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Unsaturated sulfur-containing polymers from modular alcohol click chemistry†

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The traditional polymerization methods utilizing thiol–yne Michael addition have made significant progress in the past decades, despite suffering from the poor availability of dithiols. Here, a modular and efficient click reaction for connecting primary and secondary alcohols with activated alkynes *via* carbonyl sulfide (COS) was developed. The click reaction is successfully applied to synthesize different kinds of polythiocarbonates by the step-wise polyaddition of diols, dipropiolates, and COS. Diols are a diverse and abundant class of compounds that can be obtained from biomass and COS is released as industrial waste, while dipropiolates can be obtained through a one-step condensation reaction of diols with propiolic acid. In addition to the ease of obtaining the monomers, this method is atom-economical, metal-free, and involves mild conditions. Overall, the polymers have broad prospects for green materials given their facile synthesis, readily available feedstocks, desirable performance.

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Introduction

An effective method for synthesizing sulfur-containing polymers is through the Michael addition of thiols and alkynes.^{1–12} For example, functional hyperbranched polymers of prop-2-ynyl-3-mercaptopropanoate have been prepared by photo-initiated thiol–yne click polymerization under the assistance of the initiator of 2,2-dimethoxy-2-phenylacetophenone (DMPA),¹³ and linear main chain polymers can be prepared by the UV-initiated click polymerizations of terminal monoynes with dithiols.¹⁴ With applications in high performance polymer,^{15–17} optical,^{18,19} luminescent,²⁰ opto-electronic,²¹ self-healing,^{2,22} metal adsorption²³ and other fields, these polymers are in high demand. However, the utilization of thiols is unpleasant since they are expensive with a persistent irritating odor and they have lower ignition points and flash points compared to alcohols.

Conversely, diols represent readily available and sustainable building blocks with an extremely rich variety, and many of them can be synthesized from renewable biomass resources.²⁴ In general, diols are typically condensed with diacids to synthesize polymers, but due to the need for high temperature

and vacuum conditions to remove water, the energy consumption of this process is relatively high, and the atom-economy is poor.²⁵ Therefore, there is a high demand for the atom-economic utilization of diols in polymerization reactions under mild conditions.

Carbonyl sulfide (COS) is a waste product from mining of fossil resources, which can cause acid rain and destruction of the ozone layer.^{26,27} COS can be separated by selective adsorption to obtain a high purity gas. Additionally, COS is industrially mass produced from CO and sulfur, and has been widely used as a fumigant for grain storage.²⁸ In very recent years, the synthesis and applications of sulfur-containing polymers using COS^{29–46} were investigated by our group and others.^{47,48} Using metal or organic catalysts, different kinds of well-defined polythioethers and polythiocarbonates have been obtained. During the polymerization process using COS and epoxides, we realized that there might be an intermediate with a thiol group formed. This intermediate could potentially undergo a click reaction with olefins or alkynes.

Next, we discovered that the carbonothioate intermediate formed with a base as catalyst using COS and an alcohol can react with electron-deficient C≡C bonds (Fig. 1) to generate thiocarbonates. Based on the newly developed click reaction, this study discloses the step-wise polyaddition of diols, dipropiolates, and COS to synthesize a series of poly(thiocarbonate ester)s with C=C remaining in the main chain. Dipropiolates are accessible by the esterification of diols and propiolic acid, which serve to incorporate in-chain ester groups as potentially biodegradable and chemically breakable points. Compared with the well-known polyaddition of dithiols and monoynes, the strategy avoids the use of unpleasant and expensive thiols.

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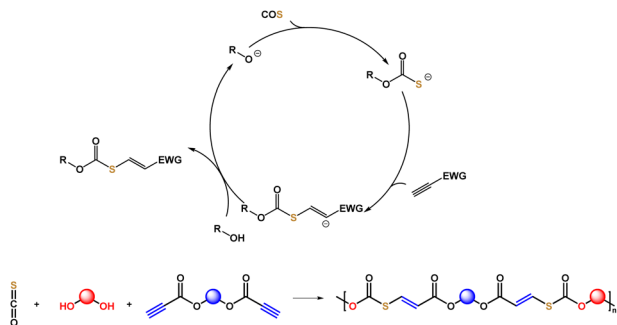


Fig. 1 Connecting alcohols with activated alkynes via a bridge molecule of carbonyl sulfide (COS).

Utilization of COS for manufacturing valuable sulfur-containing polymers is also of significance for both polymer chemistry and environmental science. Our method is atom-economical, performed under mild conditions, and uses common organic bases as catalysts.

Results and discussion

We first examined the alcohol-COS-alkyne coupling as the model reaction using 5 common activated alkynes (methyl propiolate (MP), ethyl propiolate, 3-butyne-2-one, 4-phenyl-3-butyne-2-one, and 3-phenyl-2-propynenitrile) and 5 representative alcohols (methanol, ethanol (EtOH), 1-propanol, isopropanol, and *tert*-butanol) (Fig. 2). All of these chemicals were used

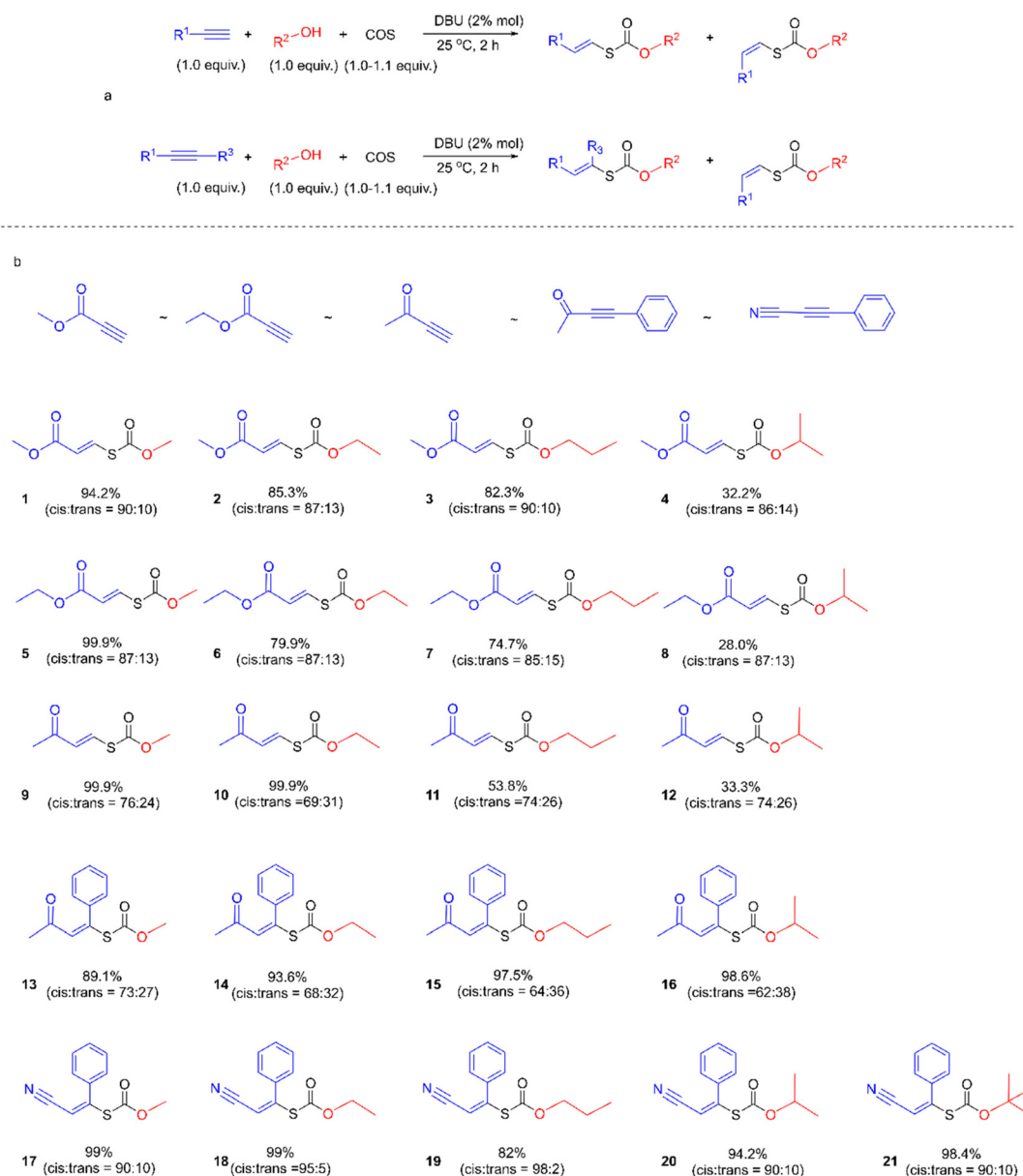


Fig. 2 Substrate scope for the coupling of alcohols, COS, and activated alkynes.

directly after purchase without purification. Since alkoxides formed from the alcohol and the base catalyst could attack the triple bonds of the alkyne units, the sequence of the feedstocks is quite important for the control of selectivity. With COS added before the methanol and DBU (see more details in the ESI†), the nucleophilic attack of the alkynes by alkoxide is avoided. The desired coupling was achieved with high efficiency under mild and robust conditions. The conversion of activated alkynes increased in the order methyl propiolate ~ ethyl propiolate ~ 3-butyn-2-one < 4-phenyl-3-butyn-2-one < 3-phenyl-2-propynenitrile due to the degree of electron deficiency of the C≡C bond and the benzene ring. The resonance of the vinylic carbanion with the benzene ring would help stabilize intermediates, resulting in increased conversion of alkynes with a benzene ring (4-phenyl-3-butyn-2-one and 3-phenyl-2-propynenitrile). A range of commercially available organobases are effective catalysts for this method (Table 1). For instance, under the same reaction conditions (Scheme 1), 1,5-diazabicyclo(5,4,0)undec-5-ene (DBU), 1,5,7-triazabicyclo(4,4,0)dec-5-ene (TBD), 7-methyl-1,5,7-triazabicyclo(4,4,0)dec-5-ene (MTBD), 4-dimethylaminopyridine (DMAP), potassium *tert*-butoxide (*t*-BuOK), *N,N,N',N'*-tetraethyl ethylenediamine (TEEDA), tri-*tert*-butylphosphine (*t*-Bu₃P) and tributyl-

phosphine (*n*-Bu₃P) afforded the product **1** in 99.9%, 99.9%, 99.9%, 76.2%, 88.6%, 97.4%, and 25.2% yields (entries 1–8, Table 1), respectively. A simple silica gel column process yielded purified **1** by removing excess methanol and catalysts (¹H-NMR, Fig. 3). TBACl and PPNCl did not present catalytic activity (entries 9 and 10, Table 1), even in solvents like DMF and DMSO. Besides the mechanism of typical basic catalysts that we provide (Fig. 5), there may be another reaction route for the nucleophilic catalysts. Nucleophilic catalysts first attack the carbon atom of COS, and then the ethanol inserts to gain an intermediate similar to **S6**, thus the sterically hindered catalysts would benefit the insertion of ethanol. Higher temperatures led to increased efficiency. By elevating the reaction temperature to 60 °C and using 2% DBU, we obtained **1** in 98% yield within 5 min.

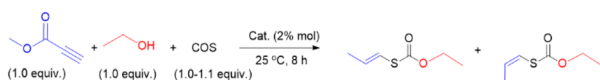
Since the double bonds in the generated products do not undergo further Michael addition reactions, the products are a mixture of *cis*–*trans* isomers coexisting simultaneously. Thus, we investigated the control of the content of *cis*–*trans* isomers in the products under different conditions, including varying temperatures, catalysts, and solvents. The content of isomers makes no difference at 25, 40, and 60 °C (entries 7–9, Table 1), indicating that the Gibbs free energy of the isomers are nearly the same. The results indicate that the catalysts and the solvents have a weak relationship with the *cis*–*trans* isomer content of the reaction product. With different catalysts such as *n*-Bu₃P and TEEDA, the content of *trans* isomers changed slightly from 9.1% (entry 8, Table 1) to 13.8% (entry 6, Table 1). With different solvents such as MeCN and ethyl acetate, the content of *trans* isomers changed slightly from 10.7% (entry 14, Table 1) to 18.0% (entry 20, Table 1).

We next sought to investigate the general applicability of this method to various alcohols using methyl propiolate as a Michael acceptor (Fig. 4). Under mild conditions (2% DBU, at 25 °C, for 2 h), diverse and densely functionalized alcohols (*N*-Boc-4-piperidinemethanol, ethyl glycolate, 4-bromophenethyl alcohol, furfuryl alcohol, and *m*-anisyl alcohol (with DCM as solvent)) produced several thiocarbonates with C=C

Table 1 The isomer content obtained under different reaction conditions^a

Entry	Cat.	Solvent	<i>C</i> _{trans} ^b	<i>C</i> _{cis} ^c	Conv. ^d
1	DBU	DCM	11.5	88.5	99.9
2	TBD	DCM	11.5	88.5	99.9
3	MTBD	DCM	11.5	88.5	99.9
4	DMAP	DCM	9.9	90.1	99.9
5	<i>t</i> -BuOK	DCM	11.5	88.5	76.2
6	TEEDA	DCM	13.8	86.2	88.6
7	<i>t</i> -Bu ₃ P	DCM	9.9	90.1	97.4
8	<i>n</i> -Bu ₃ P	DCM	9.1	90.9	25.2
9	TBACl	DCM	0	0	0
10	PPNCl	DCM	0	0	0
11	DBU	—	11.5	88.5	99.9
12 ^e	DBU	—	11.5	88.5	99.9
13 ^f	DBU	—	11.5	88.5	99.9
14	DBU	MeCN	10.7	89.3	99.9
15	DBU	Acetone	11.5	88.5	99.9
16	DBU	<i>n</i> -Hexane	12.3	87.7	99.9
17	DBU	DMF	13.0	87.0	99.9
18	DBU	DMSO	13.8	86.2	99.9
19	DBU	THF	18.0	82.0	99.9
20	DBU	Ethyl acetate	18.0	82.0	99.9

^a The reactions were conducted at 25 °C in 8 h. ^b The content of *trans*-isomers determined by ¹H-NMR spectroscopy. ^c The content of *cis*-isomers determined by ¹H-NMR spectroscopy. ^d The conversion of MP determined by ¹H-NMR spectroscopy. ^e The temperature was 40 °C. ^f The temperature was 60 °C.



Scheme 1 The model reaction of MP/EtOH/COS in Table 1.

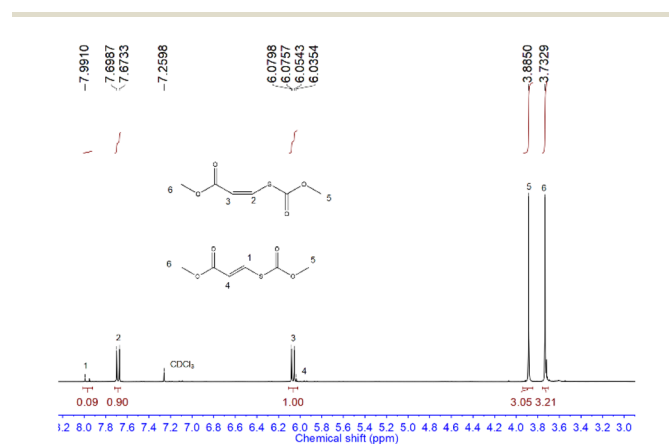


Fig. 3 ¹H-NMR spectrum for the product **1** from COS, MP, and methanol.

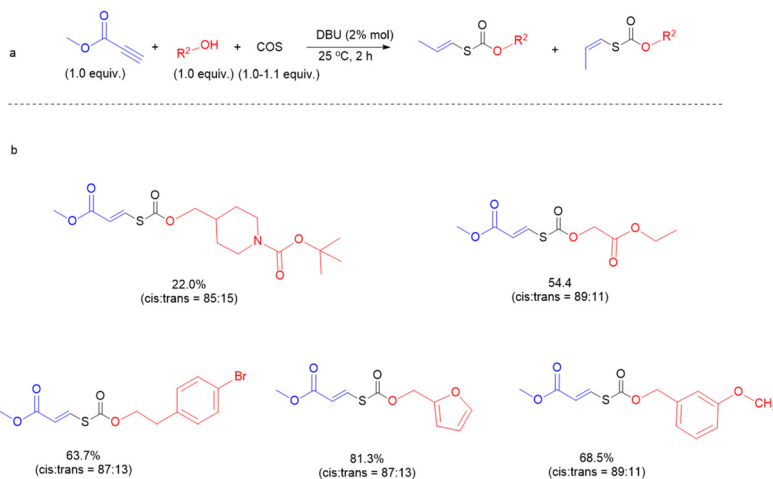


Fig. 4 Substrate scope for the coupling of alcohols, COS, and activated alkynes.

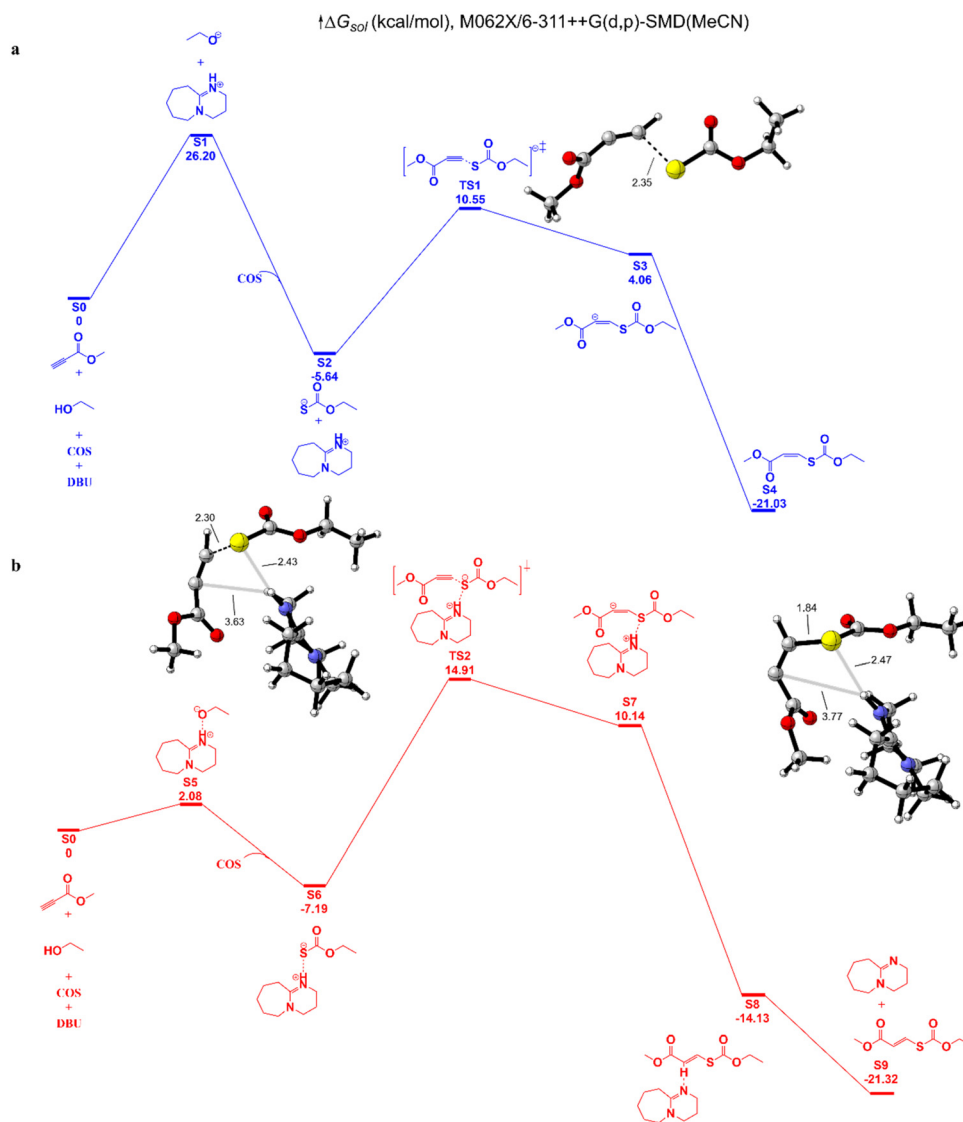


Fig. 5 Free energies associated with DBU-catalyzed coupling of COS, MP, and ethanol. In route (a), the proton of the hydroxy group is abstracted by DBU; in route (b), the hydroxy group forms a hydrogen bond with the nitrogen atom of DBU.

bonds in 22.0%, 54.4%, 63.7%, 68.5%, and 81.3% yields and the ratio of C_{trans} to C_{cis} is about 1 : 7 (Fig. S39–S43†), indicating that this reaction is tolerant of many primary alcohols with reactive functions such as halide, ester, pyridyl and furyl groups. Notably, click chemistry has emerged as one of the most powerful tools for constructing carbon–heteroatom bonds in organic chemistry, materials science, bioconjugation, etc.^{49–51}

We then explored the hypothetical mechanism through density functional theory (DFT) calculations (Fig. 5). With DBU as the catalyst, MP and ethanol are used as representative reactants. Under the deprotonation of DBU, the hydroxyl group selectively attacks the C=S bond of COS to generate the carboanion. Insertion of MP *via* the transition state determines the reaction rate in route b, with a barrier of 22.1 kcal mol⁻¹, while the barrier for the hydroxyl group and DBU in route b is 26.2 kcal mol⁻¹. In both routes the *cis* conformations are dominant, therefore the *cis*-isomers are preferentially formed. The Gibbs free energies of *cis/trans* isomers are nearly the same with a 0.29 kcal mol⁻¹ difference, so under the influence of a base catalyst, the *cis-trans* isomers could transform reversibly.

After understanding the alcohol–COS–activated alkyne coupling reaction, we sought to perform the step-wise polyaddition of diols, dipropiolates, and COS (Fig. 6). We chose MeCN as the solvent for polymerization because of its good performance in the polymerization (monomer solubility, boiling point, moisture content, etc.). All of these diols are

commercially available and used as received. 1,6-Hexanediol dipropiolates (HDP) and 2-ethyl-1,3-hexanediol dipropiolates (EHDP) are synthesized from 1,6-hexanediol, 2-ethyl-1,3-hexanediol and propiolic acid. Under mild conditions (2% DBU, 60 °C, 12 h), we obtained the title polymers **P1** to **P18** in 99% yields. These polymers have weight-average molecular weights of 3.2 to 42.1 kDa and dispersities of 1.4 to 3.0. The low M_w polymer of linear primary diol DD maybe due to the relative insolubility of DD in MeCN, while in a good solvent for DD such as DMSO and DMF, the resulting polymer tends to cross-link. The polymerization proceeding for 12 h was long enough for the secondary diols to react with COS and alkynes (the low conversion of alkynes in **4** was because the reaction of isopropanol, COS and methyl propiolate was conducted at 25 °C in only 2 h). Thus, the difference in the M_w also depends on the solubility of the diols. Because of the poor solubility of diols with long carbon chains in solvents like MeCN and DCM in which polymers have better solubility, it is quite hard to gain polymers with higher molecular weight from such diols, thus we didn't make many attempts for the polymerization of long carbon chain diols, COS and dipropiolates. But it's suggested that those polymers may have stronger crystallinity from previous work. At low temperature (*e.g.*, 25 °C), the M_w of **P4** gained in 12 h would decrease to about 8.8 kDa (with $D = 1.9$). Reducing the reaction time is also not conducive to the increase of M_w , (*e.g.*, 4 h), and the M_w of **P4** gained under the same conditions is about 11.3 kDa (with $D = 2.4$). All of these polymers possess well-defined and pre-designed chain struc-

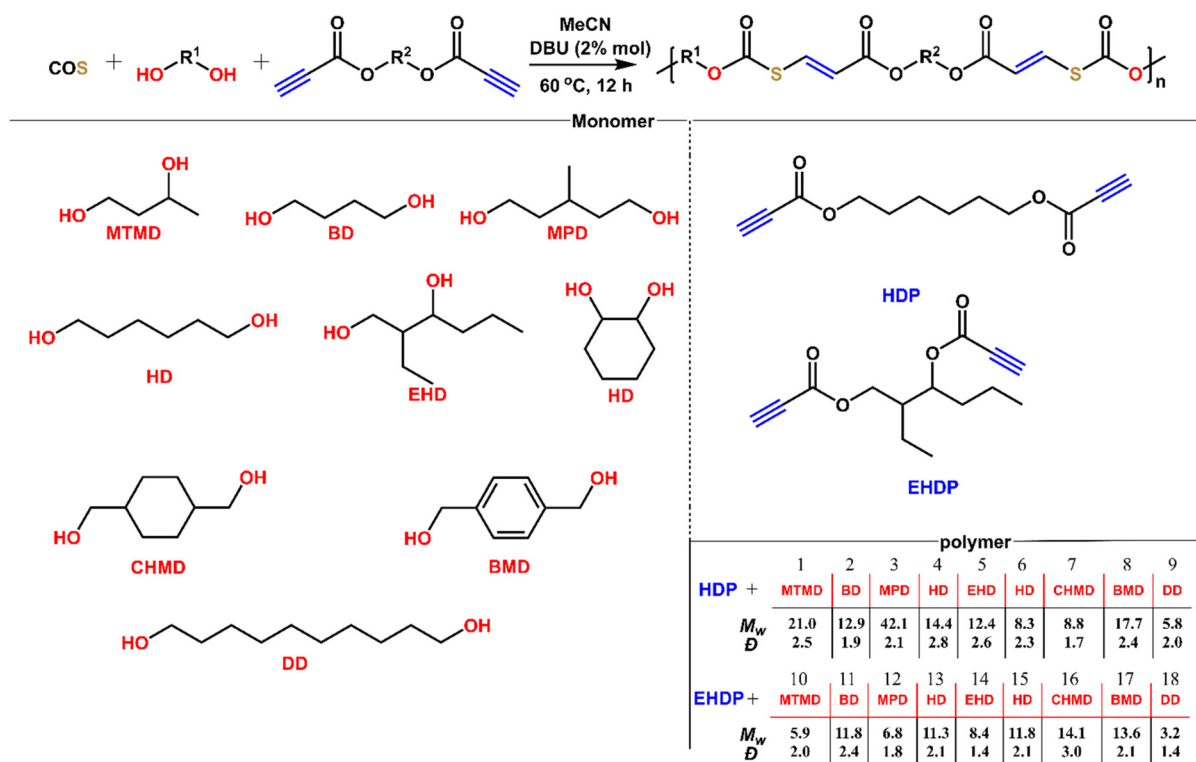


Fig. 6 Synthesis of a series of polymers from diols, dipropiolates, and COS.

tures according to NMR analysis (Fig. S47–S66[†]), in which each repeating unit contains thiocarbonate and ester groups and C=C bonds. The controlled experiment confirmed that

the polymerization did not occur without a catalyst. Accordingly, the readily accessible monomers, mild polymerization conditions, and high efficiency reveal a facile and versatile method for polymer synthesis.

The thermodynamic properties of polymers were tested using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the results are shown in Table 2 and Fig. 7. The T_g of the polymer is mainly affected by the functional groups of the polymer and the number of methylene $-\text{CH}_2-$ units in the polymer main chain. The stronger the rigidity of the polymer chain and side groups, the higher the T_g . For example, for **P4** and **P7**, cyclohexane is more rigid than $-(\text{CH}_2)_4-$, so the T_g rises from 20.7 to 37.4 °C. The possible reason for T_g first increasing and then decreasing with the number of $-\text{CH}_2-$ units in the main chain (entries 1, 4 and 9, Table 2) is that the chain regularity increases while the density of the rigid groups (ester groups and thiocarbonate groups) decreases. The improvement of chain regularity will also increase the crystallization ability of the polymer. For instance, for linear primary diols such as HD, no obvious melting peak is observed in the DSC curve (Fig. S70[†]), indicating its low crystallization ability, while DD, a linear primary diol containing ten $-\text{CH}_2-$ groups, shows obvious crystallization ability (Fig. S75[†]), with a crystallization temperature (T_c) of 93.3 °C. At the same time, the thermal stability of the polymer increases with the length of the main chain (entries 2, 4 and 9, Table 2), indicating that the polymer's stability is mainly affected by the thiocarbonate groups. The greater the

Table 2 Polymerizations of HDP&EHDP/COS/diols catalysed by DBU at 60 °C^a

Entry	Diols	No.	M_w^b	D	T_g^c	$T_{d,5\%}^d$
1	MTMD	P1	21.0	2.5	10.0	218.5
2	BD	P2	12.9	1.9	9.7	230.9
3	MPD	P3	42.1	2.1	3.4	244.3
4	HD	P4	14.4	2.8	20.7	243.8
5	EHD	P5	12.4	2.6	8.4	230.9
6	CHD	P6	8.3	2.3	37.4	202.3
7	CHMD	P7	8.8	1.7	15.1	264.8
8	BMD	P8	17.7	2.4	22.1	232.8
9	DD	P9	5.8	2.0	5.3	281.2
10	MTMD	P10	5.9	2.0	-4.9	225.3
11	BD	P11	11.8	2.4	-24.4	236.2
12	MPD	P12	6.8	1.8	-6.7	215.9
13	HD	P13	11.3	2.1	2.8	244.6
14	EHD	P14	8.4	1.4	-10.2	219.4
15	CHD	P15	11.8	2.1	58.9	230.2
16	CHMD	P16	14.1	3.0	40.7	253.8
17	BMD	P17	13.6	2.1	41.2	214.6
18	DD	P18	3.2	1.4	-10.3	265.7

^aThe reactions were conducted in 12 h with [HDP]:[diol]:[COS]:[DBU] = 50:50:55:1 with MeCN as solvent. ^bThe molecular weight and distribution of polymers were determined by GPC with polystyrene standards. ^cThe glass transition temperature was determined by DSC. ^dThe decomposition (5 wt% polymer) temperature was determined by TGA.

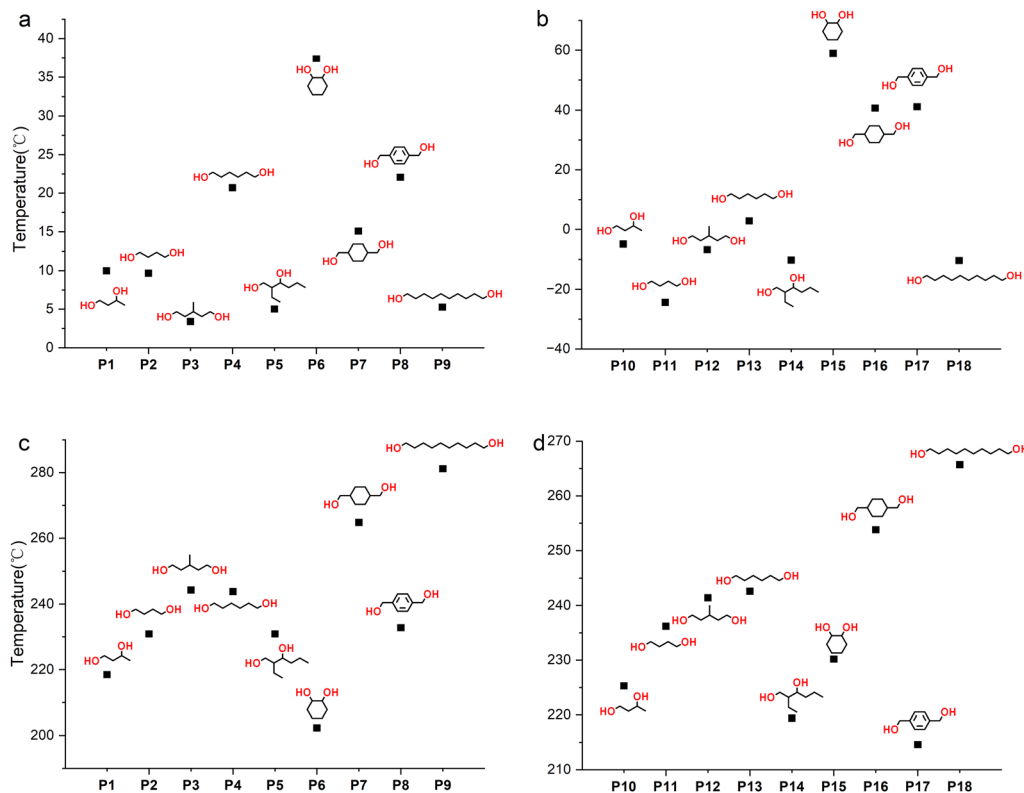


Fig. 7 (a) T_g values of **P1** to **P9**. (b) T_g values of **P10** to **P18**. (c) T_d values of **P1** to **P9**. (d) T_d values of **P10** to **P18**.

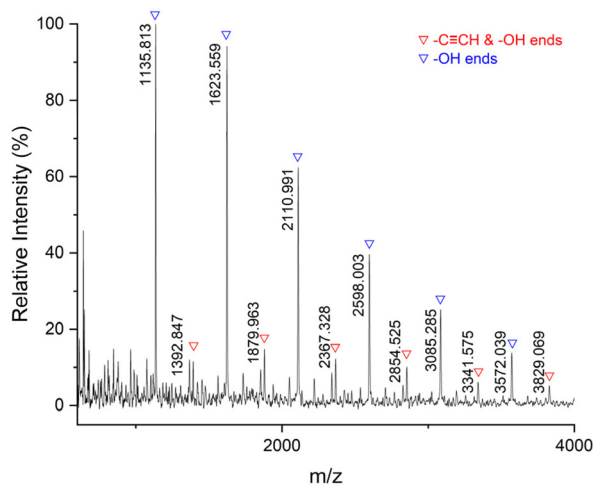


Fig. 8 MALDI-TOF-MS spectrum for P7 (entry 7, Table 2).

density of thiocarbonate groups, the easier it is for the polymer to decompose at high temperatures.

Subsequently, we tested the MALDI-TOF-MS of P7 (Fig. 8). There are mainly double $-OH$ terminal species $[(C_{22}H_{30}O_8S_2)_n + C_8H_{16}O_2 + Na^+] = [486.14 \times n + 144.12 + 22.99]$, accompanied by a small amount of $-C\equiv CH$ and $-OH$ terminal species $[(C_{22}H_{30}O_8S_2)_n + C_{21}H_{30}O_7S + H^+] = [486.14 \times n + 426.17 + 1.01]$. The thiocarbonate groups are not included at the ends of the polymer chains because the thiocarbonate groups are unstable and dissociate more easily.

Conclusions

Through the coupling reaction of hydroxyl/COS/activated $C\equiv C$ bonds, which is modular and efficient, we have obtained several small molecules (**1** to **21**) and macromolecules (**P1** to **P18**) in high yield. The significance of this method lies in its avoidance of unpleasant and expensive thiols, utilizing diols as readily available and sustainable building blocks. The process is performed under mild conditions, utilizing common organic bases as catalysts, ensuring atom-economical and environmentally conscious polymerization. The produced polymers possess in-chain esters, thiocarbonate units and $C=C$ bonds. These polymers are expected to become green materials in practice given their widely available raw materials and facile synthesis.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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