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Highly efficient access to well-defined linear polymers with substantial vinyl pendants *via* ATRP of divinyl monomers†

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Reported herein is a highly efficient access to well-defined linear polymers with substantial vinyl pendants *via* activators generated by electron transfer (AGET) atom transfer radical polymerization (ATRP) of dissymmetric divinyl monomers by side armed bisoxazoline (SaBOX)/copper catalysts. High conversions (>90%) of the divinyl monomers allyl methacrylate (AMA) and vinyl methacrylate (VMA) without gelation through ATRP were realized with a relatively high concentration ratio of monomer to initiator in feed ([M]$_0$/[I]$_0 \geq$ 100), yielding completely soluble homopolymers with relatively high molecular weights and narrow molecular weight distributions (M_n's = 1.49–3.69 × 10^4, Đ's = 1.2–2.0). Besides, random MMA copolymers with different amounts of pendant vinyl groups (18–54 mol%) were conveniently obtained by employing AMA or VMA as the comonomer.

Introduction

Well-defined polymers with vinyl pendants have received significant attention in considering their transformability to a variety of valuable materials, such as cross-linked, hyperbranched, and functionalized polymers.[1–11] Well-defined polymers of divinyl monomers, for instance, allyl methacrylate (AMA) and vinyl methacrylate (VMA), are obtainable with high conversions by some polymerization approaches, such as group transfer polymerization, anionic polymerization[12–14] as well as recently developed Lewis pair polymerization and coordination polymerization.[15–18] However, compared to the stringent reaction conditions required for the above polymerization approaches, atom transfer radical polymerization (ATRP) is obviously advantageous in making polymers with more diverse functionalities and architectures as well as copolymers with a controllable extent of repeating units under less stringent reaction conditions.[19–24] In this context, the development of an effective ATRP approach for divinyl monomers is very attractive and promising.[25–27] Similar to conventional and other controlled radical polymerization methods,[28–35] gelation is also usually inevitable during the ATRP of divinyl monomers,[6,7,36,37] especially in the late stage, since the ratio of the monomer to the radical species decreases gradually along with the conversion of the monomer.

Although many attempts have been made to solve this problem, it is still very challenging to suppress the intermolecular crosslinking in the ATRP of divinyl monomers, due to the nondistinctive propagation of the growing radical species to double bonds in the monomer and the polymer chain. With a relatively high concentration ratio of monomer to initiator in feed ([M]$_0$/[I]$_0 \geq$ 100), the homogeneous polymerization systems for the ATRP of AMA were only able to be safeguarded in the early stage of the polymerization with conversions up to 41%; otherwise cross-linked insoluble polymers were produced.[36,37] Parenthetically, even though the copolymerization of a crosslinker (*e.g.*, divinylbenzene or ethylene glycol diacrylate) in controlled radical polymerization processes showed a delayed gelation onset, it is difficult to produce completely soluble copolymers at high conversions of more than 70%.[38–45] In current work, by the employment of the side armed bisoxazoline (SaBOX) ligand (**L4d** in Scheme 1), we obtained well-defined linear polymers with abundant vinyl or allyl ester groups under the conditions of activators generated by electron transfer (AGET) ATRP of AMA and VMA. Remarkably, even with conversions of AMA and VMA higher than 90%, the resultant polymers were completely soluble in common organic solvents.

Results and discussion

Conventional ATRP and (AGET) ATRP of divinyl monomers with ligand PMDETA

As shown in Table S1 (page S5 in the ESI†), under conventional ATRP conditions employing *N,N,N′,N″,N″*-pentamethyldiethyl-

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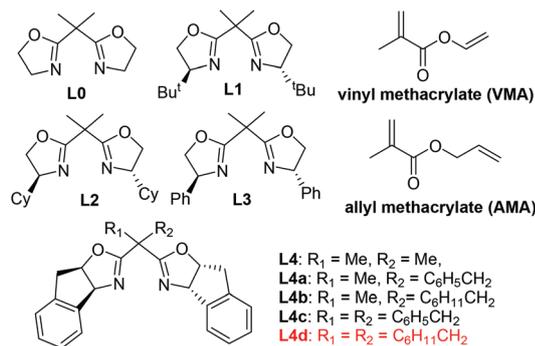
Scheme 1 The BOX ligands screened.

Fig. 1 Conversion as a function of time for the (AGET) ATRP of AMA (a) and VMA (b) to monitor the gel point, employing ligands with different BOX scaffolds under the conditions shown in Table 1: the "×" in the signals means slight gelation just occurred.

enetriamine (PMDETA) as the ligand,[36] the homopolymerizations of AMA and VMA led to cross-linked polymers in the very early stages of the reaction with conversions of 38% and 17% at the gel point, respectively. The use of (AGET) ATRP has shown a better controllability in the polymerization attributed to the suppressed radical side reactions.[46,47] Under the commonly used (AGET) ATRP conditions (elemental copper as the reducing agent, 2-bromopropionitrile (2-BPN) as an initiator, and CuBr$_2$/PMDETA as the catalyst),[48] no gelation was observed during the whole polymerizations of AMA and VMA in 40 h; however, the conversion does not change with time in the initial stages. The polymerizations exhibited poor control on the MWs and gave limited conversions of 37% and 45%, respectively. This result inspired us to explore the regio-selective polymerization of dissymmetric divinyl monomers by SaBOX ligands, which showed high efficiency in the (AGET) ATRP of MMA.[49]

Effect of the BOX scaffold on the (AGET) ATRP of divinyl monomers

We first investigated the scaffold effect of common BOX ligands (Scheme 1) on the (AGET) ATRP of AMA and VMA. The total monomer conversions during the polymerizations mediated by BOX ligands are presented as a function of time in Fig. 1 and 2 to monitor the gel point. The occurrence of gelation generally brings about significant increase of molecular weight as well as the broadening of molecular weight distribution, and even the observation of gels. The monomer conversion at the gel point is defined as the monomer conversion when slight gelation has just occurred (the signals with "×" in Fig. 1 and 2) and is obtained on the monomer basis using ¹H NMR or weighing.[36,37] As shown in Table 1 and Fig. 1, the structure of the BOX scaffold had a significant influence on both reactivity and the conversion at the gel point. For example, by employing simple BOX **L0** as the ligand, the polymerizations for both AMA and VMA proceeded quickly and continually with time until gelation occurred at moderate conversions (62% and 63% for AMA and VMA, respectively). With ligand **L1**, however, a deceleration for both AMA and VMA polymerizations occurred at low conversions of 37% and 39%, respectively. After the initial periods, the conversions increased
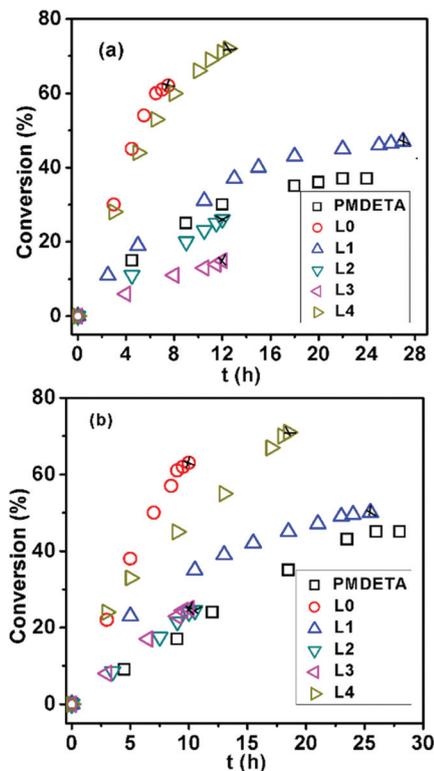
very slowly with time and insoluble cross-linked fractions were observed with conversions up to 47% and 50%, respectively. When **L2** and **L3** were employed, insoluble cross-linked fractions appeared even in the initial reaction period with very low conversions (≤26%). The optimal scaffold proved to be **L4**, which promoted the polymerizations for both AMA and VMA and no deceleration process was detected, leading to the high conversions of 72% and 71% at gel points for AMA and VMA, respectively. These results suggest that indane-BOX **L4** is more suitable for the ATRP of dissymmetric divinyl monomers than PMDETA and other examined BOX ligands, thereby achieving a higher polymerization rate and delayed gelation onset.

Side arm effect on the SaBOX/copper mediated (AGET) ATRP of divinyl monomers

Based on the side arm effect observed in the (AGET) ATRP of MMA,[49] which means that the side arms (the pendant groups) installed on the bridge carbon of BOX prove to strongly influence both the activity of the catalyst and the control on molecular weights, we focused our further study on such an effect in the (AGET) ATRP of AMA and VMA with side armed indane-BOX ligands (Scheme 1). All the polymerizations of both monomers proceeded quickly and continually with time until gelation occurred. As shown in Table 1 and Fig. 2, one pendant group, either cyclohexylmethyl (**L4b**) or benzyl (**L4a**),
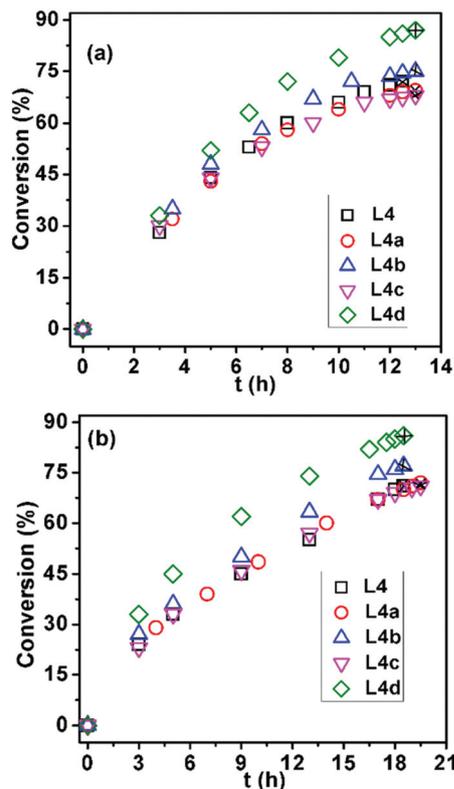
Fig. 2 Conversion as a function of time for the (AGET) ATRP of AMA (a) and VMA (b) to monitor the gel point, employing indane-BOX ligands with different side arms under the conditions shown in Table 1: the "×" in the signals means slight gelation just occurred.

installed on the indane-BOX has little effect on both activity and the conversion at gelation onset. The introduction of two benzyl groups (**L4c**) also made only little difference. In contrast, when SaBOX **L4d** with two cyclohexylmethyl arms was used instead of **L4**, the AMA and VMA conversions at the gel point improved from 72% to 87% and from 71% to 86%, respectively. In a dilute system, the conversion at the gel point could be further improved to 93% and 91% for AMA and VMA, respectively (runs 10 and 20 in Table 1). First-order kinetic plots for all the polymerizations are shown in Fig. S1 and S2 (pages S6 and S7 in the ESI†). As shown in Fig. S3–4 (pages S8 and S9 in the ESI†), the evolution of molecular weight as a function of conversion for all the polymerizations indicated that before the occurrence of crosslinking, the molecular weights for all the polymerizations gradually increased with monomer conversion. When the crosslinking occurred at high conversions, the molecular weights significantly increased. This is consistent with the previous literature reports.[6,35–37]

Synthesis and characterization of well-defined homopolymers with vinyl pendants

Next, **L4d** was employed as the ligand to synthesize well-defined polymers. As summarized in Table 2, a high conversion of 83% was achieved by employing **L4d** as the ligand under the same conditions and the MW distribution remained relatively narrow ($Đ$ = 1.2), indicating a well-defined structure of the resultant polymers. Through increasing the solvent/monomer ratio to 2/1, well-defined PAMA was produced with a high conversion of 91%. As shown in Fig. 3a and Fig. S5 (page S10 in the ESI†), the ^{1}H NMR analysis suggested the complete

Table 1 Gel points in the ATRP of AMA and VMA using different BOX ligands[a]

| Run | M | THF/M (v/v) | Ligand | Gel point | | $M_{n, GPC}$[c] (10^3) | $Đ$[c] | $M_{n, theory}$ (10^3) |
				t (h)	Conv.[b] (%)			
1	AMA	1/1	**L0**	7.5	62	16.1	2.6	7.96
2		1/1	**L1**	27.0	47	20.6	2.5	6.06
3		1/1	**L2**	12.0	26	nd[d]	nd[d]	3.42
4		1/1	**L3**	12.0	15	nd[d]	nd[d]	2.03
5		1/1	**L4**	12.5	72	19.2	2.7	9.22
6		1/1	**L4a**	12.5	69	18.0	2.5	8.84
7		1/1	**L4b**	13.0	75	20.4	2.8	9.48
8		1/1	**L4c**	13.0	68	20.3	3.1	8.72
9		1/1	**L4d**	13.0	87	20.5	2.7	11.1
10		2/1	**L4d**	19.0	93	25.6	3.5	11.9
11	VMA	4/1	**L0**	10.0	63	19.1	2.5	7.20
12		4/1	**L1**	25.5	50	30.5	2.5	5.74
13		4/1	**L2**	10.5	24	nd[d]	nd[d]	2.82
14		4/1	**L3**	10.0	25	nd[d]	nd[d]	2.94
15		4/1	**L4**	18.5	71	20.6	3.1	8.09
16		4/1	**L4a**	19.5	72	19.2	2.7	8.21
17		4/1	**L4b**	18.5	77	25.9	2.9	8.77
18		4/1	**L4c**	19.5	71	27.5	2.8	7.96
19		4/1	**L4d**	18.5	86	24.9	2.4	8.78
20		10/1	**L4d**	36.0	91	29.8	3.6	10.3

[a] Conditions: $n(M):n(BPN):n(CuBr_2):n(ligand):n(Cu(0)) = 200:2:1:2:4$, at 20 °C; THF was employed as the solvent. [b] The monomer conversion at the gel point (the signals with "×" in Fig. 1 and 2), which is the monomer conversion when slight gelation just occurred and obtained on the monomer basis using ^{1}H NMR or weighing.[36,37] [c] Molecular weights and polydispersity indices of the soluble part of the product determined using GPC in THF at 25 °C *vs.* narrow PMMA standards, $Đ = M_w/M_n$.[16,35] [d] nd = not determined.

Table 2 Synthesis of well-defined homopolymers with plentiful vinyl groups[a]

Run	M	THF/M (v/v)	t (h)	Conv.[c] (%)	$M_{n, GPC}$[d] (10^3)	$Đ$[d]	$M_{n, theory}$ (10^3)
1	AMA	1/1	12.0	83	14.9	1.2	10.6
2	AMA	2/1	24.0	91	19.2	1.5	11.6
3[b]	AMA	2/1	24.0	85	35.1	1.5	21.6
4	VMA	4/1	18.0	84	15.3	1.3	9.55
5	VMA	10/1	35.5	89	20.2	2.0	10.1
6[b]	VMA	10/1	35.0	82	36.9	1.8	18.5

[a] Conditions: $n(BPN):n(CuBr_2):n(L4d):n(Cu(0)) = 2:1:2:4$, $n(M):n(BPN) = 100:1$. THF was employed as the solvent, at 20 °C. [b] $n(M):n(BPN) = 200:1$. [c] Monomer conversion measured using ^{1}H NMR of the crude reaction mixtures. [d] Molecular weights and polydispersity indices determined using GPC in THF at 25 °C vs. narrow PMMA standards, $Đ = M_w/M_n$.
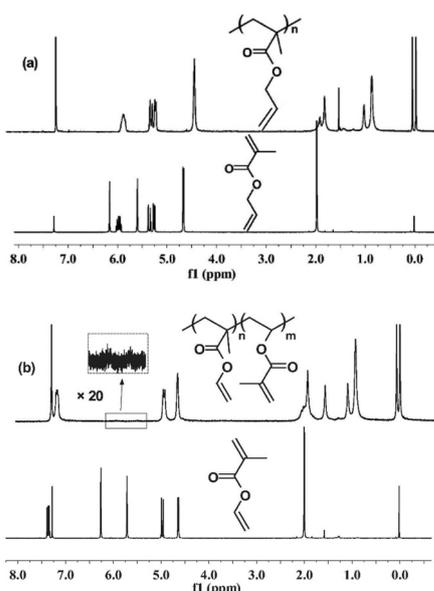
Fig. 3 Overlay of ^{1}H NMR (CDCl₃, 25 °C) spectra of the monomer AMA and the polymer PAMA (a, run 2 in Table 2) as well as overlay of ^{1}H NMR (CDCl₃, 25 °C) spectra of the monomer VMA and the polymer PVMA (b, run 5 in Table 2).

retention of the allyl ester groups ($δ$ 5.91, 5.31, and 5.20 ppm). The ^{13}C NMR spectrum of PAMA further demonstrated the linear structure of the polymer and no grafted structure or methacrylate vinyl groups were detected (Fig. S7 in page S11 of the ESI†). This is different from the previous report about the ATRP of AMA, which produced polymers with significant amounts of methacrylate vinyl groups.[37] In the case of the polymerization of VMA mediated by **L4d**, a high conversion of 84% could be achieved and the resultant polymers possess a narrow MW distribution ($Đ$ = 1.3). Further increasing the solvent/monomer volume ratio to 10/1 led to a higher conversion of 89%, while maintaining a completely homogeneous solution. As shown in Fig. 3b and Fig. S6 (page S10 in the ESI†), subsequent analysis of the isolated material by ^{1}H NMR

spectra indicated that the produced polymers contained substantial pendant vinyl ester groups ($δ$ 4.92, 4.63, and 7.15 ppm) with a very small amount (ca. 1%) of the remaining methacrylate vinyl groups ($δ$ 5.51 and 5.92 ppm). The ^{13}C NMR spectrum of the polymer PVMA demonstrated the linear structure of the polymer and no grafted structure was detected (Fig. S8 in page S11 of the ESI†).[37] The PVMA produced at a high conversion of 89% showed a broader $Đ$ of 2.0 and an M_n higher than the theoretical value. As no gelation phenomenon was observed during the whole polymerization process, the possible reason for the broadened $Đ$ value and high M_n was presumed to be the poor MW control under highly diluted conditions. This is consistent with the results of the (AGET) ATRP of MMA employing different monomer and catalyst concentrations (Table S2 in page S12 of the ESI†). Besides, as indicated by Fig. S9 (page S13 in the ESI†), the molecular weights of the polymers gradually increased with the monomer conversion during the polymerizations shown in runs 2 and 5 of Table 2.

The low molecular weight PAMA and PVMA were prepared using **L4d**, and we analyzed the structure of these polymers using MALDI-TOF MS (Fig. 4), which confirmed the linear structure of the polymers. Since resonances of the vinyl-terminated end-group were not observed in the ^{1}H and ^{13}C NMR spectra, we believe that the minor peaks in the MALDI-TOF mass spectra should result from the dehydrobromination of the bromo terminated polymer chains during the MALDI-TOF MS analysis.[50] Furthermore, the narrow and symmetric nature
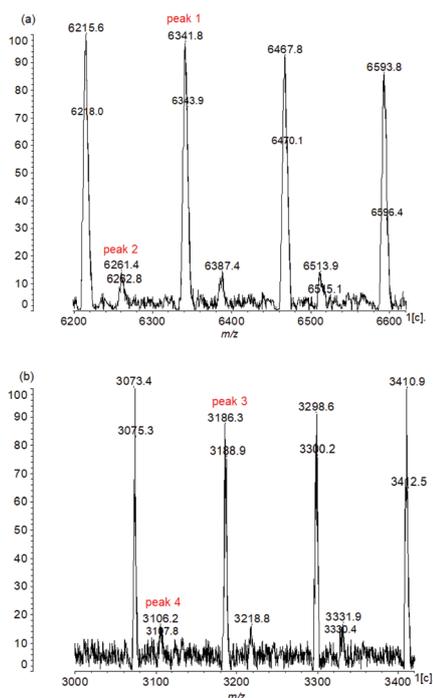
Fig. 4 MALDI-TOF mass spectra of PAMA (M_n = 6226) and PVMA (M_n = 5361); peak 1: CN(CH₃)CH(AMA)₄₉BrNa⁺; peak 2: CN(CH₃)CH(AMA)₄₈CH═C(CH₃)COCH₂CH═CH₂Na⁺; peak 3: CN(CH₃)CH(VMA)₂₇BrNa⁺; and peak 4: CN(CH₃)CH(VMA)₂₆CH═C(CH₃)COCH═CH₂Na⁺.

Table 3 Copolymerization of MMA with AMA or VMA using **L4d**/copper catalyst[a]

Run	MMA (mmol)	Comon.	Comon. (mmol)	t (h)	Comon. conv.[b] (%)	MMA conv.[b] (%)	Comon. incorp.[c] (%)	$M_{n, GPC}$[d] (10^3)	$Đ$[d]	$M_{n, theory}$ (10^3)
1	4.375	AMA	0.625	29	84	72	17	11.6	1.2	7.76
2	3.750		1.250	29	85	74	30	12.6	1.3	8.39
3	2.500		2.500	19	91	85	54	15.1	1.4	10.1
4	4.375	VMA	0.625	24	88	78	21	12.4	1.2	8.22
5	3.750		1.250	24	88	79	33	16.8	1.5	8.56
6	2.500		2.500	19	90	80	54	17.1	1.6	9.07

[a] Reaction conditions: n(MMA and comonomer):n(BPN):n(CuBr$_2$):n(ligand):n(Cu(0)) = 200:2:1:2:4, at 20 °C; THF was employed as the solvent (1.5 mL). [b] Monomer conversion measured using ^{1}H NMR. [c] Comonomer incorporation measured using ^{1}H NMR. [d] Number-average molecular weights and polydispersity indices determined using GPC at 25 °C in THF vs. narrow PMMA standards, $Đ = M_w/M_n$.

of the carbonyl group stretching, centered around 1722 and 1740 cm^{-1} in the FTIR spectra (Fig. S10 and S11 in page S14 of the ESI†) of the resultant PAMA and PVMA from runs 2 and 5 in Table 2, respectively, confirmed the absence of cyclic or crosslinking structures, which clearly differed from the previously reported results of the ATRP of AMA and VMA.[29,30,36] In addition, PAMA and PVMA with higher MWs (M_n's > 35 000) and relatively narrow MW distributions ($Đ$s = 1.5–1.8) were also readily synthesized by increasing the ratio of monomer to initiator.

Synthesis and characterization of well-defined copolymers with vinyl pendants

The homopolymers of AMA or VMA undergo a relatively fast cross-linking reaction in air even at room temperature. To obtain a wide variety of switchable materials that are relatively stable, the copolymerizations of MMA with AMA or VMA utilizing **L4d** were conducted under the polymerization conditions similar to those employed for the homopolymerizations (Table 3). Random MMA copolymers with different amounts of pendant vinyl groups (18–54 mol%) were obtained by employing AMA or VMA as the comonomer and varying the comonomer/MMA ratio from 1/7, 1/3 to 1/1. The copolymers of MMA prepared with AMA or VMA were well-defined with high incorporation of the comonomers. The ^{1}H NMR spectra (ESI Fig. S12–17†) of the copolymers (poly-(MMA-co-AMA) and poly-(MMA-co-VMA)) suggested the complete retainment of the allyl ester moiety ($δ$ 5.91, 5.31, and 5.20 ppm) and vinyl ester moiety ($δ$ 4.88, 4.60, and 7.14 ppm) and the complete disappearance of the methacrylate vinyl protons. For the MMA/ VMA copolymerizations, the signals corresponding to the methacrylate vinyl protons could not be detected in the ^{1}H NMR spectra of the products, which is different from the results of the VMA homopolymerizations. The double bond in the methacrylate vinyl group is much more active than the one in the vinyl ester group, and thus, the former one participated in the polymerization far more preferentially than the latter one. In the MMA/VMA copolymerization, the relative amount of the vinyl ester group is lower than that in the VMA homopolymerization, and in turn, the probability of polymerization for the double bond in the vinyl ester group is very low in the copolymerization. Therefore, the signals corresponding to the

methacrylate vinyl protons could not be observed in the ^{1}H NMR spectra of the MMA/VMA copolymers.[4,34,40] GPC analysis showed that the resulting copolymers exhibited M_n's in accord with the calculated M_n's, and relatively narrow MW distributions ($Đ$'s = 1.2–1.6).

Experimental section

Polymerization

All polymerizations were set up and performed under an atmosphere of oxygen-free, dry nitrogen using standard Schlenk-line techniques or inside a nitrogen-filled glovebox. In an ampule equipped with a magnetic stirrer bar, a mixture of CuBr$_2$, ligand and Cu(0) powder in a solvent was stirred at room temperature for 2 h under the atmosphere of nitrogen. After this, the monomer and initiator were added into the ampule. The ampule was placed at room temperature (20 °C). After stirring for the allotted period of time, an aliquot (ca. 0.1 mL) was collected and quenched with CDCl$_3$ (0.5 mL). The conversion was determined by integration of the remaining monomer with respect to the polymer backbone resonances in the ^{1}H NMR spectrum of the crude product. After completion of the reaction, the contents of the ampule were dissolved in THF or CH$_2$Cl$_2$. The reaction mixture was filtered off through a glass funnel with neutral alumina. The filtrate was concentrated under reduced pressure. The residuals were redissolved in 5.0 mL THF or CH$_2$Cl$_2$. This solution was added to an approximately 50-fold excess of rapidly stirred methanol. The precipitate that formed was then collected by filtration and washed with methanol. The precipitate was dried to constant weight in a vacuum oven at room temperature and then the dried samples were stored in the dark at −30 °C.

Conclusions

In summary, we developed a highly effective (monomer conversion over 90%) and controllable (M_n's = 1.49–3.69 × 10^4, $Đ$'s = 1.2–2.0) (AGET) ATRP of divinyl monomers employing an SaBOX ligand designed on the basis of the side arm effect, which successfully delayed the gelation onset from the monomer conversion of 41% to over 90% and produced well-

defined linear polymers with plentiful pendant vinyl groups. Various BOX/copper catalysts have been investigated, showing a remarkable sensitivity of the polymerization rate and the gelation onset to a subtle ligand structural change. This study may provide a new strategy to synthesize well-defined, switchable, and potentially useful polymers with high efficiency *via* the ATRP of divinyl monomers.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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