Supporting Information

Reactive separation of β-bromoethylbenzene from α-β-bromoethylbenzene mixtures: A Zn²⁺-mediated radical polymerization mechanism

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Contents

1. Experimental methods

1.1 Reagents

α-bromoethylbenzene (97%), β-bromoethylbenzene (98%), styrene (99.5%), ZnO (99.9%), $Zn(NO_3)_2 \cdot 6H_2O$ (99.9%), zinc (99.9%), $(CH_3COO)_2Zn \cdot 2H_2O$ (99.9%), $ZnCl_2$ (98%), $ZnSO_4 \cdot H_2O$ (99%), Fe_2O_3 (99.5%), $AlCl_3$ (99%), copper (99.9%), $Cu(NO_3)_2 \cdot 3H_2O$ (99%), Cu_2O (99%), TiO_2 (Anatase, 99.8%), γ-Al_2O_3 (99.9%), $AgNO_3$ (99.8%), KI (99.5%), $FeSO_4 \cdot 7H_2O$ (99%), n-octane (99%), dodecane (99%), n-hexane (99%), acetonitrile (99%), ethanol (99.5%) were purchased from Aladdin. FeO (90%), starch, nitric acid (68%), toluene (99%), N,N-dimethylformamide (DMF, 99.9%), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 98%) radical and diphenyl diselenide $((PhSe)_2, 96\%)$ radical were obtained from Macklin. Commercial reagents were used without any purification unless special instructions.

1.2 Activity tests

Nominal quality of ZnO, α-bromoethylbenzene, and/or β-bromoethylbenzene

were added into a clean test tube in sequence, then seal the tube with a rubber plug, and insert a thin PTFE tube below the liquid level. N_2 was injected through the PTFE tube to replace the air. 10 minutes later, place the test tube in an oil bath that had been preheated to a constant temperature, and start stirring. After the reaction, take out the test tube and immediately add 10 mL of n-hexane to disperse the pristine post-reaction solution. α-Bromoethylbenzene, β-bromoethylbenzene, and styrene were quantitatively analyzed by gas chromatography equipped with an HP-5 capillary column with an inner diameter of 0.32 mm, with toluene as the internal standard. And other products were qualitatively detected by GC-MS and quantitatively analyzed by the area normalization method. The selectivities of all products were calculated based on the conversion of α-bromoethylbenzene.

1.3 Reaction mechanisms of radical traps

A usual test of participation of radical mechanisms is the addition of radical traps, in the assumption that they will slow or stop radical reactions.[1]

Radical traps are essentially highly chemically unstable. Add a sufficient amount of radical traps to the system that generates radicals, and radical traps will quickly couple with the radical intermediates generated in the reaction process, to form more stable covalent bonds, which stabilizes the originally active radical intermediates with lone pair electrons.

The life of the coupling products of radical traps and radical intermediates is prolonged, hence the captured coupling products can be detected by mass spectrometry, nuclear magnetism, etc., to determine the structure of radical intermediates in the system.

At the same time, the coupling of radical traps with radical intermediate generated in reaction is a diffusion-controlled process.[2] The addition of radical traps will reduce the chemical reactivity of radical intermediates, leading to a significant decline in the concentration of the highly chemically active intermediates in the system, hindering the vital radical transfer process and reducing the reaction efficiency.

2. Effect of reaction conditions on the selective transformation of α-bromoethylbenzene by ZnO

2.1 Effect of the composition ratio of α-bromoethylbenzene to β-bromoethylbenzene in the feedstock

Effect of the composition ratio of α-bromoethylbenzene to β-bromoethylbenzene in the feedstock on the selective transformation was investigated by charging 1 mg ZnO into the mixture of α- and β-bromoethylbenzene with the variable mass fraction of α-bromoethylbenzene ($m_\alpha/m_{\alpha+\beta}$) from 0 to 100 wt%, and the results are shown in **Fig. S1**.

When $m_\alpha/m_{\alpha+\beta}$ is 0, that is, in pure β-bromoethylbenzene, the activity of ZnO to β-bromoethylbenzene is poor as previously discussed. As $m_\alpha/m_{\alpha+\beta}$ increases from 0.3 to 0.8, the conversion of β-bromoethylbenzene gradually rises from 6.3% to a maximum of 21.6%. The up-regulation of β-bromoethylbenzene conversion with the increasing ratio of α-bromoethylbenzene in the system may be because the higher concentration of α-isomer will improve the transformation efficiency of β-bromoethylbenzene, or because of the incremental unit concentration ratio of ZnO to β-bromoethylbenzene.

The conversion of α-bromoethylbenzene fluctuates more intensively with the alterable ratio of α-bromoethylbenzene to β-bromoethylbenzene in the feedstock. When $m_\alpha/m_{\alpha+\beta}$ rises from 0.05 to 0.4, the conversion of α-bromoethylbenzene grows from 72.9% to the maximum of 89%, which certificates that an appropriate augment in the concentration of α-isomer will boost the transformation efficiency. While continuing to increase $m_\alpha/m_{\alpha+\beta}$ to 0.9, the conversion of α-bromoethylbenzene drops to 52.7%, which is due to the feeding amount of ZnO is certain, whereas the concentration of α-bromoethylbenzene is gradually increasing, and the transformative capacity of the per-unit amount of ZnO in per unit time has reached saturated. Therefore, excessively increasing the concentration of α-bromoethylbenzene will result in a decrease in the transformation efficiency.

It is noteworthy that there is a mutation of α-bromoethylbenzene conversion from 73.7% to 52.7% when $m_\alpha/m_{\alpha+\beta}$ is between 1 to 0.9, which indicates that the dispersion effect of the added β-bromoethylbenzene suppresses the transformation reaction. This

phenomenon supports the reaction mechanism proposed in this work and will be fully discussed in **Section 2.5**.
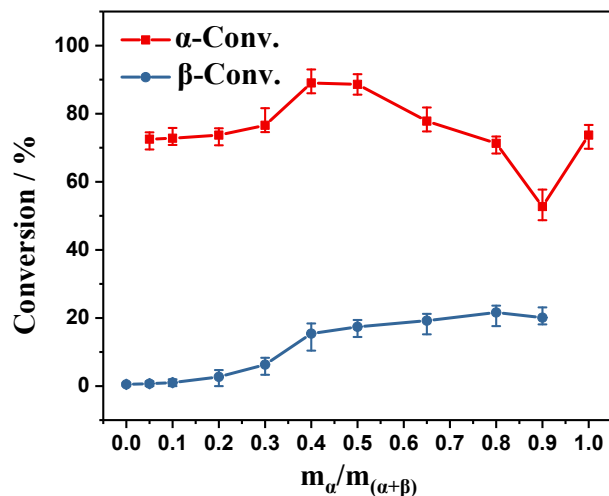
Fig S1. Effect of substrate composition on the transformation performance of ZnO. Reaction conditions: 1 g α-β-bromoethylbenzene mixtures with varied mass ratios, 1 mg ZnO, 60 °C, N_2 bubble, 60 min.
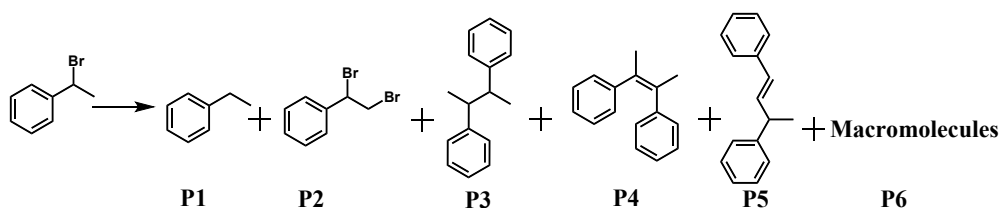
Scheme S1. Products for the reactions shown in Figs. 1b, 2a, 3, S1-S5, S12, and S15.

Table S1. Quantification of the radical polymerization products selectivity in **Fig. S1**.

$m_α/m_{α+β}$	P1/%	P2/%	P3/%	P4/%	P5/%	P6/%
0.05	12.6	5.8	12.7	10.4	26.6	30.9
0.1	10.9	4.2	10.8	9.6	28.2	36.3
0.2	11.3	5.7	13.1	8.8	25	36.1
0.3	10.8	5.2	12.5	9.5	27.1	34.9
0.4	11.2	4.1	11.8	10.6	24.7	37.6
0.5	11.8	4.9	12.2	9.6	23.1	38.4
0.65	10.4	5.4	12.6	11.1	22.7	37.8
0.8	10.9	5.7	11.9	10.0	21.7	39.8
0.9	10.3	4.7	12.6	9.7	23.2	39.5
1	8.5	3.6	10.4	13.1	26.7	37.7

Determined by the area normalization method. Reaction conditions: 1 g α-β-bromoethylbenzene mixtures with varied mass ratios, 1 mg ZnO, 60 °C, N_2 bubble, 60 min.

2.2 Effect of ZnO feeding amount

According to the previous tests on the synthesis of β-bromoethylbenzene from styrene and HBr, the yield of the by-product α-bromoethylbenzene was about 5-15%. To simulate the application of ZnO to the practical refinement of the crude β-bromoethylbenzene product, the content of α-bromoethylbenzene in the mixture of α- and β-isomers was set as 10 wt% unless otherwise specified.

α-Bromoethylbenzene and β-bromoethylbenzene display quite different responses with the variable ZnO from 0 to 2.5 mg. As shown in **Fig. S2**, the conversion of α-bromoethylbenzene rises rapidly from 8.7% to 100% as the gradual increase of ZnO feeding amount, while the conversion of β-bromoethylbenzene increases from 0% to 0.4% only when more than 1.8 mg ZnO is charged, indicating the conversion efficiency of β-bromoethylbenzene is much lower than that of α-isomer.

Furthermore, equivalent ZnO was charged into pure α-bromoethylbenzene or pure β-bromoethylbenzene, respectively, to directly compare the transformation selectivity of α or β- bromoethylbenzene by per unit mass of ZnO, and the results are shown in the illustrations in **Fig. S2**. As the dosage of ZnO increases from 0 to 1 mg, the conversion of α-bromoethylbenzene enhances from 7.6% to 73.7%, in contrast, the conversion of β-bromoethylbenzene increases by only 0.2%. The above results indicate that ZnO exerts a particular transformation selectivity for α-bromoethylbenzene, rather than β-bromoethylbenzene, which emphasizes the achievement of ZnO on the selective removal of by-product α-bromoethylbenzene in the mixture of α- and β-isomers.

Previous researches have mentioned that the main product of the elimination of halogenated aromatics by Zn-series catalysts is aromatic olefins.[3] However, this point reported in the literature does not receive approval from the transformation products distribution in our experiments (**Table S2**). Only when without ZnO, styrene with a selectivity of 23.9% can be detected. Furthermore, once ZnO is added, the selectivity of styrene quickly declines to 0 and remains undetectable with an even higher ZnO feed. Qualitative analysis of the products marks that the majority of the products are macromolecules containing more than two benzene rings.
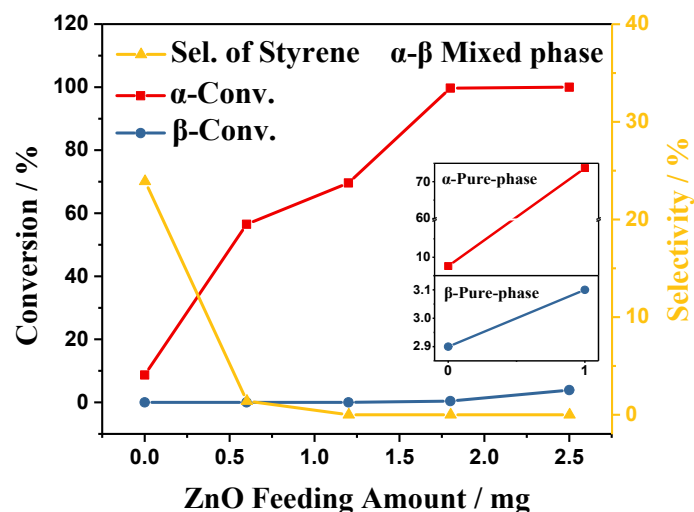
Fig S2. Effect of feeding amount on the transformation performance of ZnO. Reaction conditions: 1 g α or β pure phase, or 2 g mixed phase consisting 0.2 g α-bromoethylbenzene and 1.8 g β-bromoethylbenzene, 60 °C, N_2 bubble, 60 min.

Table S2. Quantification of the radical polymerization products selectivity in **Fig. S2**.

ZnO/mg	P1/%	P2/%	P3/%	P4/%	P5/%	P6/%
0	8.0	1.8	6.7	9.3	19.2	26.5
0.6	11.6	5.2	10.8	10.1	26.2	34.5
1.2	10.2	4.6	11.5	10.8	27.5	35.4
1.8	9.5	3.1	12.3	11.4	25.5	38.2
2.5	9.7	4.3	9.8	9.5	28.1	38.6

Determined by the area normalization method. Reaction conditions: 1 g α or β pure phase, or 2 g mixed phase consisting 0.2 g α-bromoethylbenzene and 1.8 g β-bromoethylbenzene, 60 °C, N_2 bubble, 60 min.

2.3 Effect of temperature

Effect of temperature on the selective transformation of α-bromoethylbenzene by ZnO, as shown in **Fig. S3**, is demarcated by 40 °C as the boundary. When the temperature is lower than 40 °C, the improvement of α-bromoethylbenzene conversion from 9.5% to 10.8% is quite limited as the increasing temperature. While an uprush of α-bromoethylbenzene conversion to 58.7% is recorded, when the temperature is raised to 50 °C. Then the conversion of α-bromoethylbenzene remains the upward trend as the rising temperature and reaches 100% at 120 °C.

In contrast, the augment in temperature has a weaker effect on the transformation of β-bromoethylbenzene by ZnO. The conversion of β-bromoethylbenzene keeps roughly unchanged when the temperature is below 80 °C, and increased to 3.7% at 120 °C, while α-bromoethylbenzene has been completely consumed at this temperature. Therefore, the best selective transformation effect and activity for α-bromoethylbenzene can be ensured in the range of 80-120 °C.

The selectivity of styrene is detected as only 0.67-0.77% below 40 °C and vanishes away with the increasing temperature between 50-120 °C. Other products are shown in **Table S3**.

Fig S3. Effect of temperature on the transformation performance of ZnO. Reaction conditions: 0.2 g α-bromoethylbenzene, 1.8 g β-bromoethylbenzene, 1 mg ZnO, N_2 bubble, 60 min.

Table S3. Quantification of the radical polymerization products selectivity in **Fig. S3**.

Temperature/°C	P1/%	P2/%	P3/%	P4/%	P5/%	P6/%
22	11.5	4.8	10.4	11.3	30.7	25.4
40	10.1	4.6	9.8	13.5	31.4	28.6
50	10.6	5.7	10.6	11.8	28.9	32.4
60	11.2	4.2	11.9	10.8	26.2	35.7
80	10.6	5.1	11.3	10.8	24.6	37.6
120	9.8	4.4	11.5	9.6	22.2	42.5

Determined by the area normalization method. Reaction conditions: 0.2 g α-bromoethylbenzene, 1.8 g β-bromoethylbenzene, 1mg ZnO, N_2 bubble, 60 min.

2.4 Effect of reaction time

Effect of reaction time is shown in **Fig. S4**, α-bromoethylbenzene is rapidly consumed within 80 min. On the contrary, the conversion of β-bromoethylbenzene is affected weakly by the prolongation of reaction time and enhances slightly only when the residence time is more than 120 min. Therefore, β-bromoethylbenzene should be separated in time after the ZnO-induced reactive separation process to avoid the loss of the target product. And the suitable reaction time range is 80-120 min at 60 °C.

The selectivity of styrene at the initial 20 minutes reaches the highest of 1.6% during the entire reaction, and gradually reduces to 0.1% with the prolongation of reaction time. Meanwhile, the yield of styrene progressively diminishes from 0.7% to 0.1%, demonstrating that as the reaction progresses, apart from the formation of styrene being suppressed, the generated styrene is incrementally consumed as well. Other products are shown in **Table S4**.
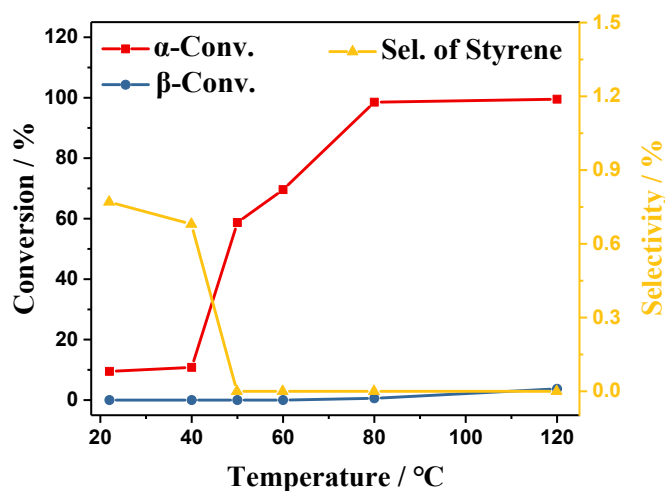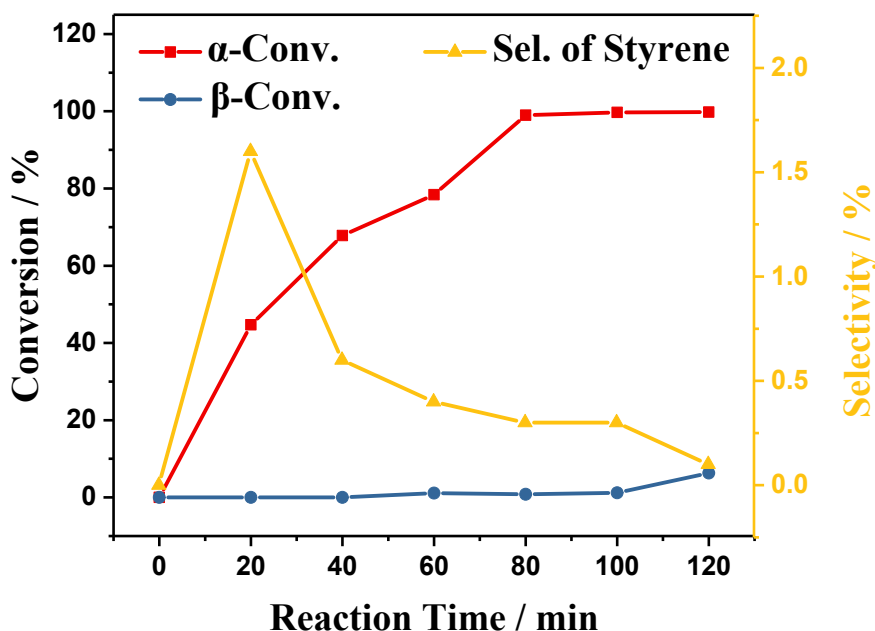

Fig S4. Effect of reaction time on the transformation performance of ZnO. Reaction conditions: 0.1 g α-bromoethylbenzene, 0.9 g β-bromoethylbenzene, 1 mg ZnO, N_2 bubble, 60 °C.

Table S4. Quantification of the radical polymerization products selectivity in **Fig. S4**.

Reaction time/min	P1/%	P2/%	P3/%	P4/%	P5/%	P6/%
0	10.8	5.9	10.1	10.7	32.4	28.7
20	11.3	4.5	11.7	10.4	29.2	31.6
40	11.9	4.8	10	9.3	30.1	33.2
60	10.9	4.2	10.8	9.6	28.2	36.3
80	11.6	5.1	10.2	10.3	26.5	36.3
100	10.2	4.9	11.5	10.1	25.4	37.9
120	9.3	3.7	10.2	11.7	29.1	36

Determined by the area normalization method. Reaction conditions: 0.1 g α-bromoethylbenzene, 0.9 g β-bromoethylbenzene, 1mg ZnO, N_2 bubble, 60 °C.

2.5 Effect of solvents

Solvents with different physicochemical properties were investigated in the radical polymerization of α-bromoethylbenzene, as shown in **Fig. S5**. Any additional solvent in the reaction remarkably cuts down the conversion of α-bromoethylbenzene, which is due to the cage effect brought by solvents.[4] That is, the surrounding solvent molecules produce a "cage", in which the diffusion of radicals is hindered, resulting in the inhibition of the radical transfer process. Moreover, radicals in the "cage" are prone to collide to cause radical termination, leading to a decline in the reactivity of radicals. Besides, this conclusion can also explain the mutation of α-bromoethylbenzene conversion shown in **Fig. S1** when $m_\alpha/m_{\alpha+\beta}$ alters between 0.9 and 1.

The polarity of solvents also intensely affects the reactivity of radicals.[5] The conversion of α-bromoethylbenzene in alkanes is higher than that in DMF and acetonitrile solvents, but the selectivity of styrene is the reverse. Alkanes are far less polar than DMF and acetonitrile, therefore radical reactions are more likely to occur in alkanes, resulting in the lower styrene selectivity. While the stronger polarity of DMF and acetonitrile inhibits radical reactions, but promotes the ionic process of halogenated hydrocarbon elimination, leading to an augment in the selectivity of styrene.

In addition, compared with the stable β-bromoethylbenzene, the solvolysis of α-bromoethylbenzene is conducted in ethanol to produce (1-ethoxy)-ethylbenzene with a selectivity of 90%. Therefore, the purification of β-bromoethylbenzene can be achieved

by ethanol as the additive because of the difference in boiling points between (1-ethoxy)-ethylbenzene and β-bromoethylbenzene.
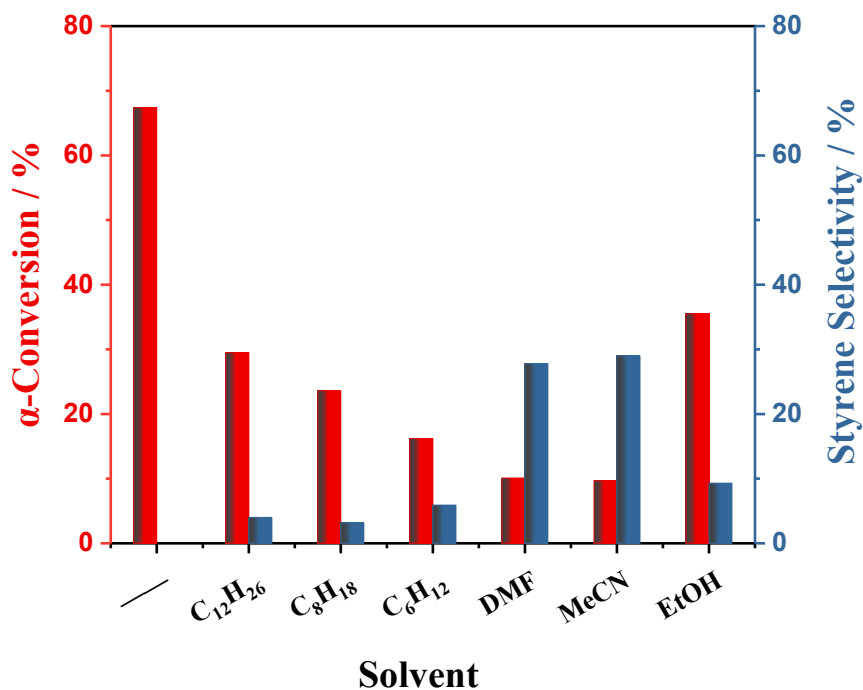

Fig S5. Effect of solvent on the transformation performance of ZnO. Reaction conditions: 0.5 g α-bromoethylbenzene, 0.5 g solvent, 1 mg ZnO, N$_2$ bubble, 60 min.

Table S5. Quantification of the radical polymerization products selectivity in **Fig. S5**.

Solvent	P1/%	P2/%	P3/%	P4/%	P5/%	P6/%
/	8.5	3.6	10.4	13.1	26.7	37.7
C$_{12}$H$_{26}$	6.3	3.1	11.2	12.6	27.9	33.1
C$_8$H$_{18}$	7.1	3.9	10.6	11.9	29.6	30.9
C$_6$H$_{12}$	6.7	3.4	11.1	12.3	31.2	26.4
DMF	4.2	2.2	8.4	8.6	18.9	14.7
MeCN	3.3	1.4	9.7	7.1	22	16.1
EtOH	0.7	0.3	0.8	1.4	1.8	0.5

Determined by the area normalization method. Reaction conditions: 0.5 g α-bromoethylbenzene, 0.5 g solvent, 1 mg ZnO, N$_2$ bubble, 60 min.
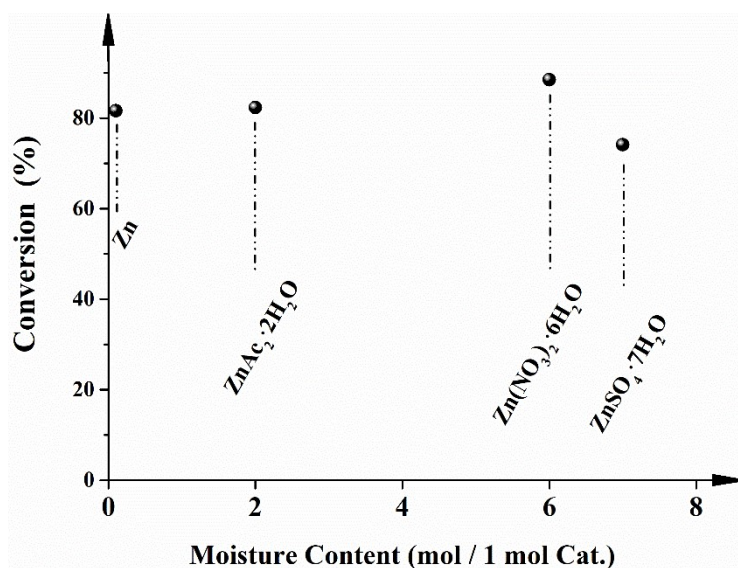
Fig S6. The relationship between the conversion of α-bromoethylbenzene and the moisture content of the catalysts used in Fig. 1b.

As shown in Fig. S6, the moisture content of the catalysts used in Fig. 1b has no effect on the radical polymerization activity (i.e., the conversion of α-bromoethylbenzene), suggesting that the presence of crystal water or a trace amount of physically adsorbed water on catalysts will not affect the Zn^{2+}-mediated radical polymerization rate.

3. General methods for the identification of bromine and products analysis

First, 1 mL of the original post-reaction solution of α-bromoethylbenzene and ZnO at 60 °C for 1 h was added into a test tube. The mixture of α-bromoethylbenzene and ZnO had turned orange after being treated at 60 °C for 60 min, so that the formation of Br_2 was presumed. Then drop about 2 mL of 0.1 mol/L KI aqueous solution into the test tube with shaking. After that, 5 mL of the clear starch aqueous solution was added into the test tube, and shake it well. At this time, the post-reaction solution in the test tube rapidly turned blue, confirming our conjecture. The schematic figure of the detection process was exhibited in **Scheme. S2**. In summary, it suggests that the brown-yellow substance produced during the reaction is bromine.
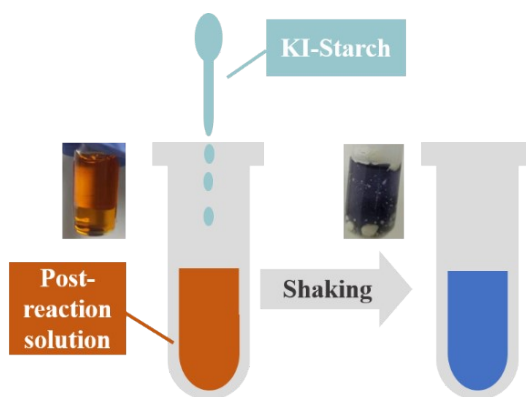
Scheme S2. Identification of bromine in the post-reaction solution using a KI-starch method.

The reactant had been completely coking after 60 minutes at 120 °C. Qualitative analysis of the products suggested a rather complex and diverse product composition. The structures of the main products are shown in **Fig. S7**.
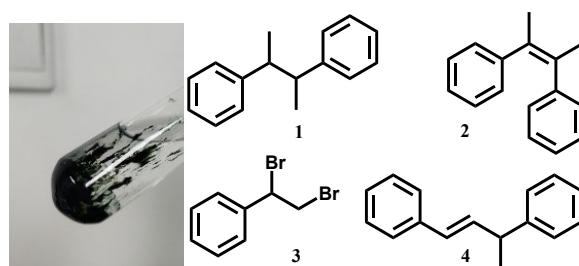

Fig S7. The coking product obtained from α-bromoethylbenzene and ZnO under 120 °C for 60 min and the specific structures of partial products.
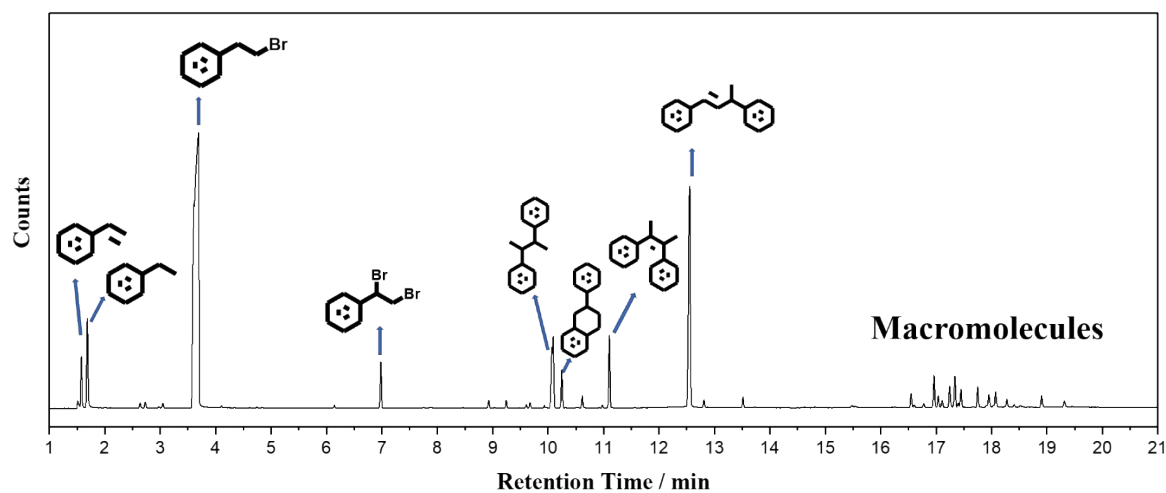
Fig S8. Gas chromatogram of the products obtained after the reaction of α- and β-bromoethylbenzene mixtures and ZnO at 60 ℃ for 120 min. Qualitative analysis of the products dissolved in DMF and n-hexane was recorded by GCMS. Detection conditions: HP-5MS capillary column, 110-350 ℃.
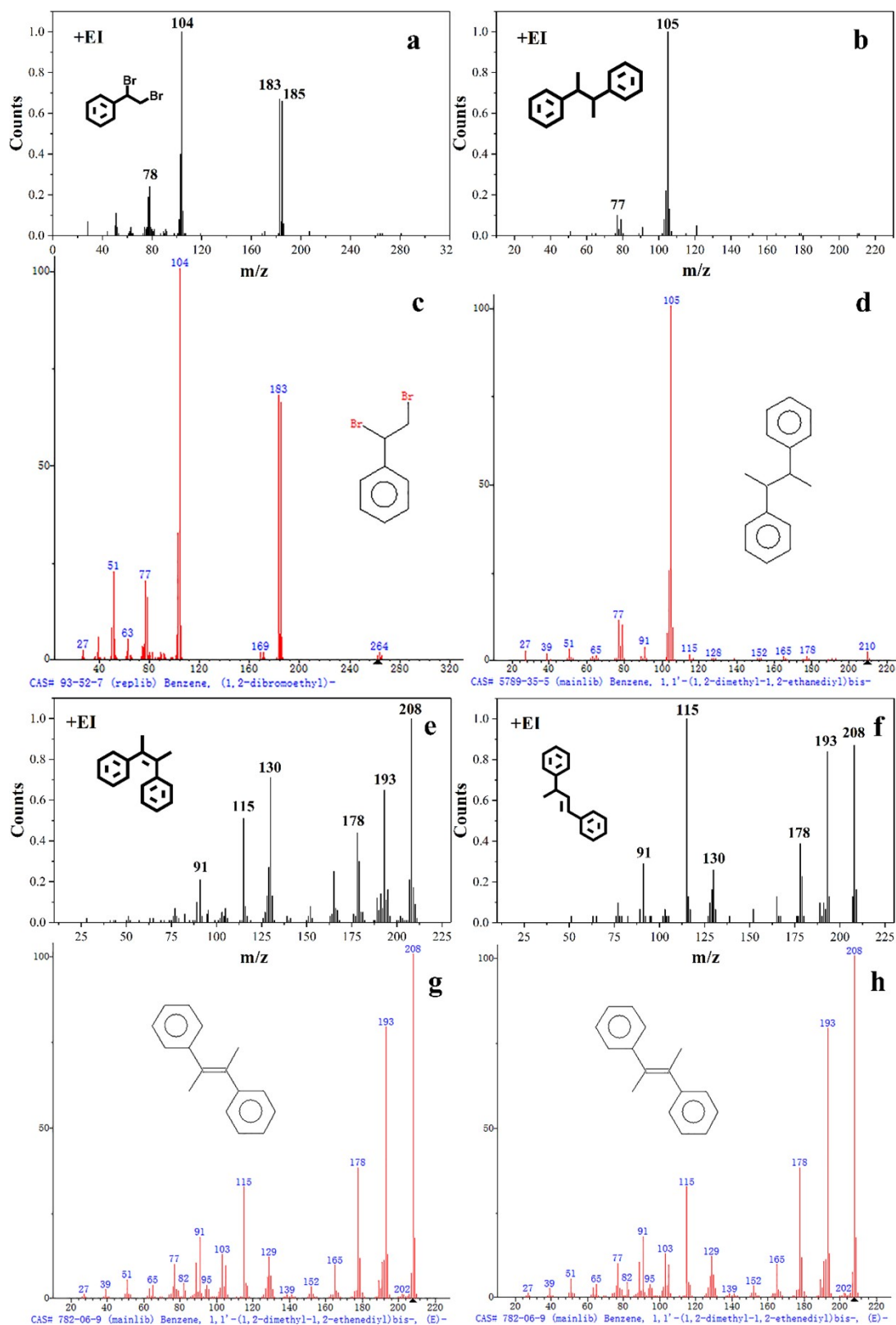
Fig S9. Experimental mass spectra of partial radical polymerization products and their respective standard mass spectra originated from the National Institute of Standards and Technology (https://webbook.nist.gov/chemistry/).
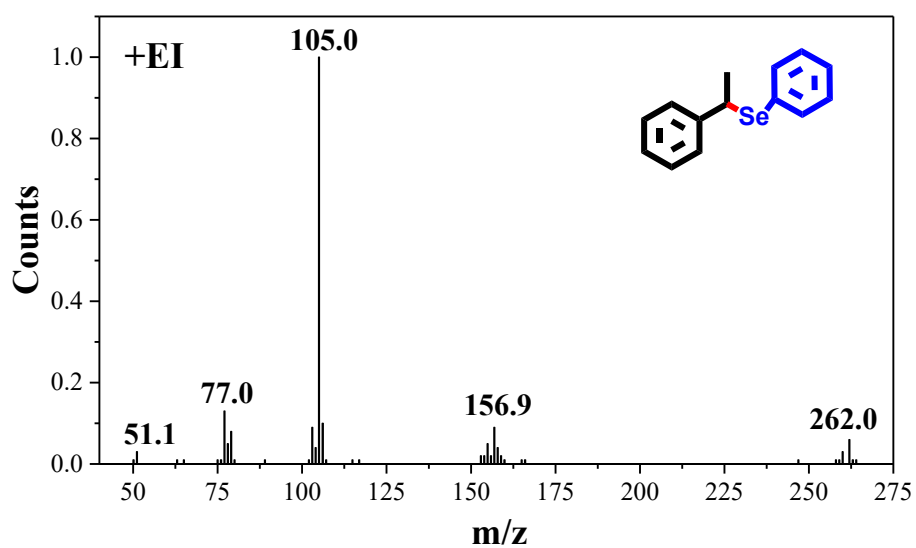
Fig S10. Mass spectra of the captured coupling product of (PhSe)2 radical trap and α-methylbenzyl radical.

The qualitative analysis of the captured coupling product of $(PhSe)_2$ radical trap and α-methylbenzyl radical referred to the distribution of mass fragments of the standard compound in published work (i.e., α-Methylbenzyl phenyl selenide, $C_{14}H_{14}Se$, mass spectrum: m/e 262 (M, 5%), 157 (5), 105(100), 77 (21)).[6]
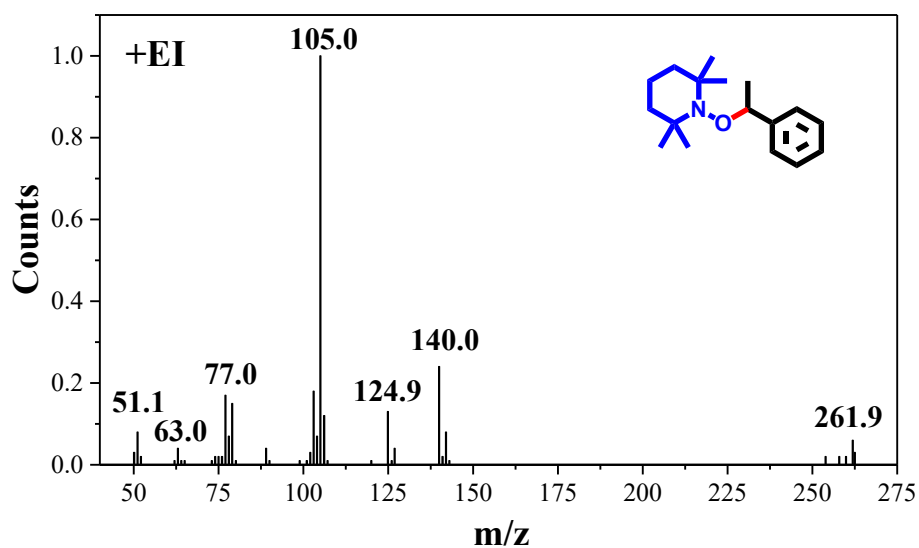

Fig S11. Mass spectra of the captured coupling product of TEMPO radical trap and α-methylbenzyl radical.

The qualitative analysis of the captured coupling product of TEMPO radical trap and α-methylbenzyl radical was determined by the identification of the feature of this compound, namely molecular ion peak detected as 261.9 as many published works reported that: "The formation of the TEMPO adduct of the 1-phenylethyl radical was confirmed by the presence of its molecular ion signal in the ESI-MS spectrum of the product solution". (2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine, $C_{17}H_{27}NO$, mass spectrum: found 261.9 (M^+) Molecular weight: 261.4).[7]
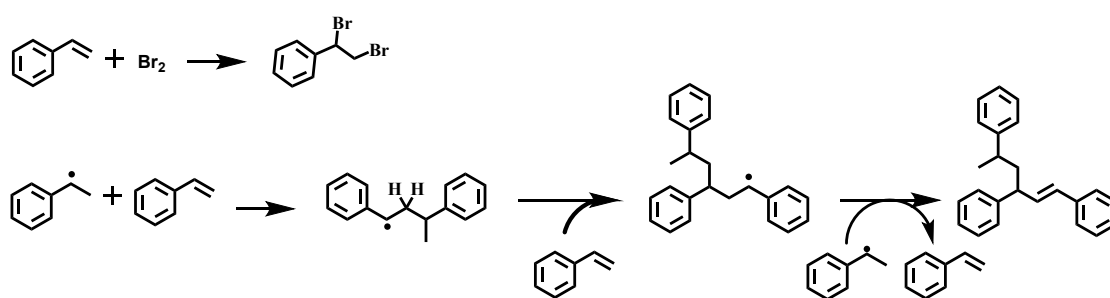
Scheme S3. The proposed formation mechanism of 1,2-dibromoethylbenzene and representative macromolecule involves the polymerization of styrene.
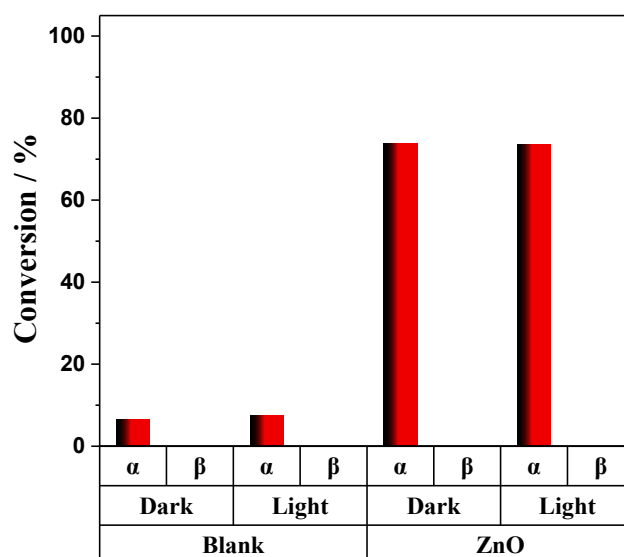

Fig S12. The control experiments performed in dark and in the presence of light. Reaction conditions: 0.2 g α-bromoethylbenzene, 1.8 g β-bromoethylbenzene, 1 mg ZnO or none, N_2 bubble, 60 °C, 60 min.

Table S6. Quantification of the radical polymerization products selectivity in **Fig. S12**

Conditions	Catalyst	P1/%	P2/%	P3/%	P4/%	P5/%	P6/%
Dark	Blank	4.1	0.8	5.3	6.7	11.0	12.9
Light	Blank	8.0	1.8	6.7	9.3	19.2	26.5
Dark	ZnO	12.9	5.7	12.3	10.2	24.8	34.1
Light	ZnO	11.2	4.2	11.9	10.8	26.2	35.7

Determined by the area normalization method.

In order to exclude radicals generated by light, the control experiments in dark have been performed. The product distribution and the conversion of α-bromoethylbenzene with or without ZnO are barely changed in the presence or absence of light, indicating that compared to ZnO the effect of light on this radical reaction can be negligible.
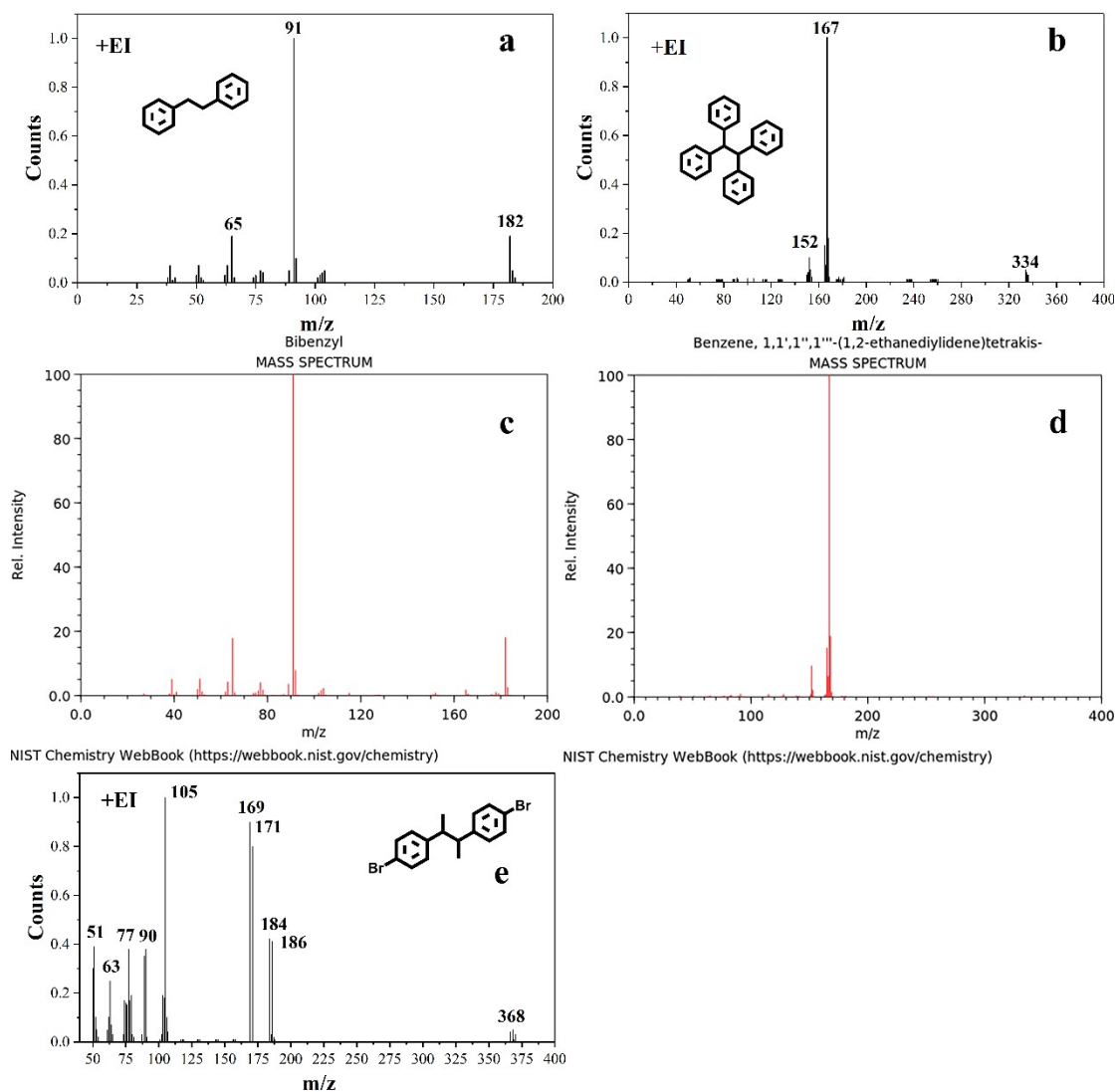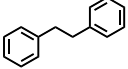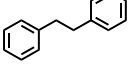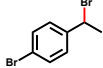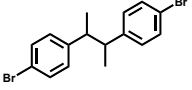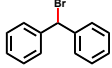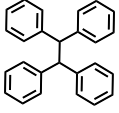
Fig S13. Experimental mass spectra of partial radical polymerization products and their respective standard mass spectra originated from the National Institute of Standards and Technology (https://webbook.nist.gov/chemistry/).

The representative radical polymerization products obtained from various substrates were qualitatively analyzed by GCMS. The distribution of mass spectra fragments of the tested mass spectrum of 1,2-diphenylethane (Fig. S13a) and 1,1,2,2-tetraphenylethane (Fig. S13b) matches well with their respective standard mass spectrum (Fig. S13c-d), affirming their formation in radical polymerization experiments. The generation of 4,4'-dibromo-α,α'-dimethyl-bibenzyl was confirmed by the presence of its molecular ion signal as 368 in the ESI-MS spectra of the product solution (Fig. S13e), i.e., 4,4'-dibromo-α,α'-dimethyl-bibenzyl, $C_{16}H_{16}Br_2$, mass

spectrum: found 368 (M$^+$) Molecular weight: 368.1).

Table S7. Substrate scope of Zn^{2+}-mediated radical polymerization.[a]

Substrate	Conversion (%)	Representative product [c]	Selectivity (%) [d]
	90.8		19.4
	99.2		21.7
	97.9		11.1
	99.5 [b]		7.8

[a] Reaction conditions: 0.3 g Substrate, N2 bubble, 80 °C, 3 mg ZnO, 60 min. [b] 5 mg ZnO, 120 min. [c] Only one of the representative radical polymerization products is shown. [d] Determined by the area normalization method.

The extension of this Zn^{2+}-mediated radical polymerization process to other substrates was eventually evaluated and the experimental results are shown in Table S7 and Fig. S13. The substitution of electron-donating groups (such as -H, -Ph, -X) for the benzene ring's H atom of α-bromoethylbenzene or -CH$_3$ of the benzylidene group does not hinder the radical polymerization catalyzed by Zn^{2+}, which is due to the stabilization of radical intermediates through electron conjugation by the electron-donating groups.[8] Consequently, the Zn^{2+}-mediated radical polymerization possesses a broad tolerance of functional groups.

Table S8. Quantification of the radical polymerization products selectivity in **Fig. 1b**.and **Fig. 3**.

Catalyst	P1/%	P2/%	P3/%	P4/%	P5/%	P6/%
ZnO	11.2	4.2	11.9	10.8	26.2	35.7
Zn	23.0	2.9	10.3	10.7	22.7	30.4
$(CH_3COO)_2Zn$	11.9	4.8	10.7	9.8	26.5	36.3
$Zn(NO_3)_2$	12.2	4.7	12.4	9.6	28.1	33.0
$ZnCl_2$	11.6	5.4	12.3	10.1	27.8	32.8
$ZnSO_4$	11.8	4.4	11.5	11.4	26.5	34.4
$AlCl_3$	5.9	4.2	11.2	10.3	27.3	41.1
$FeCl_3$	10.4	4.6	11.1	10.9	26.8	36.2
$Fe(NO_3)_3$	9.0	3.8	12.4	10.6	25.5	38.7
Fe_2O_3	10.2	4.3	11.9	11.2	26.9	35.5
$FeSO_4$	5.9	0.9	10.4	8.5	15.0	26.5
FeO	5.6	1.7	11.6	7.8	13.8	22.3
$Cu(NO_3)_2$	7.4	1.4	12.1	8.1	14.2	23.8
Cu_2O	6.2	2.1	10.8	9.2	15.4	27.1
Cu	6.8	2.0	11.2	9.4	13.2	25.4
TiO_2	5.6	0.6	10.7	8.5	14.6	19.8
γ-Al_2O_3	5.1	1.1	11.3	7.7	13.9	17.5

Determined by the area normalization method. Reaction conditions: 0.2 g α-bromoethylbenzene, 1.8 g β-bromoethylbenzene, 0.012 mmol catalyst, N_2 bubble, 60 °C, 60 min.

Table S9. Quantification of the radical polymerization products selectivity in **Fig. 2a**.

Substrate	P1/%	P2/%	P3/%	P4/%	P5/%	P6/%
Styrene + α	9.3	5.1	11.5	12.8	23.9	37.4
Styrene + α + ZnO	6.8	3.6	13.7	11.9	25.8	38.2

Determined by the area normalization method. Reaction conditions: 1 g styrene and 0.5 g α-bromoethylbenzene, N_2 bubble, 60 °C, 60 min.
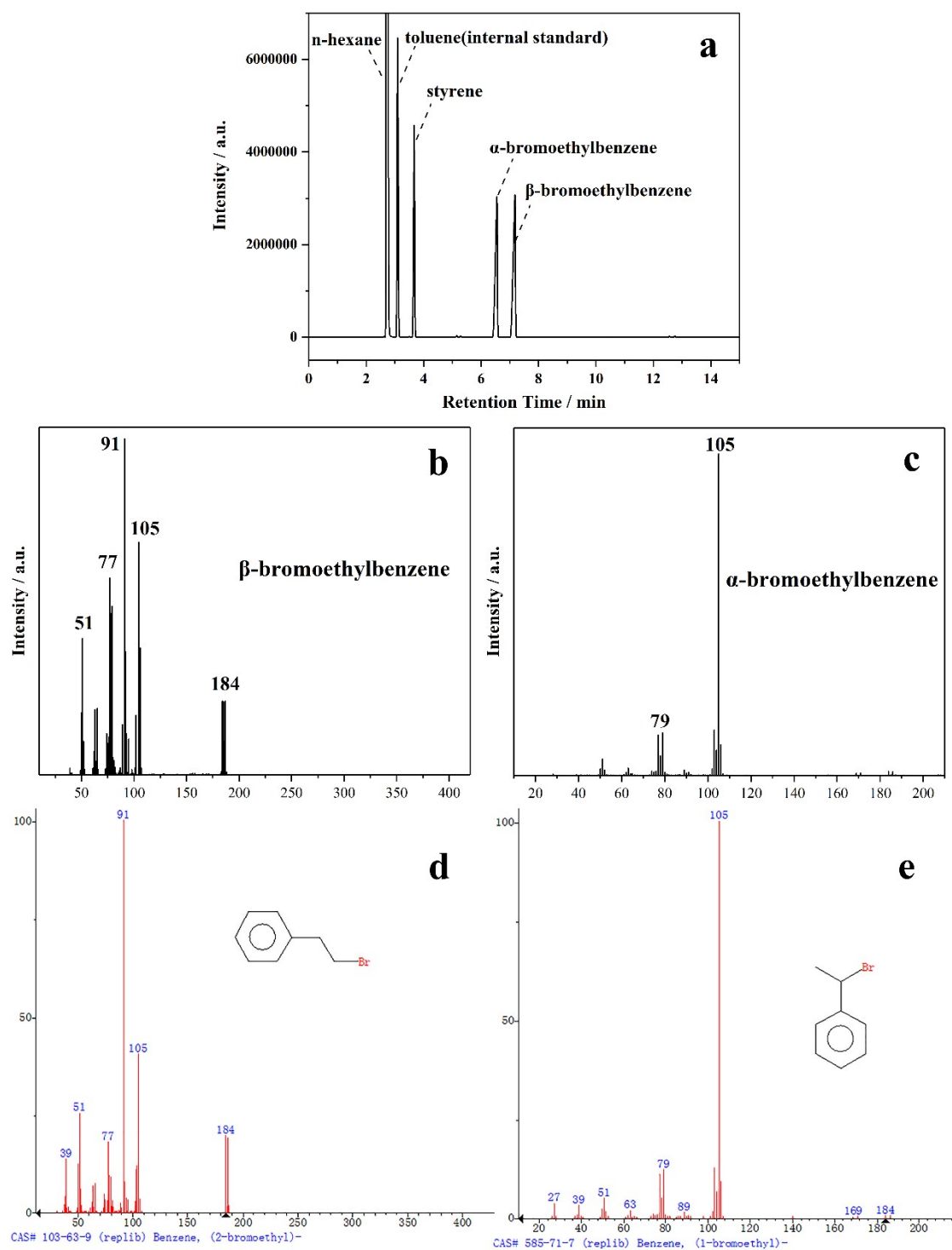
Fig S14. a. Gas chromatograms of the standard-solution of α-β-bromoethylbenzene mixtures. Detection conditions: HP-5 capillary column, 110-260 ℃. b-c. Experimental mass spectra of α- and β-bromoethylbenzene. d-e. Standard mass spectra of α- and β-bromoethylbenzene originated from the National Institute of Standards and Technology (https://webbook.nist.gov/chemistry/).
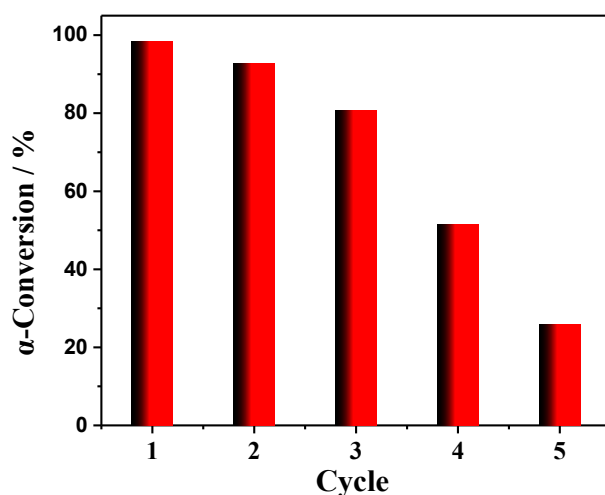
Fig S15. Conversion of α-bromoethylbenzene in the long-term stability experiment. Reaction conditions: 0.2 g α-bromoethylbenzene, 1.8 g β-bromoethylbenzene, 1 mg ZnO, N_2 bubble, 80 °C, 60 min.

Table S10. Quantification of the radical polymerization products selectivity in **Fig. S15.**

Cycle	P1/%	P2/%	P3/%	P4/%	P5/%	P6/%
1	10.6	5.1	11.3	10.8	24.6	37.6
2	9.0	4.7	10.8	10.1	26.5	38.9
3	6.7	4.1	8.5	11.8	25.4	43.5
4	3.3	2.8	4.6	8.3	22.7	58.3
5	2.1	1.3	3.9	4.2	15.1	73.4

Determined by the area normalization method. Reaction conditions: 0.2 g α-bromoethylbenzene, 1.8 g β-bromoethylbenzene, 1 mg ZnO, N_2 bubble, 80 °C, 60 min.

Since the homogeneous active species (Zn^{2+}) is hard to be separated from the macromolecules with two or more aromatic rings and higher boiling points, a long-term stability experiment by repeatedly feeding α-bromoethylbenzene instead of recycling tests was conducted to verify the long-term performance of the catalyst. After ending each 60-minute cycle, another 0.2g of α-bromoethylbenzene was immediately added to the reaction mixture to start a new cycle. The conversion of α-bromoethylbenzene in

the Nth cycle was calculated on basis of the following equations:

$$Conversion\ in\ the\ N^{th}\ cycle\ (\%)$$
$$= (1 - \frac{\alpha\ remaining\ in\ the\ N^{th}\ cycle - \alpha\ remaining\ in\ the\ ($$
$$\alpha\ fed\ in\ the\ N^{th}\ cycle$$
$$) \times 100$$

As shown in Fig. S15 and Table S9, the conversion of α-bromoethylbenzene decreases during the long-term experiment. This might be due to the continuous accumulation of macromolecules in the reaction system (further polymerization or even coking), leading to a decreased amount of Zn^{2+} species in the solution phase.

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