Poly(vinyl ketone)s by Controlled Boron Group Transfer Polymerization (BGTP)**

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Controlled radical polymerizations have been intensively studied during the past ten years, and several methods have been developed: ATRP (atom-transfer radical polymerization),^[1] RAFT (reversible addition–fragmentation chain-transfer polymerization),^[2] iodo,^[3] tellurium, antimony, and bismuth group transfer,^[4] cobalt-mediated processes,^[5] and NMP (nitroxide-mediated polymerization).^[6] Various polymers with defined molecular weight and polydispersity (PDI) below the theoretical limit (1.5) can be conveniently prepared using these techniques. To our knowledge, only one report on the successful controlled radical polymerization of vinyl ketones has appeared.^[7] Herein, we will introduce a new method for controlled polymerization of vinyl ketones that is based on a radical boron group transfer process.^[8,9]

We recently showed that formal homolytic substitution at boron in catecholboron enolates **1** with the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)^[10] delivers resonance-stabilized α -enoyl radicals **2** that undergo TEMPO trapping to afford α -oxygenated ketones **3** [Eq. (1)].^[11]



It is well known that organocatecholboron compounds react only with heteroatom- and not with C-centered radicals. Interaction of the Lewis acidic boron atom with an electron lone pair of the heteroatom-centered radical seems to be of

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key importance for this selectivity.^[8] As α -enoyl radicals carry spin density at oxygen, we assumed that reversible interchange of the catecholboron moiety between an α -enoyl radical and a catecholboron ketone enolate might be feasible. To develop a boron group transfer radical polymerization (BGTP), this degenerate transfer process has to be kinetically competent with the addition of the α -enoyl radical to the monomer present in solution [Eq. (2)]. In our concept, the boron group transfer requires spin density at oxygen, while the growth of the polymer chain relies on the spin density at the carbon atom of the α -enoyl radical.



We tested our hypothesis with enolate **4a** as a polymerization regulator, which was prepared in situ by the reaction of the corresponding α , β -unsaturated ketone with catecholborane.^[11] NMR spectroscopy studies revealed that **4a** was formed within one hour at room temperature as a single isomer, which was tentatively assigned as *E* isomer (over 95% yield; see the Supporting Information). Initial polymerization experiments were conducted with methyl vinyl ketone (MVK) and V-70 as a stable, low-temperature radical initiator (Scheme 1). Enolate **4a**, MVK, and V-70 in dry THF (50 vol%) were heated to 70°C, and the resulting polymer



Scheme 1. Polymerization of various α , β -unsaturated ketones.

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precipitated upon addition of Et_2O /pentane. Mean molecular weight (M_n) and polydispersity index values were determined by gel permeation chromatography (GPC) relative to linear poly(methyl methacrylate) standards. The results are summarized in Table 1.

Table 1: Polymerization of MVK with 4a (1.3 equiv) under different conditions to give PMVK 5.

Entry	MVK (equiv)	V-70 (equiv)	t [h]	Yield [%]	M _n (calcd) [gmol ⁻¹]	<i>M</i> _n (GPC) [g mol ⁻¹]	PDI
1	50	1.0	1	73	2110	2800	1.27
2	50	1.0	6	74	2130	2700	1.24
3	100	1.0	1	72	4020	5600	1.28
4	100	1.0	6	70	3910	5400	1.27
5	100	1.0 ^[a]	6	97	5370	7800	2.21
6	100	-	1	< 2	_	-	_
7	100	1.0 ^[b]	1	< 2	_	-	_
8	100	1.0 ^[c]	12	39	4350	9300	1.44
9	200	1.0	1	69	7630	11 900	1.33
10	200	1.0	6	67	7420	13 700	1.32
11 ^[d]	200	1.0	6	53	5850	8300	1.45
12	200	0.75	1	59	6490	12800	1.32
13	200	1.5	1	70	7730	13 000	1.32
14	100	1.0 ^[e]	6	57	3140	5500	1.30
15	100	1.0 ^[e]	12	67	3680	8100	1.44
16	100	0.2	1	20	5530	7200	1.49
17	100 ^[f]	1.0	6	48	2710	3300	1.27
18	100 ^[g]	1.0	6	79	4390	5700	1.35
19	100 ^[h]	1.0	6	79	4390	6500	1.42
20	100[i]	1.0	6	68	3800	5500	1.37
21	100 ^[j]	1.0	6	28	1650	1600	1.26

[a] **4a** was not added. [b] Galvinoxyl radical (5 equiv, 5 mol% with respect to MVK) was added. [c] Conducted at 30°C. [d] Toluene was used as a solvent. [e] Conducted with AIBN. [f] MVK in THF at 10 vol%. [g] Conducted in neat MVK. [h] Conducted with **4b**. [i] Conducted with **4c**. [j] Conducted with **4d**.

We were pleased to observe that 4a indeed regulates the polymerization of MVK and provides direct validation of our hypothesis. A low PDI of 1.27 clearly demonstrated a controlled process when the reaction was conducted for 1 h with 50-fold excess of MVK over V-70 (Table 1, entry 1). Polymerization was fast, as extending the reaction time to 6 h delivered a similar yield and molecular weight (Table 1, entry 2). Polymers with larger M_n values were readily obtained by increasing the monomer/initiator ratio to 100/1. Importantly, the polymerization remained controlled with unchanged PDI (Table 1, entries 3 and 4). As expected, the polymerization was not controlled in the absence of regulator 4a and under otherwise identical conditions, which is clearly shown in the significant increase of the PDI above the theoretical limit of 1.5 (Table 1, entry 5). Moreover, attempted polymerization in the absence of V-70 did not work, thus supporting the radical nature of the process (Table 1, entry 6). Along this line, polymerization in the presence of the galvinoxyl radical (5 equiv, 5 mol% relative to MVK) was inhibited, which clearly shows that a radical mechanism must be operative (Table 1, entry 7). Reaction at 30°C for 12 h provided poly(methyl vinyl ketone) (PMVK) in low yield with a rather high M_n value (Table 1, entry 8). PMVK with M_n values of up to 14000 gmol⁻¹ was isolated upon further increasing the monomer/initiator ratio to 200/1. For these experiments, the PDI slightly increased to around 1.3 (Table 1, entries 9 and 10).

In the optimization of the reaction, replacing THF by toluene had a detrimental effect on the polymerization and resulted in lower molecular weights and worse reaction control (Table 1, entry 11; see discussion below). Varying ratios of regulator/initiator, at constant monomer concentration, only showed an effect on yield (Table 1, entries 9, 12, 13). Interestingly, M_n was not altered to a large extent in these experiments, and thus a ratio of 1.3:1 for 4a/V-70 was used for the following investigations. Replacing V-70 with α , α' -azobisisobutyronitrile (AIBN) as a radical initiator delivered lower polymer yields compared to the V-70 initiated reactions (Table 1, entries 14 and 15), and lowering the amount of V-70 to 0.2 equiv provided a lower conversion, higher $M_{\rm n}$, and larger PDI values (Table 1, entry 16). Optimization of the concentration in the reaction was not successful: when the reaction was conducted under more dilute conditions, a lower yield and molecular weight was obtained (Table 1, entry 17), whereas at higher concentration, little effect on the polymerization was observed (Table 1, entry 18).^[12]

We then studied what effect the Lewis acidity of the boron atom in **4** had on the polymerization. With the *tert*-butylsubstituted regulator **4b**, PMVK with a slightly larger PDI was formed (Table 1, entry 19). The more electrophilic fluorosubstituted derivative **4c** did not improve the result (Table 1, entry 20), whereas the methoxy-substituted congener **4d** led to a sharp decrease in yield (Table 1, entry 21).

Next, we tested whether our new method supports the controlled polymerization of aryl vinyl ketones (Table 2). Pleasingly, with phenyl vinyl ketone, polymers with a PDI of 1.3 were obtained (Table 2, entry 1). Increasing the reaction time to 6 h did not change the result, thus indicating that polymerization was complete under the applied conditions within one hour (Table 2, entry 2). Polymerization in absence of **4a** afforded a large PDI, which again clearly shows the ability of **4a** to act as a regulator in these processes (Table 2, entry 3). However, control was not perfect for a larger targeted M_n (Table 2, entry 4). Gratifyingly, *p*-methoxyphenyl vinyl ketone and *p*-bromophenyl vinyl ketone could be conveniently polymerized by BGTP (Table 2, entries 5–8).

Renaud and co-workers showed that alkyl catecholboron derivatives undergo efficient formal homolytic substitution at

Table 2: Polymerization of various aryl vinyl ketones with 4a (1.3 equiv) and V-70 (1 equiv) in THF (50 vol%) to give 6–8.

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Entry	Ketone (equiv)	R	<i>t</i> [h]	Yield [%]	M _n (calc) [g mol ⁻¹]	M _n (GPC) [g mol ⁻¹]	PDI
1	50	Ph	1	78	4100	7000	1.33
2	50	Ph	6	78	4100	6700	1.33
3	50 ^[a]	Ph	6	84	4410	10300	3.15
4	100	Ph	1	73	7560	12800	1.53
5	50	4-MeOC ₆ H₄	6	86	5500	8400	1.39
6	50 ^[a]	4-MeOC ₆ H ₄	6	72	4490	15 900	2.92
7	50	$4-BrC_6H_4$	6	71	5870	6900	1.43
8	50 ^[a]	$4-BrC_6H_4$	6	79	6520	18300	4.22

[a] 4a was not added.

boron with α -carbonyl radicals deriving from ketones.^[8] However, analogous reactions with α -carbonyl radicals deriving from amides and esters were reported to not work. This result is in agreement with our observations that controlled polymerization of n-butyl acrylate and *N*-isopropylacrylamide by using **4a** as a regulator was not observed. The spin density at oxygen in these α -carbonyl radicals is probably too low to effect formal homolytic substitution at boron with catecholboron enolates.^[8]

We showed the controlled character of the **4a**-mediated MVK polymerization by determining conversion as a function of time and analyzing molecular weight as a function of monomer conversion (Figure 1). Both plots had the typical behavior expected for a controlled process, further validating the experimental results shown in Table 1.



Figure 1. a) Monomer conversion versus time. b) Molecular weight and PDI versus monomer conversion (conditions: MVK (200 equiv), **4**a (1.3 equiv), V-70 (1 equiv), THF, 70 °C). \blacksquare M_n , —— linear fit, \triangle PDI.

To understand the new polymerization concept in more detail and to support the suggested mechanism depicted in [Eq. (2)], we performed mechanistic studies by using HR-ESI mass spectrometry. Polymerizations with 4a (MVK/4a = 20:1) were conducted in either benzene or in THF. ESImass spectrometric analysis showed a clean polymerization process with two (in THF) or three main peak series (in benzene) separated by one monomer mass (Figure 2). These three series could be clearly identified, and they differ in the radical chain initiation and termination. Only a small fraction of polymers carry the enoyl radical, which is derived from 4a, as the initiating moiety in their backbone (series indicated by $a \bullet$ in Figure 2). Thus, most of the polymers were initiated by the more reactive radical derived from the V-70 (\blacktriangle and \blacklozenge). This fact was further supported by ¹H NMR spectroscopic analysis of the polymers: a signal for the methoxy group of the enoyl moiety was lacking, and only the resonance of the methoxy substituent of the V-70-derived unit was clearly



Figure 2. Part of an ESI-MS spectrum of a MVK polymerization regulated with **4a** in benzene.

identified (see the Supporting Information). Furthermore, ¹H NMR spectroscopy allowed to estimate M_n of the polymers independently to the GPC method. The NMR analysis provided systematically lower M_n values (by about 1200 g mol⁻¹; Supporting Information, Table S1). Decreasing the amount of V-70 to 0.2 equiv provided the polymer in lower yield, with a larger M_n showing that initiation occurred mostly by the V-70 derived radicals (Table 1, entry 16).

Currently, we do not fully understand why only a very small fraction of polymers was initiated by the enoyl radical deriving from 4a. A possible explanation might be the probable low reactivity of the enoyl radical deriving from 4a towards MVK. As dimerization products of two of the enoyl radicals deriving from 4a were not identified, it seems that these enoyl radicals are able to efficiently undergo formal homolytic substitution at boron with a polymeric B-enolate to regenerate 4a. This process keeps the concentration of the 4a-derived enoyl radicals low and does not lead to chain termination. In fact, after polymerization and precipitation, we isolated from solution 42% of p-methoxyphenethyl phenyl ketone that probably derived from hydrolysis of 4a. Importantly, for reactions performed in benzene, a peak series assigned to an aldol condensation product (\blacktriangle) was identified (Figure 2). This aldol-terminated polymer was derived from a catecholboron enolate by intramolecular aldol condensation.^[13] This side reaction strongly supports our suggestion that the growing polymer chain carries a catecholboron enolate moiety.^[14] Interestingly, polymeric aldol condensation products were identified only in traces for reactions con-

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ducted in THF (see the Supporting Information), which is likely to be the reason why a better polymerization control was achieved in THF as compared to the reactions conducted in toluene (see above).

To further support our mechanism, we investigated the thermal stability of the B-enolate using ¹H NMR spectroscopy. At 70°C, we did not see any decomposition of the Benolate, which indicates that reversible O-B homolysis does not occur and thus a mechanism in analogy to the NMP process,^[6] in which reversible radical generation by homolysis controls the process, is most likely not operative. This was further supported by the experiment lacking the V-70 initiator (see Table 1, entry 6), where polymerization did not occur. We also checked whether the catecholboron moiety can be transferred to the α -cyanoalkyl radical derived from V-70. To this end, a mixture of 4a and V-70 was heated to 70 °C in THF for 1 h. Product analysis revealed a 86% yield of p-methoxyphenethyl phenyl ketone resulting from hydrolysis of 4a along with 67% of 2,3-bis-(2-methoxy-2-methylpropyl)-2,3dimethylsuccinonitrile, which derived from in-cage dimerization of the initiating radicals. The reduced V-70-derived radical (4-methoxy-2,4-dimethylpentanenitrile), which could be formed by either disproportionation or by boron-group transfer followed by hydrolysis, was identified as being only present in traces by GC-analysis. Therefore, boron-group transfer from 4a to the V-70-derived α -cyanoalkyl radical can be ruled out.

In conclusion, we presented a novel method for controlled radical polymerization of alkyl and aryl vinyl ketones. This process comprises an unprecedented boron group transfer reaction as the key step. To date, controlled radical polymerization of this substance class has been limited to the RAFT process; compared to RAFT-mediated MVK-polymerizations, BGTP is faster and also gives good control over the reaction. Mass spectrometry studies support the suggested mechanism and elucidate possible termination processes.

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