



Super-Grignard reagents ($R_2Mg \cdot LiCl$) mediated covalent-anionic-radical polymerization capable of low \mathcal{D} and reactive hydrogen compatibility

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ARTICLE INFO

Article history:

Received 23 October 2022

Revised 10 November 2022

Accepted 27 January 2023

Available online 3 February 2023

Keywords:

$R_2Mg \cdot LiCl$

Grignard reagent

Living polymerization

Covalent-anionic-radical polymerization

Block copolymerization

ABSTRACT

The precise synthesis of polymer with narrow molecular weight distribution (\mathcal{D}) and well-defined architectures is very essential to exploring the functions and properties of polymer materials. Here, a universal polymerization method capable of low \mathcal{D} and reactive hydrogen compatibility is reported by introducing super-Grignard reagents ($R_2Mg \cdot LiCl$) into polymer chemistry. Under mild conditions, various monomers, including nonpolar polystyrene and 4-methoxystyrene that cannot be initiated by Grignard reagents, and polar methacrylate, are successfully polymerized with full monomer conversion and low \mathcal{D} . This approach is amenable to wide varieties of initiators, polymerization temperature, and feed ratio, which makes it attractive for applications in polymer synthesis. By adding methanol and water during the polymerization process, the reactive hydrogen compatibility of this method is confirmed, which makes this method avoid the rigorous restriction on polymerization conditions of anionic polymerization. Moreover, chain extension polymerization and block copolymerization are achieved and demonstrate the livingness of chain propagation, enabling the facile synthesis of well-defined macromolecular architectures. This work therefore expands the methodology libraries of living polymerization, which may cause inspirations to polymer science.

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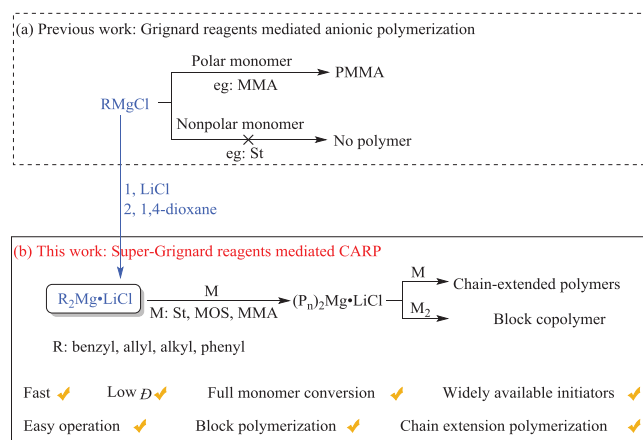
The 20th century witnessed the booming of synthetic polymeric materials which have become an indispensable part of human life due to their easy processing and diversified properties [1–4]. The development of polymerization methods is an important foundation to match the growing demand for synthetic polymeric materials [5–9]. In particular, the precise synthesis of polymer with narrow molecular weight distribution (\mathcal{D}) and well-defined architectures has been extensively studied for decades and contributed to the synthesis of commercial polymer products [10–14].

To achieve polymers with low \mathcal{D} , polymer chemists have paid considerable research efforts and living polymerization methods have been developed in the past decades [15–20]. In 1956, Szwarc used sodium naphthalenide as initiators at low temperature for the anionic polymerization of styrene (St), achieving the preparation of a “living polymer” which enables continued propagation when new monomer was added without chain termination and chain transfer

reactions [21–24]. The appearance of “living polymer” opens the door to the precise synthesis of well-defined polymer, and scientists realized the significance of this method to the development of polymer field. However, various living polymerization methods based on different polymerization species and mechanisms were reported until the end of the 20th century due to the existence of chain termination and chain transfer reaction [25–28]. For examples, Webster group achieved silyl ketene acetals mediated group transfer polymerization of α,β -unsaturated carbonyl compounds in 1983 [29,30]. Higashimura group achieved HI/I_2 mediated living cationic polymerization of isobutyl vinyl ether in 1984 [31,32]. Grubbs group achieved metallacyclobutanes mediated living ring-opening metathesis polymerization of norbornene in 1986 [33,34]. And various reversible deactivation radical polymerizations (RDRP) were reported in 1990s, such as alkyl halides and transition-metal complexes mediated atom transfer radical polymerization, nitroxides mediated nitroxide-mediated radical polymerization, and thiocarbonyl chain transfer agents mediated reversible addition-fragmentation chain transfer polymerization [35–46]. Although great progress has been witnessed in living polymerization field, there are still some difficulties to develop a method with multiple advantages, including widely available initiators and monomers,

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Scheme 1. (a) Grignard reagents and (b) super-Grignard reagents mediated polymerization.

mild polymerization conditions, easy operation, low \bar{D} and full monomer conversion, etc. For example, relatively rigorous experimental conditions (high purity monomer, reactive hydrogen forbidden, high vacuum system, low temperature, etc.) are required in living anionic polymerization, and bimolecular termination is unavoidable at high conversion in living radical polymerization. Consequently, developing new polymerization species different from solely anionic, cationic, or radical species is highly significant and desirable to promote polymer synthesis and polymeric materials. Recently, we reported a versatile Barbier covalent-anionic-radical polymerization (Barbier CARP) method by introducing the Barbier covalent-anionic-radical species into living polymerization, enabling polymers with low \bar{D} through polymerization of nonpolar monomer (e.g., St), where polymerization species exhibits all-in-one covalent-anionic-radical characteristics [47].

Grignard reagents, a well-known class of nucleophilic reagents prepared by Victor Grignard in 1900, can act as initiators for anionic polymerization of polar monomers (e.g., methyl methacrylate (MMA)) rather than nonpolar monomers (e.g., St and derivatives) (Scheme 1a) [22,48–50]. Recently, Knochel has gained great progress in the development of novel Grignard reagents, e.g., $R_2Mg \cdot LiCl$. In comparison with traditional Grignard reagents, $R_2Mg \cdot LiCl$ (referred as super-Grignard reagents) exhibit exceptional reactivity and allow challenging halogen-magnesium exchange reactions efficiently to prepare Grignard reagents, which even exhibit excellent compatibility with functional groups, such as carbonyl group and nitrile group [51]. Different from the outstanding

achievements of super-Grignard reagents in organic chemistry, super-Grignard reagents are rarely used in polymer synthesis, especially in the design of the living polymerization method. Based on the unique reactivity of super-Grignard reagents, we aim to introduce super-Grignard reagents into polymer chemistry with the development of a universal living polymerization capable of wide varieties of monomers and initiators, which will expand the methodology libraries of living polymerization and is therefore significant.

Herein, we report a universal polymerization method capable of low \bar{D} and reactive hydrogen compatibility by introducing super-Grignard reagents into polymer chemistry, achieving polymerization of polar monomers and nonpolar monomers under mild polymerization conditions (Scheme 1b). Different from anionic polymerization, this polymerization species exhibits all-in-one covalent-anionic-radical characteristics with reactive hydrogen compatibility. Through this super-Grignard reagents mediated CARP, narrow distributed polymer with \bar{D} as low as 1.15 can be obtained under mild conditions with full monomer conversion. Meanwhile, block copolymerization and chain extension polymerization are successfully carried out to verify the livingness of the polymer chain end, which therefore enable potential utilizations of this polymerization in the synthesis of polymer materials.

To verify above hypothesis, polymerization of St was firstly carried out by using $i\text{-Pr}_2Mg \cdot LiCl$ as an initiator in THF under mild conditions, where relatively rigorous restrictions (e.g., low temperature, high purity and high vacuum system) are not required. As shown in Table 1, entries 1–6, narrowly distributed polystyrenes (PS) with \bar{D} as low as 1.15 were successfully prepared with full monomer conversion (>99%). The successful preparation of PS is confirmed by 1H NMR spectra, where broad polymer signals appear at 7.35~6.89, 6.86~6.21, and 2.38~1.08 ppm, accompanied with the disappearance of sharp signals of monomer at 7.40~7.21 and 6.73~5.21 ppm, respectively (Fig. S1 in Supporting information). According to MALDI-TOF-MS shown in Figs. 1A and B, the end groups of obtained PS are demonstrated to be isopropyl and hydrogen, which derives from the initiator and quencher methanol, respectively, indicating that the polymerization is initiated by $i\text{-Pr}_2Mg \cdot LiCl$ and terminated by proton hydrogen of methanol. As the temperature drops from 45 °C to 0 °C, M_n of PS increases gradually from 44.7 kg/mol to 93.9 and 179.7 kg/mol accompanied with low \bar{D} smaller than 1.20, which indicates well-controlled \bar{D} in this polymerization, even though the initiator efficiency is highly temperature dependent. Additionally, various super-Grignard reagents (alkyl, benzyl, allyl and phenyl) were carried out as initiators, where full monomer conversion can also be achieved, indicating

Table 1
Results of St polymerization by various super-Grignard reagents.^a

Entry	Initiator	α^b	T (°C)	Time	Conversion ^c	Yield ^d	M_w^e	M_n^e	M_w/M_n^e
1	$i\text{-Pr}_2Mg \cdot LiCl$	20	45	2 h	>99%	>99%	38,400	32,000	1.20
2	$i\text{-Pr}_2Mg \cdot LiCl$	50	45	2 h	>99%	>99%	52,800	44,700	1.18
3	$i\text{-Pr}_2Mg \cdot LiCl$	100	45	3 h	>99%	>99%	83,300	72,200	1.16
4	$i\text{-Pr}_2Mg \cdot LiCl$	200	45	10 h	>99%	>99%	275,000	238,400	1.15
5	$i\text{-Pr}_2Mg \cdot LiCl$	50	25	6 h	>99%	>99%	110,000	93,900	1.17
6	$i\text{-Pr}_2Mg \cdot LiCl$	50	0	20 h	>99%	>99%	213,900	179,700	1.19
7	$Et_2Mg \cdot LiCl$	50	45	1 h	>99%	>99%	145,500	122,000	1.19
8	$allyl_2Mg \cdot LiCl$	50	45	2 h	>99%	>99%	87,000	73,300	1.19
9	$Bn_2Mg \cdot LiCl$	50	45	10 min	>99%	>99%	48,800	39,600	1.23
10	$Ph_2Mg \cdot LiCl$	50	45	24 h	>99%	>99%	881,300	638,100	1.38
11	$i\text{-PrMgCl}$	50	45	24 h	–	–	–	–	–

^a Polymerization conditions: St (2 g, 1 equiv.), THF (4 mL).

^b $\alpha = [St]/[initiator]$.

^c Determined by comparison of the relative integrals in the 1H NMR spectrum of PS against St.

^d Isolated yield.

^e Determined by GPC in DMF using linear PS as calibration standard.

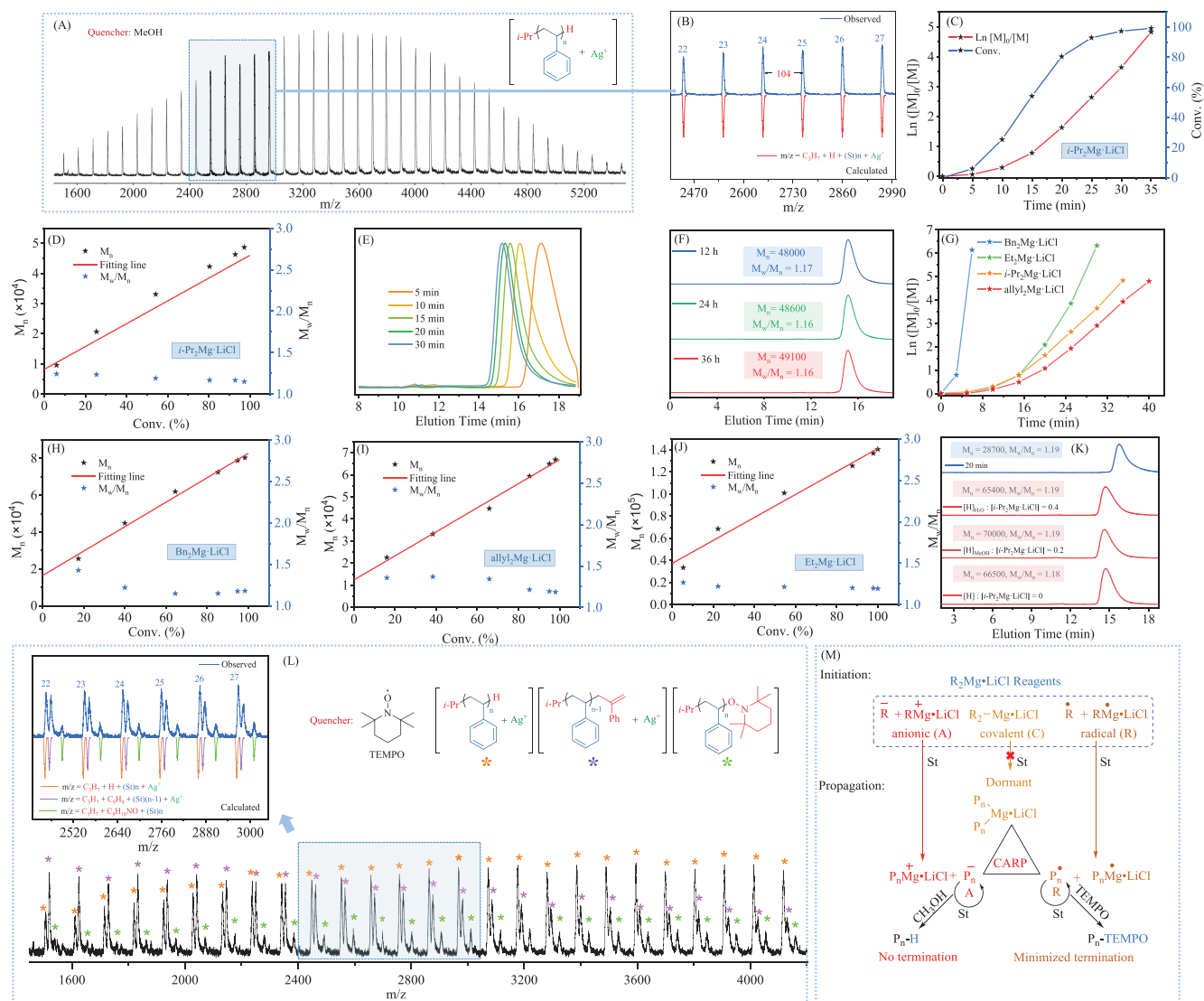


Fig. 1. (A) MALDI-TOF mass spectrum of PS quenched by MeOH with *i*-Pr₂Mg·LiCl as initiator. (B) Amplified MALDI-TOF mass spectrum of (A). (C) The relationship of ln([M]₀/[M]) vs. polymerization time, and the relationship of monomer conversion vs. polymerization time for polymerization of St by *i*-Pr₂Mg·LiCl at 45 °C. (D) The relationship of molecular weight vs. conversion for polymerization of St by *i*-Pr₂Mg·LiCl at 45 °C. (E) GPC traces of PS prepared by *i*-Pr₂Mg·LiCl at 45 °C for different polymerization times: 5 min, 10 min, 15 min, 20 min, and 30 min. (F) GPC traces of PS prepared by *i*-Pr₂Mg·LiCl at 45 °C for different polymerization times: 12 h, 24 h and 36 h. (G) The relationship of ln([M]₀/[M]) vs. polymerization time for polymerization of St by different super-Gignard reagents at 45 °C. (H) The relationship of molecular weight vs. conversion for polymerization of St by Bn₂Mg·LiCl at 0 °C. (I) The relationship of molecular weight vs. conversion for polymerization of St by allyl₂Mg·LiCl at 45 °C. (J) The relationship of molecular weight vs. conversion for polymerization of St by Et₂Mg·LiCl at 45 °C. (K) GPC curves of polymer obtained at 20 min (blue) and polymers obtained at 15 h with addition of different amounts of MeOH or H₂O (red). Polymerization conditions: 1) St (2 g, 1 equiv.), [St]/[*i*-Pr₂Mg·LiCl]=20, THF (4 mL), 45 °C, 20 min. 2) MeOH or H₂O (0.01 equiv.), r.t., 15 h. (L) MALDI-TOF mass spectrum of PS quenched by TEMPO with *i*-Pr₂Mg·LiCl as initiator. (M) Plausible mechanism of super-Gignard reagents mediated polymerization.

good diversity of initiator for this polymerization (Table 1, entries 7–10, Tables S1–S3 in Supporting information). When considering the initiator structures, polymer with higher M_n of 638.1 kg/mol and relatively large \bar{D} of 1.38 was obtained when using Ph₂Mg·LiCl as an initiator at 45 °C (Table 1, entry 10). All these results indicate low \bar{D} can be achieved and M_n can be manipulated by feed ratio, initiator structure and polymerization temperature, even though initiation efficiency is not high, which are similar to our previous study of Barbier CARP. By comparison, experimental M_n obtained by super-Gignard reagent mediated polymerization are far greater than the calculated M_n according to Eq. S1 (Supporting information), indicating only less than 8% of super-Gignard reagents participates in polymerization. In comparison, no polymer is observed for Grignard reagent *i*-PrMgCl, which is consistent with the anionic polymerization literature (Table 1, entry 11) [22].

To reveal the polymerization kinetics, this super-Gignard reagent mediated polymerization was investigated by recording monomer conversion, M_n and \bar{D} at different polymerization time. As shown in Figs. 1C–F, polymerization of St with a [St]/[*i*-Pr₂Mg·LiCl] feed ratio of 50/1 was carried out at 45 °C, where almost full monomer conversion was achieved at 35 min accompanied with low \bar{D} and the increase of M_n linearly from 9.6 kg/mol to 48.7 kg/mol. To prove that bimolecular termination is inexistent after full monomer conversion, the polymerization time was extended to 36 h, where no obvious bimolecular GPC trace was observed. Correspondingly, other super-Gignard reagents mediated polymerization kinetics were carried out under the same conditions. By analyzing the relationship of ln([M]₀/[M]) vs. polymerization time, polymerization rate order of these initiators is Bn₂Mg·LiCl > Et₂Mg·LiCl > *i*-Pr₂Mg·LiCl > allyl₂Mg·LiCl (Fig. 1G),

which is inconsistent with the amount of polymerization species calculated from M_n , indicating substituted group of initiators will affect polymerization rate and molecular weight of obtained polymers simultaneously. All these polymerization rate results also indicate the propagation process is slower at the beginning and accelerates during polymerization, and the reactivity of polymerization species (benzyl species) is much higher than that of virgin super-Grignard reagents, which explain why only a small amount of super-Grignard reagent acts as real initiator, as mentioned above. It is worth mentioning, the polymerization initiated by $\text{Bn}_2\text{Mg}\cdot\text{LiCl}$ is so fast and can be completed in about 6 min. So, its polymerization kinetics was also carried out at 0 °C so that the relationship of M_n vs. monomer conversion can be plotted, where linear relationship is achieved (Fig. 1H). The relationships of M_n with monomer conversion are also linear for other initiators, as shown in Figs. 1H-J and Figs. S2-S4 (Supporting information). So, all these results confirm the living characteristics of this super-Grignard reagents mediated polymerization with a wide variety of initiators, including *i*- $\text{Pr}_2\text{Mg}\cdot\text{LiCl}$, $\text{Et}_2\text{Mg}\cdot\text{LiCl}$, $\text{Bn}_2\text{Mg}\cdot\text{LiCl}$, $\text{allyl}_2\text{Mg}\cdot\text{LiCl}$ and $\text{Ph}_2\text{Mg}\cdot\text{LiCl}$.

To further confirm the all-in-one CARP characteristics of this super-Grignard reagents mediated polymerization, rather than traditional anionic polymerization characteristics, reactive hydrogen compatibility experiments were carried out in different baths by adding 0.2 equiv. of MeOH or H_2O at 20 min of polymerization (Fig. 1K). The sample taken out at 20 min was characterized by ^1H NMR and GPC, giving the monomer conversion of 18% and M_n of 28.7 kg/mol (blue curve). After 15 h, full monomer conversions have been achieved in all these batches with similar GPC curves (the red trace), indicating that polymerization species exhibits high compatibility with reactive hydrogens (e.g., MeOH and H_2O). Compared with the zero tolerance of reactive hydrogen of traditional anionic polymerization, the CARP characteristics of this super-Grignard reagent mediated polymerization exhibits better compatibility with polymerization conditions. Meanwhile, TEMPO capture experiments were used to demonstrate the radical characteristics of polymerization species. As shown in Fig. 1L, three groups of peaks exist in MALDI-TOF mass spectrum, two of which are considered to TEMPO terminated PS deriving and proton terminated PS, while another seem to be degraded PS derived in MALDI-TOF test according to the literature on TEMPO-mediated living radical polymerization [52]. However, when large amount of radical trapper (BHT) with reactive hydrogen containing is added during polymerization, the polymer chain is terminated by hydrogen, indicating the anionic characteristic exhibits stronger than radical characteristic (Fig. S5 in Supporting information). All these results suggest the reactive propagation species in super-Grignard reagents mediated polymerization method is not solely anionic species, but accompanied by radical characteristics.

According to above mechanism experiment results, we speculated on the possible mechanism of super-Grignard reagents mediated polymerization, as shown in Fig. 1M. In the initiation stage, the reactive species with all-in-one anionic and radical characteristics drive the addition of super-Grignard reagents on St, producing polymerization species $(\text{P}_n)_2\text{Mg}\cdot\text{LiCl}$ with covalent-anionic-radical characteristics. During the chain propagation process, polymerization species continuously react with St to achieve chain growth due to the existence of reactive all-in-one anionic and radical characteristics, while the bimolecular termination and active hydrogen quenching reaction is inhibited by the covalent characteristic, realizing the synthesis of narrow distribution polymer with low \mathcal{D} .

Generally, anionic polymerization of styrenic monomers will be suppressed when introducing an electron-donating group, such as 4-methoxystyrene (MOS), whose double bond exhibits more electron-rich due to the existence of alkoxy group. To explore

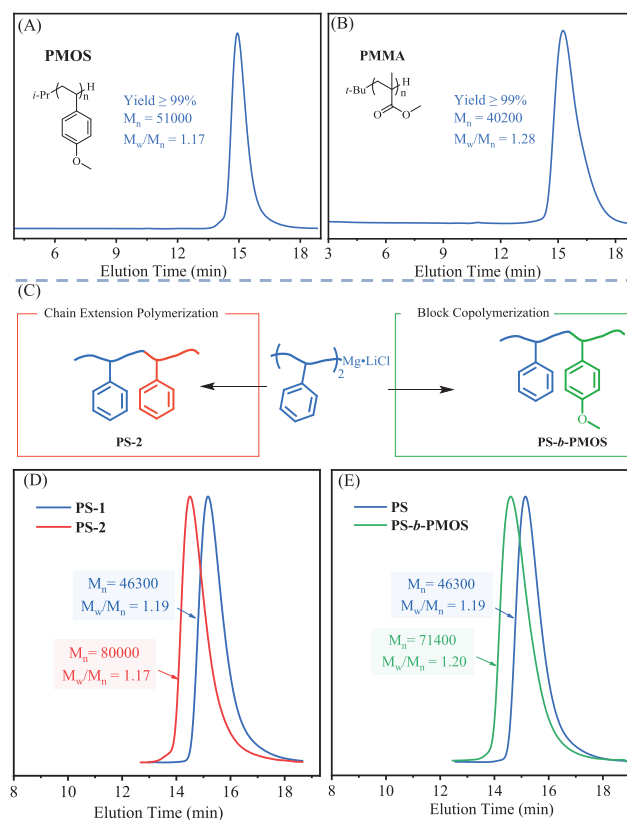


Fig. 2. (A) GPC trace of PMOS. Polymerization conditions: MOS (1 g, 1 equiv.), $[\text{St}]/[i\text{-Pr}_2\text{Mg}\cdot\text{LiCl}] = 20$, THF (2 mL), 45 °C, 24 h. (B) GPC trace of PMMA. Polymerization conditions: MMA (1 g, 1 equiv.), $[\text{St}]/[t\text{-Bu}_2\text{Mg}\cdot\text{LiCl}] = 20$, THF (4 mL), -78 °C, 3 h. (C) The scheme of chain extension polymerization and block copolymerization. (D) GPC traces of PS-1 and PS-2. (E) GPC traces of PS and PS-*b*-PMOS.

the monomer universality of this super-Grignard reagents mediated polymerization, MOS was polymerized by using *i*- $\text{Pr}_2\text{Mg}\cdot\text{LiCl}$ as an initiator. As shown in Fig. 2A and Figs. S6 and S7 (Supporting information), poly(4-methoxystyrene) (PMOS) is successfully prepared with full monomer conversion and \mathcal{D} of 1.17 under mild conditions. This result indicates that this super-Grignard reagent mediated CARP is applicable to monomers with low reactivity, e.g., MOS, where the livingness can be well maintained. Moreover, super-Grignard reagents mediated polymerization of the polar monomer methyl methacrylate (MMA) can also be achieved at -78 °C by *t*- $\text{Bu}_2\text{Mg}\cdot\text{LiCl}$, a sterically hindered super-Grignard reagent, and PMMA with M_n of 40.2 kg/mol and \mathcal{D} of 1.28 can be prepared with full monomer conversion (Fig. 2B and Fig. S8 in Supporting information). So, all these results indicate the wide monomer compatibility of this super-Grignard reagents mediated polymerization.

To explore the potential application of this CARP in the synthesis of well-defined macromolecular architectures, the chain extension and block copolymerization were performed under standard conditions (Fig. 2C). Using a feed ratio of 50:1, St was firstly polymerized at 45 °C for 30 min, and PS with M_n of 46.3 kg/mol and \mathcal{D} of 1.19 was obtained. With the addition of additional amount of St rather than quencher, the chain extension polymerization proceeded for 12 h, yielding PS-2 with higher molecular weight ($M_n = 80$ kg/mol, $\mathcal{D} = 1.17$), whose unimodal GPC curves further verify the livingness of chain propagation (Fig. 2D). Alternatively, when the second monomer MOS was added at 30 min, block copolymer PS-*b*-PMOS was prepared with over 99% monomer conversion (Fig. 2E and Fig. S9 in Supporting information). In compar-

ison with the GPC trace of PS, the chromatogram of the obtained PS-*b*-PMOS shows a pronounced increase in molecular weight to 71.4 kg/mol and maintained narrow \bar{D} of 1.20. The successful chain extension and block copolymerization indicate there is still no obvious chain termination in this CARP even if the monomer conversion reaches 99%, which attributes to the anionic characteristics of the polymerization species. Through TGA and DSC, the thermal properties of the obtained PS-*b*-PMOS were investigated, exhibiting T_d of 414 °C and T_g of 102 °C (Fig. S12 in Supporting information).

In summary, a universal polymerization method capable of reactive hydrogen compatibility was achieved with full conversion by using super-Grignard reagents as initiators for the preparation of the polymers with low \bar{D} . Under mild conditions, PS with \bar{D} as low as 1.15 is successfully prepared with full monomer conversion, where wide varieties of super-Grignard reagents, including *i*-Pr₂Mg-LiCl, Et₂Mg-LiCl, Bn₂Mg-LiCl, allyl₂Mg-LiCl and Ph₂Mg-LiCl, are used as initiators in different polymerization temperature and feed ratio. Kinetic experiments indicate that the chain ends remain reactive during polymerization. By adding methanol and water into the polymerization medium, the reactive hydrogen compatibility of this polymerization method was confirmed, exhibiting the difference from traditional anionic polymerization which needs rigorous polymerization conditions. Meanwhile, this polymerization method is compatible with other monomer, such as styrenic monomers MOS and polar monomer MMA. Moreover, chain extension polymerization and block copolymerization are carried out, and PS with higher molecular weight and PS-*b*-PMOS are prepared with over 99% monomer conversion, demonstrating the feasibility of this polymerization method in the synthesis of well-defined macromolecular architectures. All these results indicate that super-Grignard reagents mediated polymerization is a universal method for the precise synthesis of polymer with narrow \bar{D} and well-defined architectures, realizing both minimized chain termination (even when monomer conversion is over 99%) and mild reaction conditions. This work therefore expands the methodology libraries of living polymerization, which may cause inspirations to polymer science.

Declaration of competing 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.

Acknowledgments

We acknowledge funding support from National Natural Science Foundation of China (NSFC, Nos. 22271286 and 21971236) and the Haixi Institute of CAS (No. CXZX-2017-P01).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2023.108167.

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