butane}}\text{-}b\text{-PCL}$ implies the rise in molecular weight. The molecular weights of $\text{PE}_{\text{butane}}$ and $\text{PCL-}b\text{-PE}_{\text{butane}}\text{-}b\text{-PCL}$ were determined to be $M_{n,\text{GPC}}=7600$ g/mol and $M_{n,\text{GPC}}=11400$ g/mol, respectively. Consequently, all the above analyses confirmed that $\text{PCL-}b\text{-PE}_{\text{butane}}\text{-}b\text{-PCL}$ was successfully obtained and $\text{PE}_{\text{butane}}$ can be served as a macro-initiator for building the block copolymers.

Performance of PVC Film Plasticized by $\text{HTPE}_{\text{ester}}$

In recent years, polyester plasticizers have received growing attention as a result of their hypotoxicity and low migration.^[39,40] $\text{HTPE}_{\text{ester}}$ synthesized in this work was composed of flexible PE backbone and abundance of ester side groups. Fig. 4(a) shows that T_g of $\text{HTPE}_{\text{ester}}$ is -47.8 °C. Therefore, $\text{HTPE}_{\text{ester}}$ is a promising candidate for use as a plasticizer. As per Fig. 7(a), the T_g of PVC plasticized with $\text{HTPE}_{\text{ester}}$ was -7.3 °C, which is dramatically lower than that of neat PVC reported in previous work.^[41] Two factors may have contributed towards this result. Firstly, $\text{HTPE}_{\text{ester}}$ possesses relatively low T_g and good flexibility, which are beneficial for the lubrication PVC segments

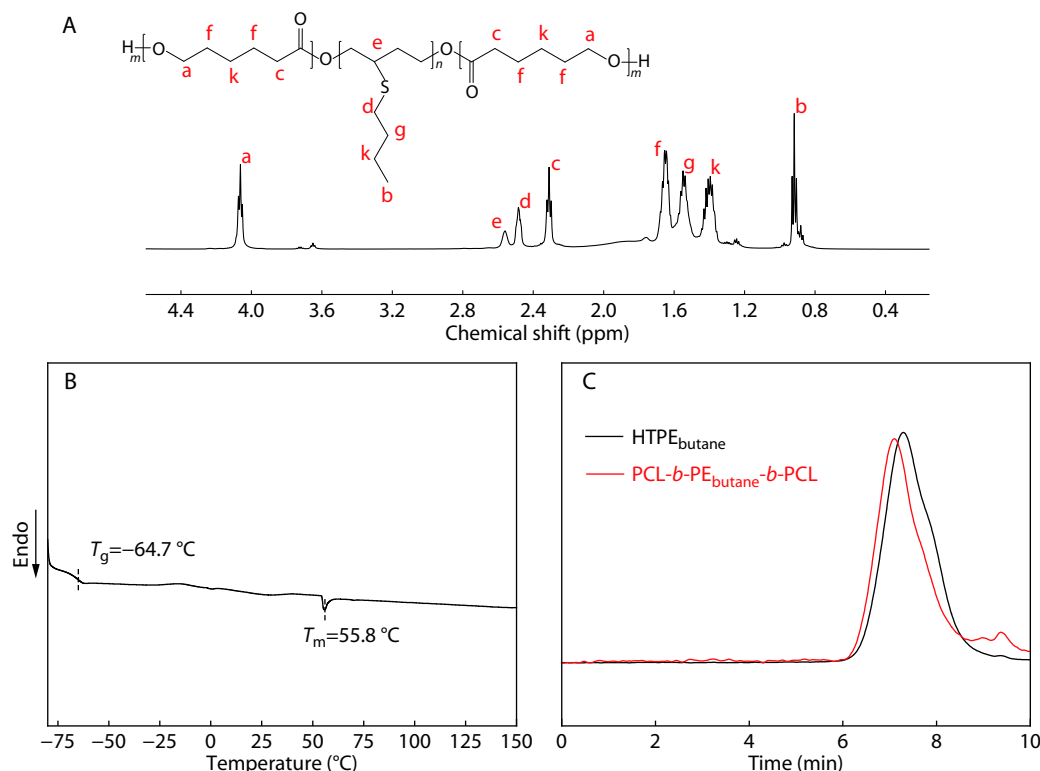


Fig. 6 (A) $^1\text{H-NMR}$ spectrum, (B) DSC curve and (C) GPC trace of $\text{PCL-}b\text{-PE}_{\text{butane}}\text{-}b\text{-PCL}$.

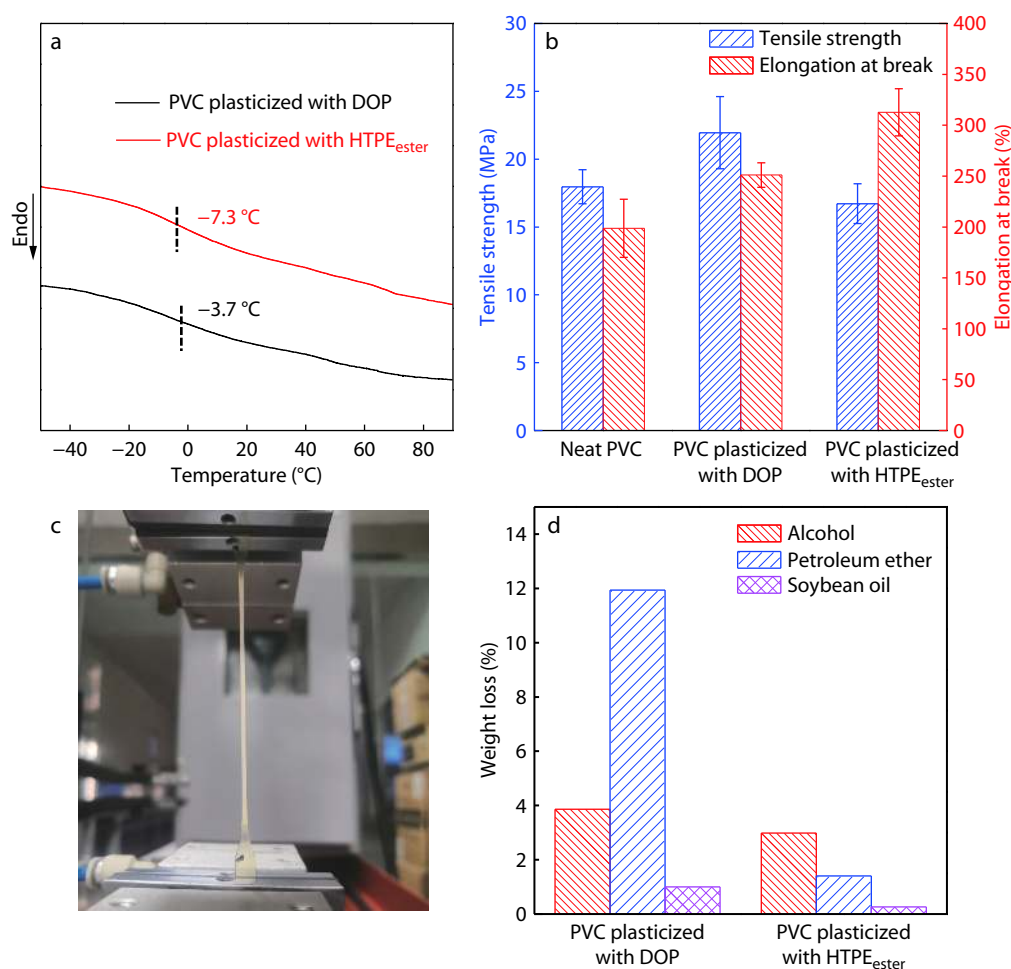


Fig. 7 (a) DSC curves of PVC films, (b) tensile strength and elongation at break of PVC films, (c) digital image of stretched PVC film plasticized by HTPe_{ester}, (d) weight loss of PVC films in extractability tests.

and further accelerating the movement of PVC segments. Secondly, the insertion of HTPe_{ester} molecules between the PVC segments weakened the interaction between PVC molecules and enlarged the free volume. Mechanical properties illustrated in Fig. 7(b) reveal that the toughness of PVC film was significantly enhanced after plasticized by HTPe_{ester}, while the tensile strength displayed negligible decrease. Additionally, Fig. 7(b) suggests that PVC film plasticized with HTPe_{ester} exhibited better ductility as compared to that with DOP. The solvent resistance properties of PVC films plasticized with HTPe_{ester} and DOP were compared, as shown in Fig. 7(d). As we expect, Fig. 7(d) indicates that HTPe_{ester} exhibited higher extraction resistance, irrespective of the use of polar ethanol or nonpolar petroleum ether. EDS, as a surface sensitive technique, was also employed to quantify the surface elements of PVC films before and after immersion into petroleum ether, and the results are presented in Figs. S10 and S11 and Table S2 (in ESI), which revealed that the content of O element was clearly decreased after immersion when DOP was used as a plasticizer, whereas it remained almost unchanged when HTPe_{ester} was used as a plasticizer. The decrease in O element can be attributed to the extraction of plasticizer from PVC film surface to solvent. Therefore, EDS tests further verify the results presented in Fig. 7(d). One of the reasonable

explanations for low migration of HTPe_{ester} is the intense interaction and entanglement between the HTPe_{ester} and PVC macromolecules, which restricted the migration of HTPe_{ester}. All the above measurements suggest that HTPe_{ester} can serve as a powerful plasticizer for PVC.

CONCLUSIONS

Herein, the strategy involving ROMP and visible light photocatalytic thiol-ene reaction has been confirmed to be a facile pathway for the synthesis of PE simultaneously bearing hydroxyl terminated and functional side groups. Three kinds of hydroxyl terminated PE bearing carboxyl, ester and butane side groups, respectively, were successfully obtained and labeled as HTPe_{ester}, HTPe_{carboxyl} and HTPe_{butane}. The structure-property relationships of functional PEs were also elucidated. The *T_g*s for all samples were in the order of HTPB < HTPe_{butane} < HTPe_{ester} < HTPe_{carboxyl}. With the increase in side group polarity, the *T_g* increased due to the enhancement of interactions between side groups. Moreover, the thermostability of functional PEs decreased as compared to that of HTPB precursor, which is resulted from that double bonds with high bond energy were completely converted to single bonds. The promising applications for functional PEs were explored. HTPe_{carboxyl} can

be used as a pH-responsive material, as the ionization of carboxyl side groups can be controlled by the ambient pH. HTPe_{butane} can serve as a macro-initiator for building the triblock copolymer due to the presence of active hydroxyl end groups. HTPe_{ester} can be used as a powerful plasticizer for PVC, which enhanced the ductility of PVC without obviously sacrificing strength.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-021-2572-5>.

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REFERENCES

- Tellers, J.; Zych, A.; Neuteboom, P.; Soliman, M.; Vachon, J. Polyolefin copolymer PE-HEMA with increased metal adhesion properties. *Eur. Polym. J.* **2020**, *131*, 109721.
- Báez, J. E.; Ramírez-Hernández, A.; Marcos-Fernández, A. Synthesis, characterization, and degradation of poly(ethylene-*b*- ϵ -caprolactone) diblock copolymer. *Polym. Adv. Technol.* **2010**, *21*, 55–64.
- Lee, H. J.; Baek, J. W.; Kim, T. J.; Park, H. S.; Moon, S. H.; Park, K. L.; Bae, S. M.; Park, J.; Lee, B. Y. Synthesis of long-chain branched polyolefins by coordinative chain transfer polymerization. *Macromolecules* **2019**, *52*, 9311–9021.
- Peng, B.; Jiang, Y.; Zhu, A. A novel modification of carbon nanotubes for improving the electrical and mechanical properties of polyethylene composites. *Polym. Test.* **2019**, *74*, 72–76.
- Ramírez-Hernández, A.; Hernández-Mota, C. E.; Páramo-Calderón, D. E.; González-García, G.; Báez-García, E.; Rangel-Porras, G.; Vargas-Torres, A.; Aparicio-Saguilán, A. Thermal, morphological and structural characterization of a copolymer of starch and polyethylene. *Carbohydr. Res.* **2020**, *488*, 107907.
- Alshumrani, R. A.; Hadjichristidis, N. Well-defined non-linear polyethylene-based macromolecular architectures. *J. Polym. Sci. Part A: Polym. Chem.* **2018**, *56*, 2129–2136.
- Ntetsikas, K.; Zapsas, G.; Bilalis, P.; Gnanou, Y.; Feng, X. Y.; Thomas, E. L.; Hadjichristidis, N. Complex star architectures of well-defined polyethylene-based Co/terpolymers. *Macromolecules* **2020**, *53*, 4355–4365.
- Kimani, S. M.; Thompson, R. L.; Hutchings, L. R.; Clarke, N.; Billah, S. M. R.; Sakai, V. G.; Rogers, S. E. Multihydroxyl end functional polyethylenes: synthesis, bulk and interfacial properties of polymer surfactants. *Macromolecules* **2014**, *47*, 2062–2071.
- Tian, B. Z.; Cai, Y. Q.; Zhang, X. W.; Fan, H.; Li, B. G. Design of well-defined polyethylene-*g*-poly-methyltrifluorosiloxane graft copolymers via direct copolymerization of ethylene with polyfluorosiloxane macromonomers. *Ind. Eng. Chem. Res.* **2020**, *59*, 4557–4567.
- Bergerbit, C.; Baffie, F.; Wolpers, A.; Dugas, P.; Boyron, O.; Taam, M.; Lansalot, M.; Monteil, V.; D'Agosto, F. Ethylene polymerization-induced self-assembly (PISA) of poly(ethylene oxide)-block-polyethylene copolymers via RAFT. *Angew. Chem. Int. Ed.* **2020**, *132*, 10471–10476.
- Han, C. J.; Lee, M. S.; Byun, D.; Kim, S. Y. Synthesis of hydroxy-terminated polyethylene via controlled chain transfer reaction and poly(ethylene-*b*-caprolactone) block copolymer. *Macromolecules* **2002**, *35*, 8923–8925.
- Demarteau, J.; Scholten, P. B. V.; Kermagoret, A.; Winter, J. D.; Meier, M. A. R.; Monteil, V.; Debuigne, A.; Detrembleur, C. Functional polyethylene (PE) and PE-based block copolymers by organometallic-mediated radical polymerization. *Macromolecules* **2019**, *52*, 9053–9063.
- Chen, M.; Chen, C. L. A versatile ligand platform for palladium- and nickel-catalyzed ethylene copolymerization with polar monomers. *Angew. Chem. Int. Ed.* **2018**, *130*, 3148–3152.
- Cui, D. M. Studies on homo- and co-polymerizations of polar and non-polar monomers using rare-earth metal catalysts. *Acta Polymerica Sinica (in Chinese)* **2020**, *51*, 12–29.
- Feng, Y. C.; Jie, S. Y.; Li, B. Synthesis of ethylene/vinyl ester copolymers with pendent linear branches via ring-opening metathesis polymerization of fatty acid-derived cyclooctenes. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 2211–2220.
- Scherman, O. A.; Walker, R.; Grubb, R. H. Synthesis and characterization of stereoregular ethylene-vinyl alcohol copolymers made by ring-opening metathesis polymerization. *Macromolecules* **2005**, *38*, 9009–9014.
- Franssen, N. M. G.; Reek, J. N. H.; Bruin, B. Synthesis of functional 'polyolefins': state of the art and remaining challenges. *Chem. Soc. Rev.* **2013**, *42*, 5809–5832.
- Rakotonirina, M. D.; Baron, M.; Siri, D.; Gaudel-Siri, A.; Quinebeche, S.; Flat, J.; Gimes, D.; Cassagnau, P.; Beyou, E.; Guillauneuf, Y. Acyloxyimide derivatives as efficient promoters of polyolefin C–H functionalization: application in the melt grafting of maleic anhydride onto polyethylene. *Polym. Chem.* **2019**, *10*, 4336–4345.
- Hong, M.; Liu, S. R.; Li, B. X.; Li, Y. S. Application of thiol-ene click chemistry to preparation of functional polyethylene with high molecular weight and high polar group content: influence of thiol structure and vinyl type on reactivity. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 2499–2506.
- Hu, H.; You, J.; Gan, W. P.; Zhou, J. P.; Zhang, L. Synthesis of allyl cellulose in NaOH/urea aqueous solutions and its thiol-ene click reactions. *Polym. Chem.* **2015**, *6*, 3543–3548.
- Song, W. Q.; Liu, Y. Y.; Qian, L. W.; Niu, L. Y.; Xiao, L. Q.; Hou, Y.; Wang, Y.; Fan, X. D. Hyperbranched polymeric ionic liquid with imidazolium backbones for highly efficient removal of anionic dyes. *Chem. Eng. J.* **2015**, *287*, 482–491.
- Tyson, E. L.; Ament, M. S.; Yoon, T. P. Transition metal photoredox catalysis of radical thiol-ene reactions. *J. Org. Chem.* **2013**, *78*, 2046–2050.
- Xu, J. T.; Boyer, C. Visible light photocatalytic thiol-ene reaction: an elegant approach for fast polymer postfunctionalization and step-growth polymerization. *Macromolecules* **2015**, *48*, 520–529.
- Zhu, X. Z.; Fan, X. D.; Zhao, N.; Liu, J.; Min, X.; Wang, Z. Z. Comparative study of structures and properties of HTPBs synthesized via three different polymerization methods. *Polym. Test.* **2018**, *68*, 201–207.
- Wang, H. T.; Bethea, T. W.; Harwood, H. J. Carbon-13 NMR spectra of isomerized polybutadienes. *Macromolecules* **1993**, *26*, 715–720.
- Wen, J. Q.; Zhang, X. Q.; Dai, Q. Q. Synthesis of polybutadienes with controllable microstructure by a novel binary Nd(3-NBSO₃)₃/alkylaluminum catalyst system. *Chinese J. Polym. Sci.* **2015**, *33*, 475–480.
- Silverstein, J. S.; Casey, B. J.; Natoli, M. E.; Dair, B. J.; Kofinas, P.

- Rapid modular synthesis and processing of thiol-ene functionalized styrene-butadiene block copolymers. *Macromolecules* **2012**, *45*, 3161–3167.
- 28 Brummelhuis, N. T.; Diehl, C.; Schlaad, H. Thiol-ene modification of 1,2-polybutadiene using UV light or sunlight. *Macromolecules* **2008**, *41*, 9946–9947.
 - 29 Zhang, W. B.; Zhang, G. H.; Du, L.; Zhang, C.; Li, L.; Zhu, J. F.; Pei, J.; Wu, J. Synthesis of hydroxyl-terminated polybutadiene bearing pendant carboxyl groups by combination of anionic polymerization and blue light photocatalytic thiol-ene reaction and its pH-triggered self-assemble behavior. *React. Funct. Polym.* **2018**, *127*, 161–167.
 - 30 Liu, D.; Jiang, P. P.; Nie, Z. X.; Wang, H. Y.; Dai, Z. D.; Deng, J. N.; Cao, Z. L. Synthesis of an efficient bio-based plasticizer derived from waste cooking oil and its performance testing in PVC. *Polym. Test.* **2020**, *90*, 106625.
 - 31 Tyson, E. L.; Niemeyer, Z. L.; Yoon, T. P. Redox mediators in visible light photocatalysis: photocatalytic radical thiol-ene additions. *J. Org. Chem.* **2014**, *79*, 1427–1436.
 - 32 Passaglia, E.; Coiai, S.; Ciardelli, F.; Galimberti, M.; Passaglia, E. Thiol-ene radical addition of L-cysteine derivatives to low molecular weight polybutadiene. *Macromol. Chem. Phys.* **2009**, *210*, 1471–1483.
 - 33 Zhang, W. B.; Fan, X. D.; Tian, W.; Chen, H.; Zhu, X. Z.; Zhang, H. T. Preparation of a P(THF-co-PO)-b-PB-b-P(THF-co-PO) triblock copolymer via cationic ring-opening polymerization and its use as a thermoset polymer. *RSC Adv.* **2015**, *5*, 66073–66081.
 - 34 Zhou, Q. Z.; Jie, S. Y.; Li, B. G. Preparation of hydroxyl-terminated polybutadiene with high *cis*-1,4 content. *Ind. Eng. Chem. Res.* **2014**, *53*, 17884–17893.
 - 35 Forens, A.; Roos, K.; Dire, C.; Gadenne, B.; Carlotti, S. Anionic polymerization of butadiene using lithium/potassium multi-metallic systems: influence on polymerization control and polybutadiene microstructure. *Chinese J. Polym. Sci.* **2019**, *38*, 357–362.
 - 36 Gao, Y. Y.; Hu, F. Y.; Liu, J.; Wang, Z. Molecular dynamics simulation of the glass transition temperature of fullerene filled *cis*-1,4-polybutadiene nanocomposites. *Chinese J. Polym. Sci.* **2018**, *36*, 119–128.
 - 37 Zhang, Y.; Zhang, X. M.; Song, Y. C.; Wang, J. H. Enhanced performance of calcium-enriched coal ash for the removal of humic acids from aqueous solution. *Fuel* **2015**, *141*, 93–98.
 - 38 Huang, Y. W.; Yan, J. Y.; Peng, S. Y.; Tang, Z. L.; Tan, C. Y.; Ling, J. B.; Lin, W. J.; Lin, X. F.; Zu, X. H.; Yi, G. B. pH/Reduction dual-stimuli-responsive cross-linked micelles based on multi-functional amphiphilic star copolymer: synthesis and controlled anti-cancer drug release. *Polymers* **2020**, *12*, 82.
 - 39 Pereira, V. A.; Fonseca, A. C.; Costa, C. S. M. F.; Ramalho, A.; Coelho, J. F. J.; Serra, A. C. End-capped biobased saturated polyesters as effective plasticizers for PVC. *Polym. Test.* **2020**, *85*, 106406.
 - 40 Sun, Z. H.; Choi, B.; Feng, A. C.; Moad, G.; Thang, S. H. Nonmigratory poly(vinyl chloride)-block-polycaprolactone plasticizers and compatibilizers prepared by sequential RAFT and ring-opening polymerization (RAFT-T-ROP). *Macromolecules* **2019**, *52*, 1746–1756.
 - 41 Chen, J.; Wang, Y. G.; Huang, J. R.; Li, K.; Nie, X. A. Synthesis of tung-oil-based triglycidyl ester plasticizer and its effects on poly(vinyl chloride) soft films. *ACS Sustain. Chem. Eng.* **2018**, *6*, 642–651.