Chemical Science

Accepted Manuscript

Chemical Science

rsc.li/chemical-science

Volume 9
Number 1
7 January 2018
Pages 1-268

ISSN 2041-6539

ROYAL SOCIETY OF CHEMISTRY

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Facile Synthesis of Recyclable Polythioimidocarbonates *via* Aromatization-driven Alternating Copolymerization of *para*-Quinone Methide and Isothiocyanates

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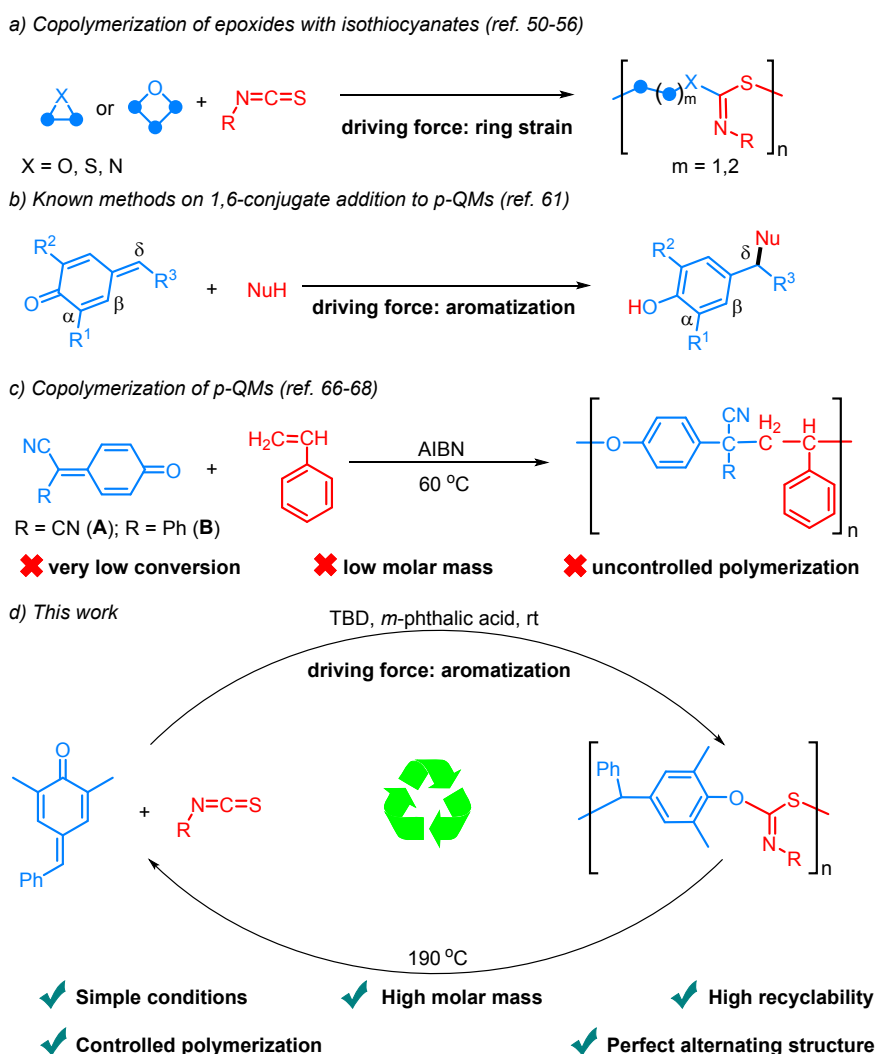
Abstract: The efficient and controllable alternating copolymerization of *para*-Quinone Methide *(p*-QM) is rare and challenging. The aromatization-driven alternating copolymerization of *p*-QM with isothiocyanates is explored for the first time under mild conditions. In the presence of the key catalyst *m*-phthalic acid and the initiator TBD, the reaction can efficiently produce completely alternating polythioimidocarbonates with narrow molecular weight distributions and high molar mass (up to 103.6 kg/mol). Experimental studies and DFT calculations suggest that *m*-phthalic acid plays a synergistic catalytic role. Remarkably, the copolymers can be recycled back into the monomers with excellent yields under vacuum at a temperature of 190 °C in just a few minutes without solvents or catalysts.

Owing to the inexpensive availability, processing versatility and exceptional mechanical properties, synthetic polymers have found numerous applications across various domains of our daily lives. The extensive production and unregulated disposal of plastics, however, have led to significant economic and environmental repercussions due to their limited degradation and recyclability.[1-6] Efforts to tackle these challenges encompass mechanical recycling,[7-9] upcycling towards value-added chemicals,[10-14] and chemical recycling to monomer.[15-18] Among these approaches, chemical recycling to monomers is particularly appealing due to its potential for regenerating polymers with virgin-quality and reducing the demand for raw materials.[19-31] To address the end-of-life challenge of polymers and safeguard finite natural resources, the development of a circular plastics economy through chemical recycling to monomer is essential for advancing sustainability efforts.[32-33]

Sulfur-containing polymers exhibit exceptional characteristics, including optical, mechanical, and metal-adsorbing properties.[34-35] Consequently, significant efforts have been dedicated to the

preparation of such polymers.[36-49] Among these methods, the ring-opening copolymerization (ROCOP) of strained heterocycles with isothiocyanates stands out as one of the most efficient approaches (Scheme 1a).[50-56] Feng, Xiong, Wu, and Zhao's group independently reported the synthesis of polythioimidocarbonates through the ROCOP of isothiocyanates and epoxides.[50-52] Subsequently, the scope of heterocycle monomer was expanded to episulfides and aziridines by other groups.[53-55] Very recently, Plajer and coworkers reported the alternating copolymerization of oxetanes and isothiocyanates in the presence of a heterobimetallic catalyst.[56] Despite these elegant achievements, the recycling of the polymers was not investigated. In addition, all the reactions are driven by the relief of ring strain. Given the numerous applications of sulfur-containing polymers and the escalating issue of plastic pollution, there is an urgent need to explore new monomers and concepts for synthesizing recyclable sulfur-containing polymers.

a) *Copolymerization of epoxides with isothiocyanates (ref. 50-56)*

X = O, S, N

driving force: ring strain

m = 1,2

b) *Known methods on 1,6-conjugate addition to p-QMs (ref. 61)*

driving force: aromatization

c) *Copolymerization of p-QMs (ref. 66-68)*

R = CN (**A**); R = Ph (**B**)

AIBN
60 °C

✖ very low conversion   ✖ low molar mass   ✖ uncontrolled polymerization

d) *This work*

TBD, *m*-phthalic acid, rt

driving force: aromatization

190 °C

✔ **Simple conditions**   ✔ **High molar mass**   ✔ **High recyclability**

✔ **Controlled polymerization**   ✔ **Perfect alternating structure**

Scheme 1. Previous works and our reaction design

para-Quinone methides (*p*-QMs), which are structurally characterized by the unique assembly of carbonyl and olefinic moieties, have been widely observed in various natural products and recognized as reactive intermediates in organic synthesis, materials chemistry and biological processes.[57-58] The canonical cyclohexadienone form exhibits a pronounced inclination towards aromatization, thereby imparting enhanced electrophilicity and facilitating 1,6-conjugate addition.[59] Significant progress has been achieved in the past decade regarding the development of highly efficient catalytic systems that facilitate the addition of diverse nucleophiles to the δ position of *p*-QMs through an aromatization driving force (Scheme 1b).[60-61] Significantly, the homopolymerization of *p*-QMs *via* 1,6-conjugate addition has also been disclosed.[62-65] However, there are very few reports on the alternating copolymerization of *p*-QMs due to their exceptionally high reactivity and tendency for homopolymerization, resulting in the formation of copolymers in a random fashion. By taking advantage of the fact that *p*-QMs (**A, B**) are not homopolymerizable with radical initiators, Iwatsuki, Itoh and coworkers reported the interesting radical alternating copolymerization of *p*-QMs (**A, B**) with styrene, but the process exhibited limited conversion rates, low molar mass, and uncontrolled polymerization (Scheme 1c).[66-67] In the case of 7-cyano-7-(ethoxy carbonyl)-1,4-benzoquinone methide, which was capable of undergoing homopolymerization in the presence of a free radical initiator, it could only copolymerize with styrene in a random fashion.[68] Therefore, the development of efficient and controllable alternating copolymerization of *p*-QMs remains a great challenge. To achieve such reactions, two challenges must be overcome: firstly, the identification of suitable co-monomers exhibiting higher activity than *p*-QMs to inhibit their homopolymerization; secondly, the exploration of an appropriate catalytic system capable of activating the monomers, enhancing reaction efficiency, and simultaneously stabilizing the chain ends to prevent undesired side reactions. Considering the high reactivity and limited tendency for homopolymerization of isocyanates, we envisioned they might be ideal co-monomers for achieving alternating copolymerization with *p*-QMs. Herein, we report the first example of aromatization-driven anionic alternating copolymerization of *p*-QM and isothiocyanates under mild conditions. In the presence of the key catalyst *m*-phthalic acid and the initiator TBD, the reaction can efficiently produce completely alternating polythioimidocarbonates with narrow molecular weight distributions and high molar mass (up to 103.6 kg/mol, Scheme 1d). By utilizing the reversibility of 1,6-conjugate addition reactions of *p*-QMs,[69-72] the copolymers can be recycled back into monomers with excellent yields under vacuum at 190 °C in just a few minutes without solvents or catalysts.

Table 1. Alternating copolymerization results of *para*-quinone methide and isothiocyanates[a]
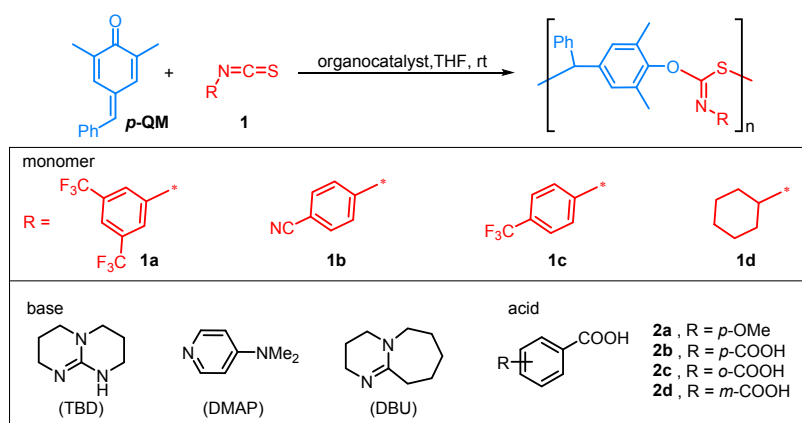
| entry	feeding	time (h)	conv. (%)[b]	$M_{n,theo}$ (kDa)[c]	$M_{n,GPC}$ (kDa)[d]	Đ[d]
1	*p*-QM/**1a**/DMAP (100/400/1)	1	93	44.9	68.9	1.57
2	*p*-QM/**1a**/DBU (100/400/1)	1	91	43.9	72.5	1.59
3	*p*-QM/**1a**/TBD (100/400/1)	1	99	47.8	60.7	1.47
4	*p*-QM/**1a**/TBD/4-Methoxyphenol (100/400/1/1)	0.6	99	47.8	27.1	1.46
5	*p*-QM/**1a**/TBD/benzyl alcohol (100/400/1/1)	5	93	44.9	45.7	1.43
6	*p*-QM/**1a**/TBD/**2a** (100/400/1/1)	1	91	43.9	54.7	1.46
7	*p*-QM/**1a**/TBD/**2b** (100/400/1/0.5)	1	91	43.9	50.9	1.47
8	*p*-QM/**1a**/TBD/**2c** (100/400/1/0.5)	1	91	43.9	40.3	1.40
9	*p*-QM/**1a**/TBD/**2d** (100/400/1/0.5)	0.8	97	46.8	51.2	1.23
10	*p*-QM/**1a**/TBD/**2d** (25/100/1/0.5)	0.2	96	11.7	13.6	1.15
11	*p*-QM/**1a**/TBD/**2d** (50/200/1/0.5)	0.3	99	23.9	29.6	1.16
12	*p*-QM/**1a**/TBD/**2d** (200/800/1/0.5)	6	96	92.5	103.6	1.25
13	*p*-QM/**1b**/TBD/**2d** (100/400/1/0.5)	2	99	36.8	28.0	1.40
14	*p*-QM/**1c**/TBD/**2d** (100/400/1/0.5)	1.5	99	41.1	29.5	1.36
15	*p*-QM/**1d**/TBD/**2d** (100/400/1/0.5)	2	89			

[a]The copolymerization was conducted in THF in a glovebox at 25 °C, $[p\text{-QM}]_0 = 0.5$ M. [b]Conversion of *p*-QM, determined by ^{1}H NMR spectroscopy. [c]Calculated molar mass based on $[p\text{-QM}]_0/[I]_0$ ratio and conversion. [d]M_n and Đ were determined by GPC analysis in THF.

The organocatalytic alternating copolymerization of *p*-QM and isothiocyanate **1a** was initially investigated with commonly used organic bases, namely 4-dimethylaminopyridine (DMAP), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (Table 1). To our delight, this alternating copolymerization proceeded smoothly and achieved more than 90% conversion in 1 h with [*p*-QM]:[**1a**]:[base] ratio of 100:400:1 in 0.5 M THF at room temperature

(for screening of the ratio of p-QM to isothiocyanate, see the SI). The obtained polymers, however, exhibited slightly broad molecular weight distributions ($Đ$) and number-average molecular weight ($M_{n,GPC}$) ranging from 60.7–72.5 kDa, which were considerably greater than the calculated theoretical $M_{n,theo}$ (Table 1, entries 1–3). The results indicated that the initiation efficiency was relatively low when organobase was employed as an initiator alone. Upon addition of 4-methoxyphenol or benzyl alcohol as chain transfer agents *via* the proton transfer reactions between the phenoxide intermediates and 4-methoxyphenol/benzyl alcohol,[73-75] the M_n of the polymer significantly decreased but molecular weight distributions of the resulting polymers were still high (entries 4–5). It may be caused by low initiating rate of organobase and side transesterification reactions. To let the molecular weight of the resulting polymer be under control further, it is necessary to relatively increase the main alternating polymerization rate and thereby suppress the side reactions. Thus, the incorporation of acid catalysts may be a potentially viable strategy: on the one hand, the utilization of an acid catalyst can activate p-QM, thereby enhancing the initiation efficiency; on the other hand, an acid catalyst can protonate phenoxide intermediate into less nucleophilic phenol, then undesired transesterification type side reactions become more difficult. However, the use of p-methoxybenzoic acid **2a**, p-phthalic acid **2b**, or o-phthalic acid **2c** as catalysts did not significantly improve the polymerization reaction ($Đ$ = 1.40–1.47, entries 6–8). Gratifyingly, m-phthalic acid **2d** provided the lowest dispersity ($Đ$ = 1.23) and exhibited good agreement between experimental and theoretical M_n (entry 9). In order to gain insights into the nature of m-phthalic acid **2d** in the copolymerization reaction, we employed ^{1}H NMR spectroscopy to observe its interaction with p-QM. The protons of p-QM exhibited a downfield shift upon treatment with 0.1 equiv. of **2d**, indicating that the p-QM monomer was activated by **2d** for the copolymerization reaction (Figure S12). Subsequently, various carboxylic acids were investigated for the copolymerization of p-QM and isothiocyanate **1a** at a fixed $[p$-QM$]_0/[$**1a**$]_0/[$TBD$]_0/[$acid$]_0$ ratio of 100:400:1:1 (Table S9). The results showed that both strong and weak carboxylic acids exhibited larger $Đ$s compared to m-phthalic acid **2d**. The good controlling behavior of **2d** may be attributed to its synergistic effect rather than its unique acidity.
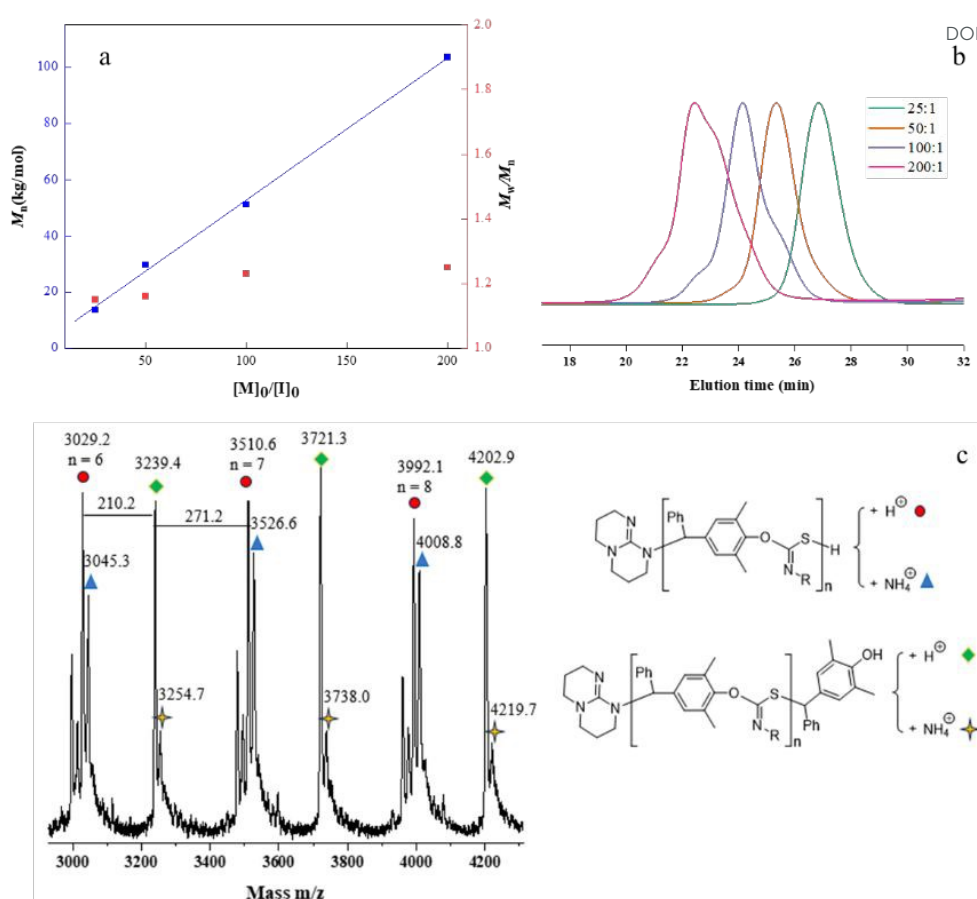
Figure 1. (a) Plots of M_n and $Đ$ *vs*. $[p\text{-QM}]_0/[\text{TBD}]_0$ ratio; (b) SEC traces of copolymers (color online); (c) MALDI-TOF MS spectrum of the low-molecular-weight P(p-QM-alt-**1a**).

The controlled nature of copolymerization was validated by conducting the reaction using varying ratios of $[p\text{-QM}]_0/[\text{TBD}]_0$ ranging from 25 to 200. The polymerizations all achieved high conversions. $M_{n,\text{GPC}}$ of the polymers increased linearly with increasing $[p\text{-QM}]_0/[\text{TBD}]_0$ ratio, while maintaining low $Đ$s (1.15−1.25) (entries 9-12, Figure 1a-1b). Notably, at $[p\text{-QM}]_0/[\text{TBD}]_0 = 200:1$, the resulting polymer can achieve a number average molecular weight of 103.6 kDa with a dispersity of 1.25 (entry 12). The alternating sequence of the resulting p-QM/**1a** copolymer was confirmed through MALDI-TOF MS. As shown in Figure 1c, the four distributions of equal intervals were observed, and the interval value (m/z = 481.4) matches the mass of p-QM and **1a** repeating units. Therefore, it can be inferred that a polymer chain exhibits a highly alternating sequence of p-QM and **1a**. The four populations correspond to two different chain ends, with two of them having an extra p-QM unit. The two populations terminate with **1a**, which can be described by the formula: $[\text{TBD}+(p\text{-QM}+\textbf{1a})_n]$ associated with two distinct cations of H^+ or NH_4^+. The other two populations end with p-QM, characterized by the equation $[\text{TBD}+(p\text{-QM}+\textbf{1a})_n+p\text{-QM}]$, and are also linked to either H^+ or NH_4^+. The presence of a TBD molecule in the polymer chains indicates that

copolymerization is initiated by TBD, which can be further confirmed by the distinct characteristic

peaks of TBD in the ^{1}H NMR spectrum of the resulting polymer when the ratio of monomer to TBD

is 15 (Figure S10). The structure of the copolymer was further analyzed by ^{1}H NMR, ^{13}C NMR and

FTIR. As shown in Figure 2a, the molar ratio of p-QM to **1a** in the copolymer is equal to 1:1 and

the characteristic resonances of p-QM homopolymerization at 5.6 ppm (Figure S11) were not

observed, indicating a completely alternating structure. The presence of a ^{13}C NMR signal at 150

ppm (Figure 2b) confirmed the formation of O(S)C=N units instead of O(N)C=S, which exhibited

a signal around 187 ppm.[76] Additionally, FTIR analysis further supported the existence of O(S)C=N

moieties. A prominent peak at 1630 cm^{-1} corresponding to C=N group was observed, while no

characteristic IR absorption of C=S group at approximately 1500 cm^{-1} was detected (Figure S3).[76]

Besides **1a**, this method can be readily adapted for the copolymerization of other aromatic

isothiocyanates with good control, including 4-CNC$_6$H$_4$ substituted isothiocyanate **1b** and 4-

CF$_3$C$_6$H$_4$ substituted isothiocyanate **1c** (entries 13-14). The resulting polythioimidocarbonates also

demonstrate a perfectly alternating structure (Figure S4-S9). However, the copolymerization of p-

QM with aliphatic isothiocyanate **1d** was unsuccessful, only yielding the p-QM homopolymer (entry

15, Figure S11). This can be attributed to the aromatic group's stronger electron-withdrawing ability

compared to that of the alkyl group, thereby resulting in higher reactivity of aromatic

isothiocyanates compared to aliphatic counterparts
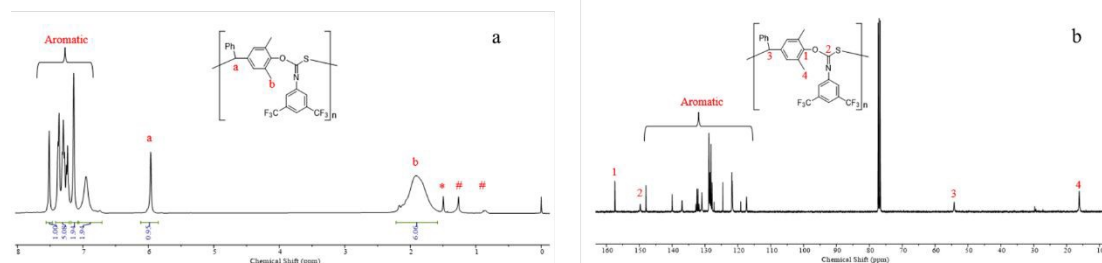
Figure 2. (a) ^{1}H NMR (CDCl$_3$) spectrum of P(p-QM-alt-**1a**) obtained by [p-QM]/[**1a**] /[TBD]/[**2d**] = 100/400/1/0.5; (b) ^{13}C NMR (CDCl$_3$) spectrum of P(p-QM-alt-**1a**) obtained by [p-QM]/[**1a**] /[TBD]/[**2d**] = 100/400/1/0.5. (*H$_2$O, #n-hexane).

To gather in-depth insight into the catalytic mechanism, we carried out several kinetic

experiments and measured the monomer conversion via ^{1}H NMR. As shown in Figure 3a, the

semilogarithmic plot displayed a linear relationship (R^2 = 0.99) indicative of a first order in p-QM

concentration. By varying the initial concentration of isothiocyanate **1a** from 1.5 to 3.0 M without

altering other reaction conditions, a zero-order dependence on **1a** concentration was confirmed

(Figure 3b). This suggests that **1a** insertion is not the rate-determining step during the

copolymerization process. Next, the initial TBD concentration was varied to explore the correlation

between k_{obs} and $[TBD]_0$, and all copolymerizations exhibited distinct first-order kinetics (Fig. S7). The plot of $\ln(k_{obs})$ against $\ln[TBD]_0$ was linear with a gradient of 1.2 (Figure 3c). It is noteworthy that an increase in the initial concentration of m-phthalic acid **2d** resulted in a decrease in the reaction rate. A double logarithm plot of the k_{obs} as a function of $[2d]_0$ was fit to a straight line with a slope of –0.2 (Figure 3d). We reasoned that the formation of an acid-base complex between **2d** and TBD could potentially reduce the reaction rate induced by TBD.[77]
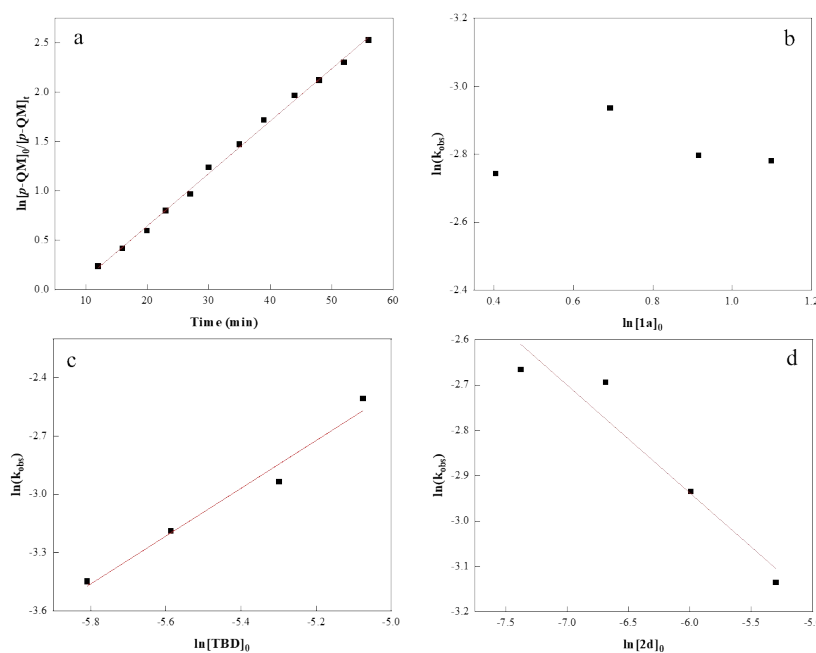
Figure 3. Kinetics for p-QM/isothiocyanate **1a** copolymerization (a) Kinetic plot of $\ln([p\text{-QM}]_0/[p\text{-QM}]_t)$ versus time at the $[p\text{-QM}]_0/[\mathbf{1a}]_0/[TBD]_0/[\mathbf{2d}]_0$ ratio of 100:400:1:0.5. (b) Plot of k_{obs} versus $[\mathbf{1a}]_0$. (c) Plot of $\ln(k_{obs})$ versus $\ln[TBD]_0$. (d) Plot of $\ln(k_{obs})$ versus $\ln[\mathbf{2d}]_0$.

Based on the experimental results obtained above, a plausible alternating copolymerization mechanism was proposed in Scheme 2. First, p-QM interacts with m-phthalic acid through hydrogen-bonding, followed by the nucleophilic attack of TBD to generate a phenol intermediate (**I**) driven by aromatization energy. The side reactions of transesterification and homopolymerization of p-QM are effectively suppressed due to the relatively weaker nucleophilicity of phenol compared to phenoxide. Subsequently, **I** reacts easily with isothiocyanates on the electron-deficient carbon to produce a sulfur anion **II** ($-C(=NR)S^-$). After the formation of a hydrogen bond between a fresh p-QM and another carboxyl group of m-phthalic acid, the activated p-QM is subjected to attack by the sulfur anion **II**. Thereafter, isothiocayanates and p-QM are alternatingly inserted to proceed the copolymerization, ultimately affording polythioimidocarbonates.
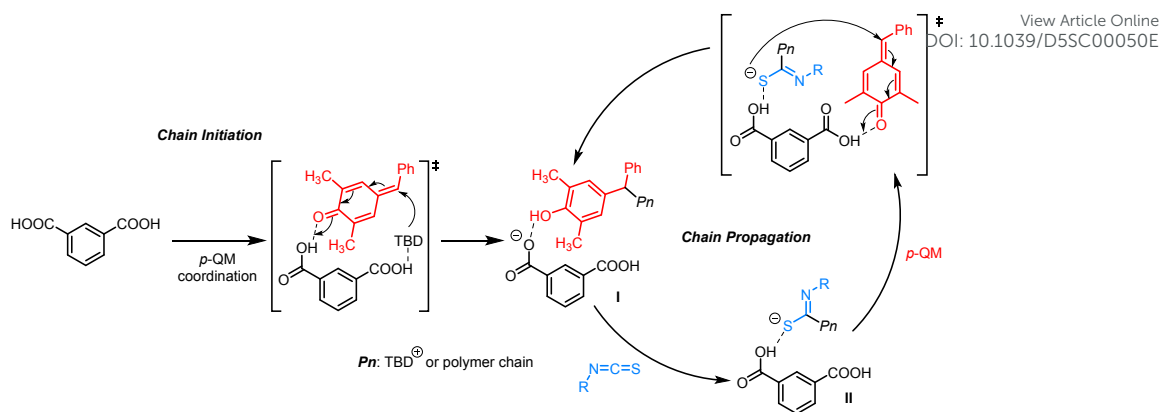
Scheme 2. Proposed mechanism for alternating copolymerization of *p*-QM and isothiocyanates

DFT calculations were also conducted to gain a better mechanistic insight into the proposed alternating copolymerization mechanism (Scheme 3).[78-79] At the initial period, the *p*-QM monomer forms a hydrogen bond with *m*-phthalic acid (**INT1**), resulting in a slight increase of Gibbs free energy compared with the initial state. After overcoming an activation free energy barrier of 14.56 kcal/mol (**TS1**), a phenol intermediate **INT2** is received through the nucleophilic addition of TBD to the activated *p*-QM with relative energy of –2.99 kcal/mol. To enhance computational efficiency, the addition product of TBD and *p*-QM was approximated as a 2,4,6-trimethylphenol. The insertion of isothiocyanate **1a** and the intermediate **INT2** spontaneously transforms into a more stable intermediate **INT3**, in which the phenol forms two hydrogen bonds with *m*-phthalic acid. A sulfur anion **INT4** is formed following the nucleophilic addition of 2,4,6-trimethylphenol to the electron-deficient carbon of isothiocyanate through **TS2** with an energy barrier of 11.97 kcal/mol. After a hydrogen bond is formed between an additional *p*-QM and *m*-phthalic acid (**IN5** to **IN6**), the nucleophilic addition of a sulfur anion to the activated *p*-QM affords **INT8** by overcoming an activation free energy barrier of 19.06 kcal/mol (**TS3** to **INT8**). Thus, the two carboxyl groups in *m*-phthalic acid play a synergistic catalytic role; one activates *p*-QM while the other stabilizes the nucleophilic phenoxide or sulfur anion during the propagation process. The energy profiles reveal that the nucleophilic addition of the sulfur anion to *p*-QM presents a significantly high total energy barrier of 19.06 kcal/mol, thereby identifying this step as the rate-determining step. This conclusion is in agreement with the kinetic study results presented in Figure 3.
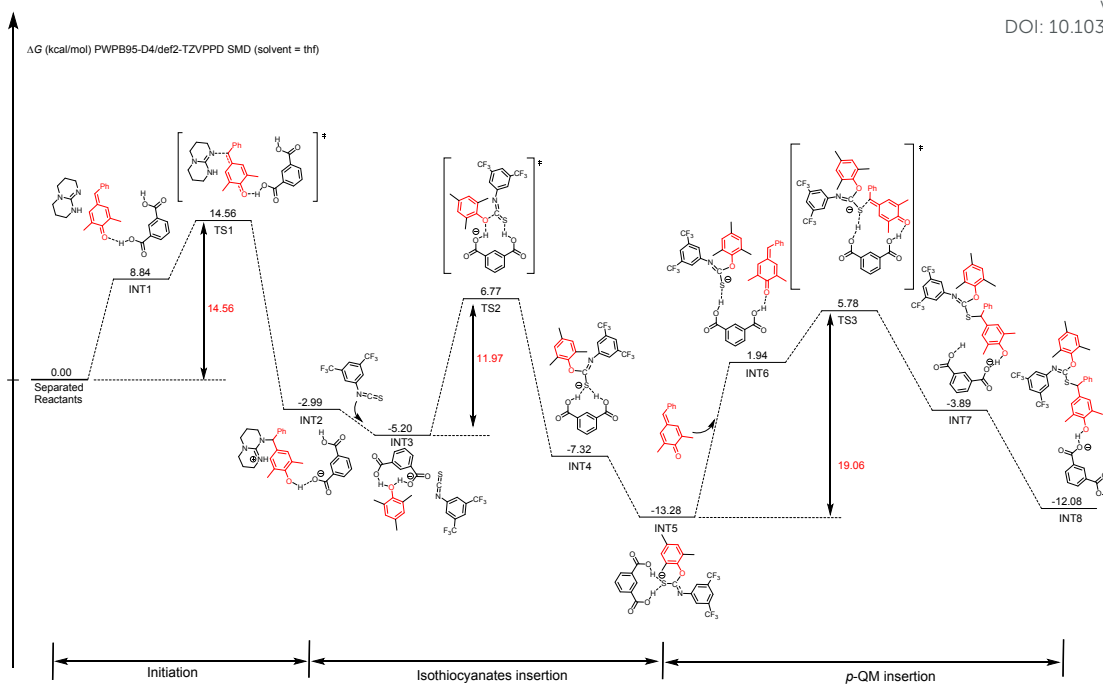
Scheme 3. Energy diagram of *p*-QM and **1a** copolymerization initiated by TBD.

To assess the recyclability of polythioimidocarbonates, we next examined the depolymerization capability using a copolymer comprising *p*-QM and **1a** as an illustrative example. This polymer was successfully depolymerized back to *p*-QM and **1a** with 92% yield using a commercially available sublimation device under vacuum at a temperature of 190 °C in just 2 minutes, without the need for solvents or catalysts (Figure 4). Thermogravimetric analysis (TGA) of these polymers showed that the thermal decomposition of all the copolymers initiates at approximately 175 °C (Figure S13B-S15B), which agrees with the recyclable behaviors at about 190 °C. The glass transition temperatures (T_gs) of these copolymers were surprisingly not observed on the differential scanning calorimetry (DSC) curves (Figure S13A-S15A). We speculated that the T_gs might be higher than their decomposition temperature because of their hard and brittle properties.
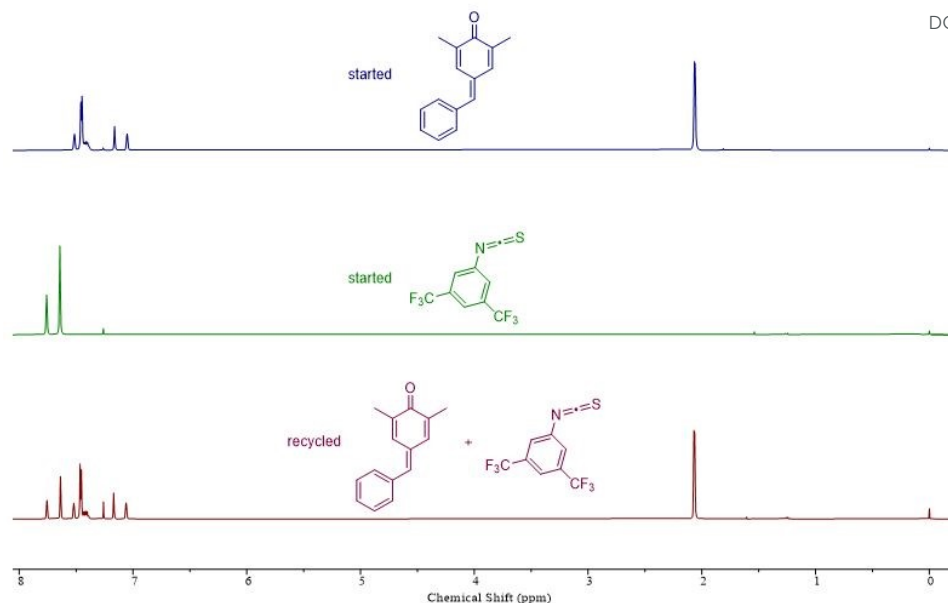
Figure 4. Recyclability study of the copolymer consisting of *p*-QM and **1a**.

In conclusion, we disclose the first example of alternating copolymerization of *p*-QM and isothiocyanates driven by aromatization under mild conditions. This method provides completely alternating polythioimidocarbonates with narrow molecular weight distributions and high molar mass. The utilization of *m*-phthalic acid as a catalyst is crucial for the reaction. Experimental studies and DFT calculations suggest that *m*-phthalic acid plays a synergistic catalytic role. Remarkably, the copolymers can be completely recycled back into the monomers with excellent yields under vacuum at a temperature of 190 °C in just a few minutes without solvents or catalysts. Further studies are currently underway in our laboratory to improve the physical properties of these copolymers and develop copolymerization of *p*-QM with other monomers.

Data availability

The data supporting this article have been included as part of the Supplementary Information.

Author contributions

C. W.-D. and D. S.-Y. performed and analyzed the experiments. Z. J., C. B., X. J., W. C.-M. and L. Q.-Z. participated in the early development of the project. C. W.-D. and W. J., and F. C.-A. conceived and designed the project. C. W.-D. overall supervised the project. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Competing intereats

The authors declare no competing interests.

Acknowledgements

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The data supporting this article have been included as part of the Supplementary Information.