Controlled Nitroxide-Mediated Radical Polymerization of Methyl and Phenyl Vinyl Ketone

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ABSTRACT: The article describes unprecedented nitroxide-mediated radical polymerization of methyl and phenyl vinyl ketone (MVK and PVK) using a sterically highly hindered alkoxyamine as initiator/regulator. It is shown that controlled polymerization of PVK is far more difficult to achieve than controlled MVK polymerization. Whereas for MVK high conversion resulting in polyvinyl ketone with low polydispersity index is readily obtained, the PVK polymerization provides good results only in the presence of free nitroxide and styrene as additives. Vinyl ketone polymerizations are analyzed by ESI mass spectrometry. These MS studies provide insights into the problems associated with the controlled nitroxide-mediated polymerization of PVK. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 2150–2160, 2012

KEYWORDS: alkoxyamines; ESI-MS spectrometry; living polymerization; nitroxide-mediated polymerization; polyvinyl ketones

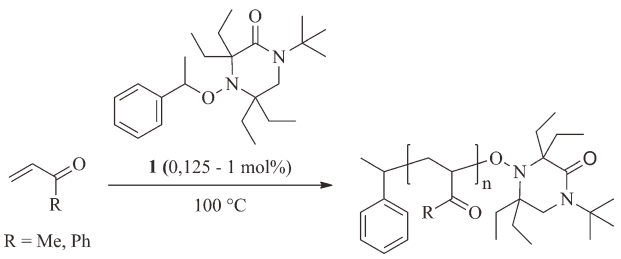
INTRODUCTION Polyvinyl ketones belong to the class of photodegradable polymers that are often used as components for packings.[1] Moreover, they have also found applications as functional materials.[2] These polymers are generally prepared with high polydispersities by conventional (uncontrolled) free radical polymerization.[3] During the past decade, controlled living radical polymerization has been intensively studied and several new methods have been developed: atom transfer radical polymerization (ATRP),[4] RAFT (reversible addition–fragmentation chain transfer polymerization),[5] I-group transfer polymerization,[6] Te, Sb and Bi-group transfer polymerization,[7] Cobalt-mediated polymerization,[8] and nitroxide-mediated polymerization (NMP)[9] have been used for the preparation of polymers with well-defined molecular weights and polydispersities below the theoretical limit [polydispersity index (PDI) $<$ 1.5]. However, Mittal et al. showed that polymerization of methyl vinyl ketone (MVK) by ATRP is not possible due to the fact that the monomer coordinates to the copper catalyst.[10] In contrast to ATRP, no metals are used in NMP.[11] To the best of our knowledge, there are only two reports on successful controlled living radical polymerization of MVK either using RAFT methodology or our recently introduced boron group transfer process.[12] Herein, we report preparation of well-defined polyvinyl ketones using NMP (Scheme 1). We will apply the recently introduced alkoxyamine **1** which was shown to be an excellent initiator/regulator for NMP of styrene, acrylates, and acrylamides.[13]

RESULTS AND DISCUSSION

Polymerization Studies

Polymerizations with alkoxyamine **1** were performed in sealed Schlenk-tubes with vinyl ketones dissolved in benzene at 100°C (MVK:benzene = 1.7:1). For MVK, the alkoxyamine concentration was systematically varied from 0.125% to 1% and results obtained are summarized in Table 1. Polymerization of MVK with **1** in benzene at 100°C occurred efficiently and well controlled (Entries 1–23). A conversion of 57% was achieved in 8 h using 1 mol % initiator loading and polymethyl vinyl ketone (PMVK) with a narrow PDI (1.08) was isolated. PMVK with larger molecular weight resulted by reducing the alkoxyamine **1** loading from 1 mol % to 0.125 mol % (Entries 4, 8, 12, 16). At low initiator loading conversion slightly decreased and polymerization remained well controlled (PDI $<$ 1.12). These experiments were repeated by running polymerizations for 6, 4, and 2 h (Table 1, Entries 1–3, 5–7, 9–11, 13–15). By lowering the initiator loading conversion and PDI slightly decreased. On increasing the polymerization time to 48 h (using 0.5 mol % initiator **1**), the conversion was increased to 73% and narrow PDI (1.08) was preserved (Entry 23).

We also tried styryl-TEMPO (Fig. 1) as initiator/regulator for the polymerization of methyl vinyl ketone (MVK in benzene, 100°C for 4 h), but no polymerization occurred and only initiator could be isolated. As for NMP of acrylates and



SCHEME 1 Nitroxide-mediated polymerization of vinyl ketones with the sterically hindered alkoxyamine **1**.

acrylamides more sophisticated nitroxides are obviously necessary to control NMP of MVK.

We analyzed the controlled character of the **1**-mediated MVK polymerization by determining the conversion as a function of time and by analyzing the molecular weight as a function of monomer conversion [Fig. 2(a,b)]. Polymerizations were run using 0.5 mol % initiator **1** (experimental data are shown in Table 1, Entries 9–12 and 17–23). All plots showed the typical behavior expected for a controlled living radical process. In addition, the plot of $\ln([M]_0/[M])$ versus $t^{2/3}$ depicted in Figure 2(c) showed the linear character expected for a NMP process which is controlled by the persistent radical effect (PRE).[9b,c,e]

TABLE 1 NMP of MVK in Benzene at 100°C—Variation of Initiator Loading and Polymerization Time

Entry	Initiator (mol %)	Time (h)	Conversion (%)	$M_{n,th}$ (g/mol)	$M_{n,exp}$ (g/mol)	PDI
1	0.125	2	16	9,600	10,800	1.17
2	0.125	4	21	12,300	18,300	1.11
3	0.125	6	29	16,800	23,900	1.07
4	0.125	8	39	23,300	31,000	1.07
5	0.25	2	24	6,800	9,800	1.18
6	0.25	4	31	8,800	14,400	1.12
7	0.25	6	35	9,600	16,300	1.10
8	0.25	8	40	11,800	18,400	1.09
9	0.5	2	23	3,200	5,500	1.22
10	0.5	4	31	4,700	7,800	1.16
11	0.5	6	38	5,600	8,700	1.14
12	0.5	8	49	6,700	9,700	1.11
13	1	2	32	2,400	3,900	1.21
14	1	4	44	3,200	4,700	1.16
15	1	6	51	3,700	5,800	1.13
16	1	8	57	4,400	6,800	1.12
17	0.5	1	16	2,200	4,600	1.23
18	0.5	3	29	4,000	6,900	1.16
19	0.5	5	33	4,900	8,200	1.13
20	0.5	7	46	6,800	9,100	1.11
21	0.5	12	52	7,500	10,700	1.09
22	0.5	20	58	8,600	13,100	1.08
23	0.5	48	73	10,500	16,100	1.08

The living character of the MVK polymerization was further investigated by using a PMVK macroalkoxyamine as initiator/regulator for subsequent styrene polymerization leading to a PMVK-*block*-polystyrene diblockcopolymer. To this end, MVK was polymerized at 100°C using alkoxyamine **1** (0.5 mol %) for 3 h in benzene. The macroalkoxyamine was isolated in 28% yield with a low PDI (1.18). The resulting PMVK macroalkoxyamine (M_n = 6700 g/mol) was then used as an initiator for polymerization of styrene (neat styrene at 100°C for 3 h) and PMVK-*block*-polystyrene diblockcopolymer obtained was analyzed by size exclusion chromatography (SEC). The PDI decreased in the copolymer (1.08) and the molecular weight increased to 14,300 g/mol as expected for a successful copolymerization (Fig. 3).

In addition, the living character was proved by using a PMVK as macroalkoxyamine for the subsequent polymerization of *n*-butylacrylate. To this end, MVK was first polymerized at 100°C using alkoxyamine **1** (0.5 mol %) for 7 h in benzene. The PMVK isolated in 45% yield with a PDI of 1.10 (M_n = 10,600 g/mol) was subsequently used as initiator/regulator for the polymerization of *n*-butylacrylate (neat *n*-butylacrylate, 125°C for 4 h). The resulting PMVK-*block*-poly *n*-butylacrylate was analyzed by SEC. We found that for the diblockcopolymer the mean molecular weight increased to 116,700 g/mol while the PDI decreased (1.07).

To get an idea about the accuracy of the SEC-determined M_n values for PMVK using a PMMA standard, we analyzed small molecular weight PMVK also by mass spectrometry for comparison. For that analysis, a PMVK sample was prepared by polymerization of MVK in benzene at 100°C for 90 min using 0.5 mol % alkoxyamine **1** as initiator and was analyzed by SEC and MALDI-MS spectrometry with DHB as matrix (Fig. 4 shows the MALDI-MS spectrum). The theoretical molecular weight ($M_{n,th}$ = 2900 g/mol) was calculated and the experimental molecular weight determined by MALDI-MS spectrometry was found to lie at 3300 g/mol ($M_{n,MALDI}$). SEC on the same sample revealed a M_n of 4900 g/mol ($M_{n,SEC}$). Since it is known that the MALDI-MS technique notoriously provides too low M_n values due to "cutting" of the polymer chains with larger molecular weights, we estimate the correct M_n value of our PMVK to be in between the MALDI-MS

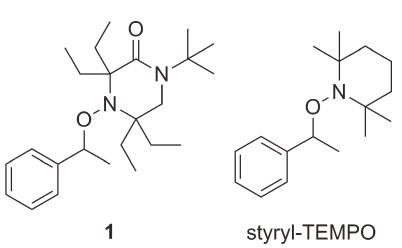


FIGURE 1 Initiators/regulators used for the controlled polymerization of MVK (the sterically highly hindered alkoxyamine **1** and styryl-TEMPO).

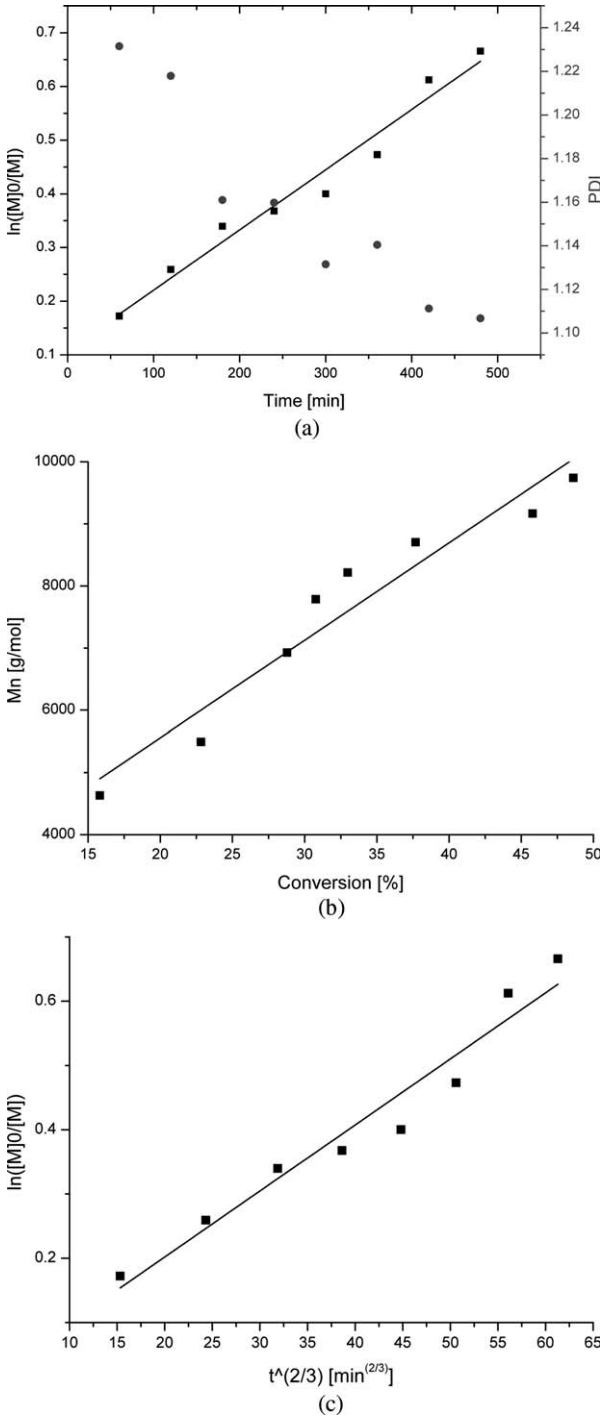


FIGURE 2 (a) Monomer conversion versus time and PDI evolution versus time (MVK in benzene, 100°C, 0.5 mol % **1**; triangles = PDI; squares = $\ln([M]_0/[M])$). (b) Molecular weight versus monomer conversion (MVK in benzene, 100°C, 0.5 mol % **1**). (c) Molecular weight versus $t^{2/3}$ (MVK in benzene, 100°C, 0.5 mol % **1**).

und the SEC results. Hence, the SEC data reported for PMVK throughout this article are likely overestimated values.

To further prove the living character of the MVK polymerization, PMVK was additionally analyzed by ESI-MS spectrometry.[14] To this end, polymerization was conducted in neat monomer (100°C, 1 mol % **1**) and was stopped after 30 min at low conversion targeting low-molecular weight PMVK suitable for mass spectrometry. After removing residual monomer, the crude product was analyzed by ESI mass spectrometry. Figure 5(a) shows a part of the MS-spectrum of a low-molecular weight PMVK. The four most prominent peak groups revealed the living nature of the 1-mediated MVK polymerization. Peaks corresponding to polymers bearing a styryl moiety as the initiating unit and the nitroxide moiety as chain terminating unit were identified (see structure in Scheme 1, R = Me). The peak series at 988.1077 correspond to a double Na^+-adduct containing 22 MVK monomers. The simulated spectrum in Figure 5(c) perfectly matches the measured high-resolution mass spectrum. The peak series at 985.6309 represent the same polymer (22 MVK entities) which is doubly charged with one Na^+-ion and one NH_4^+-ion. This assignment is supported by the calculated spectrum depicted in Figure 5(e). The peak series at 971.6343 correspond to the mono Na^+-adduct of the polymer bearing seven MVK moieties. Again, the simulated spectrum in Figure 5(b) shows a perfect match. The fourth prominent peak series at

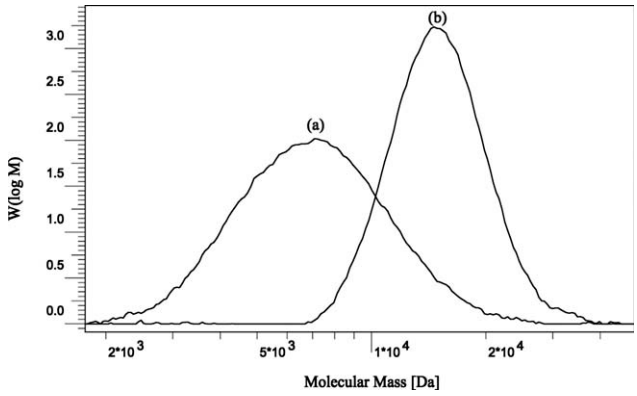


FIGURE 3 SEC-chromatograms of a PMVK (a) (MVK in benzene, 100°C, 0.5 mol % **1**) and a diblockcopolymer PMVK-*b*-PS (b) after reinitiation (neat styrene, 100°C).

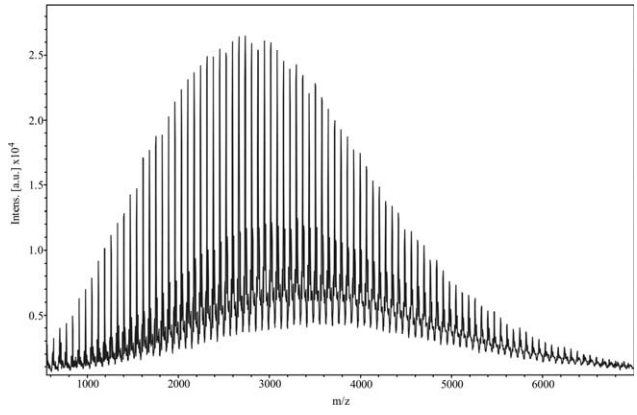


FIGURE 4 MALDI-MS spectrum of a low-molecular weight PMVK (MVK in benzene, 100°C, 0.5 mol % **1**).

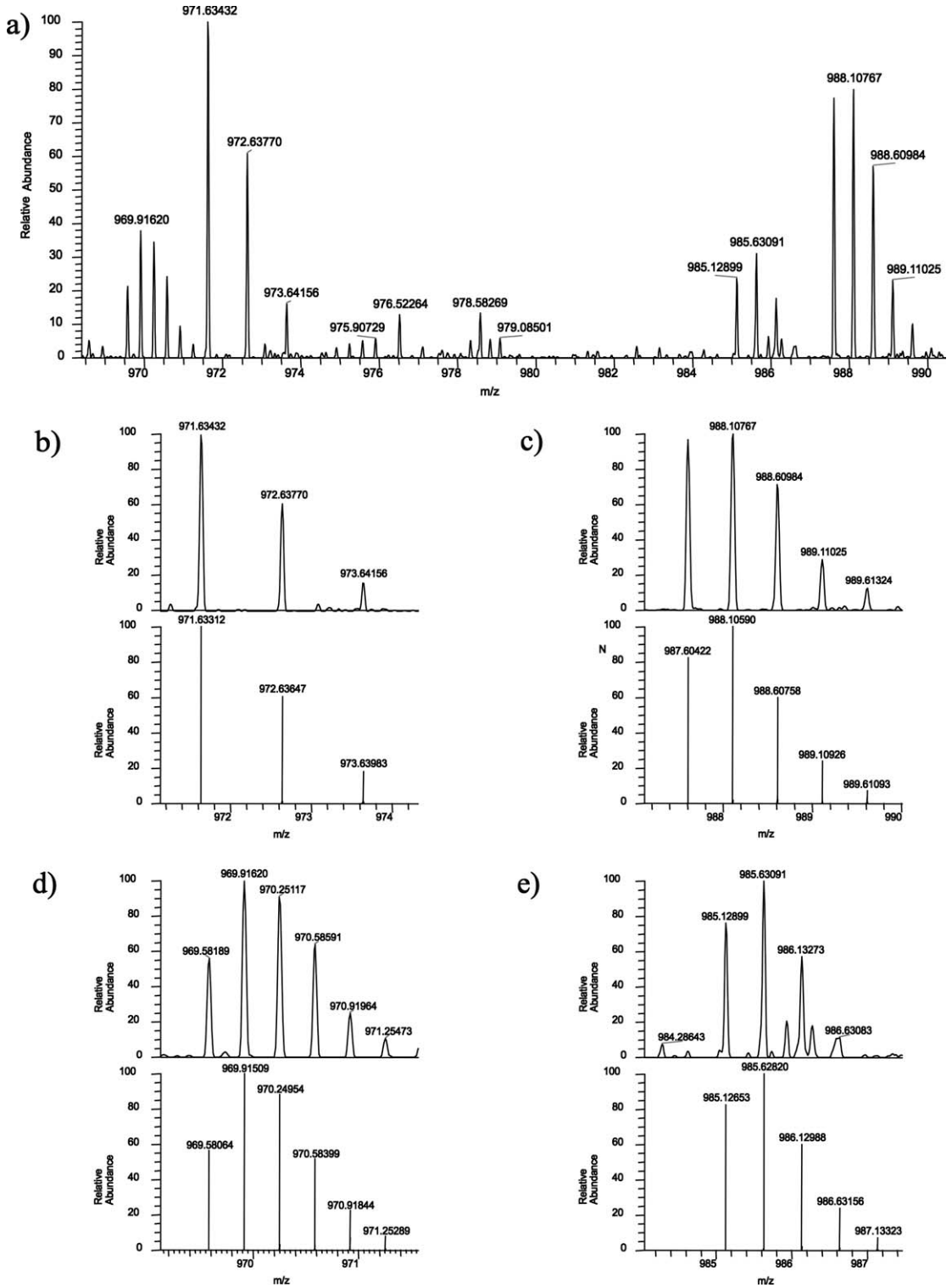


FIGURE 5 ESI–MS spectrum of a low molecular weight PMVK sample: (a) part of the ESI mass spectrum of the sample (neat MVK, 100°C, 1 mol % **1**, 0.5 h polymerization time). (b–e) measured (above) and calculated (below) spectra of distinct polymer species in different charge states: (b) Na^+-adduct with 7 MVK moieties. (c) 2 Na^+-adduct (doubly charged) with 22 MVK moieties. (d) 3 Na^+-adduct (triply charged) with 35 MVK moieties. (e) Na^+/NH_4^+-adduct (doubly charged) with 22 MVK moieties.

969.9162 belongs to a triply charged polymer (3 Na^+-adduct) containing 35 MVK entities. The assignment is further supported by the calculated spectrum presented in Figure 5(d). Hence, all the prominent peaks could be assigned to living polymers bearing the alkoxyamine moiety at the terminus of the polyketone and a styryl unit as initiating

TABLE 2 NMP of PVK in Benzene at 100°C in the Presence of **2** (0.025 mol %)—Variation of Polymerization Time

Entry	Initiator (mol %)	Time (h)	Conversion (%)	$M_{n,th}$ (g/mol)	$M_{n,exp}$ (g/mol)	PDI
1[a]	0,5	0,5	66	17,700	11,700	1.55
2	0.5	1	18	4,200	6,500	1.11
3	0.5	2	21	5,100	7,200	1.12
4	0.5	3	24	6,500	7,600	1.10
5	0.5	4	27	7,500	9,300	1.11
6	0.5	5	28	8,200	9,400	1.13
7	0.5	6	35	9,200	11,400	1.12
8	0,5	8	38	10,300	10,900	1.15
9	0,5	24	35	9,400	10,400	1.18
10[b]	0,5	6	56	13,500	14,700	1.09

[a] In the absence of **2**.
[b] 5% Styrene was added to the reaction mixture.

entity. This showed that polymerization (at least at low conversion) occurred with a high degree of livingness and that all chains were initiated by the alkoxyamine initiator **1**. Importantly, peaks derived from olefin terminated polymers, which might result from hydroxylamine elimination, were not detected in the ESI mass spectrum.

After successful polymerization of MVK, we decided to test whether alkoxyamine **1** also allows for controlled NMP of aryl vinyl ketones. We chose phenyl vinyl ketone (PVK) as a test monomer and first experiments were carried out neat or in benzene as a cosolvent at 100°C. We found that polymerization of PVK was far more difficult to control than polymerization of MVK. Polymerization of PVK under neat conditions or in benzene occurred fast and not well controlled. Reaction mixture became highly viscous in less than 30 min and SEC-analysis revealed a PDI of 1.55, indicating that polymerization was not controlled (Table 2, Entry 1). It seemed that k_p for the polymerization of PVK is too large and the concentration of free nitroxide is too small to control that process. This is reminiscent to NMP of acrylates. To solve that problem, we added a small amount of free nitroxide 2 (0.025 mol %, Fig. 6).[15] Addition of free nitroxide ensures a sufficient high concentration of the persistent radical which should lead to a better control. This is well established for NMP of methyl acrylate.[9,16] As expected, polymerization in the presence of **2** was slower and reaction delivered PPVK with a narrow PDI (Entry 2). Conversion was increased to 38% on increasing reaction time to 8 h (Entries 3–7). However, further extension of reaction time did not allow for preparation of PPVK with higher molecular weight (Entries 8–9). At around 35–40% conversion, reaction stopped. Polymerization seemed to be well controlled at low conversion as shown by plotting the monomer conversion as a function of time [Fig. 7(a)] and the molecular weight as a function of monomer conversion [Fig. 7(b)]. Moreover, the linear relation of $\ln([M]_0/[M])$ to $t^{2/3}$ alluded to a controlled NMP [Fig. 7(c)]. These polymerizations were run using 0.5 mol % initiator **1** (experimental data are summarized in Table 2, Entries 2–7).

We assumed that the low conversion might be a result of the instability of the polymeric alkoxyamine. Hydroxylamine elimination might lead to dead polymer chain ends (Scheme 2).[9] In contrast to the polymerization of MVK, for PVK the resulting α,β-unsaturated ketone is further stabilized via conjugation with the phenyl moiety. Such a competing hydroxylamine fragmentation is a problem in NMP of methyl methacrylate.

An elegant solution to that problem was provided by Charleux et al.[17] Addition of a small amount of styrene to MMA ensures the ultimate monomer moiety in the polymer to be a styrene unit, which in the dormant state (as alkoxyamine) is not prone to undergo hydroxylamine fragmentation. We therefore added 5% of styrene with respect to PVK and indeed yield was increased to 56%. Molecular weight increased to 14,700 g/mol and PDI decreased to 1.09 (Entry 10). Unfortunately, longer reaction times did not provide polymers with higher molecular weights.

To get a better picture associated with problems of NMP of PVK at higher conversion, we decided to analyze the polymerization process using ESI mass spectrometry. To this end, we targeted low-molecular weight polymers that are suitable to MS analysis (PVK:**1** = 4:1 in benzene at 100°C). Although peaks were not very prominent, we could unambiguously identify the Na^+-adducts of oligomers lacking the hydroxylamine moiety (see Scheme 2). Note that we did not see the corresponding peaks in the oligomer mixture obtained in the polymerization of MVK. This shows that the tendency for hydroxylamine elimination in a macroalkoxyamine is more pronounced for PPVK-**2** as compared with PMVK-**2**. Along with the disproportionation of the macroradical with the nitroxide leading to the hydroxylamine, we felt that the PPVK-macroradical might further react via other decomposition pathways. We therefore decided to investigate the oligomers by MS–MS-analysis. Our group recently reported on successful ESI–MS sequence analysis of oligomers prepared by NMP.[14c] Such an analysis will give us information regarding the fate of the PPVK-macroradicals in the gas phase. The MS–MS spectra were recorded on an orbitrap mass spectrometer which provides precise and high-resolution masses. In the MS–MS experiments, we used CID (collision-induced decomposition) by the specific excitation of precursor ions to produce the corresponding daughter ions (Fig. 8).

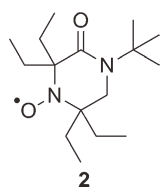


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FIGURE 6 Nitroxide used for controlled polymerization of PVK.

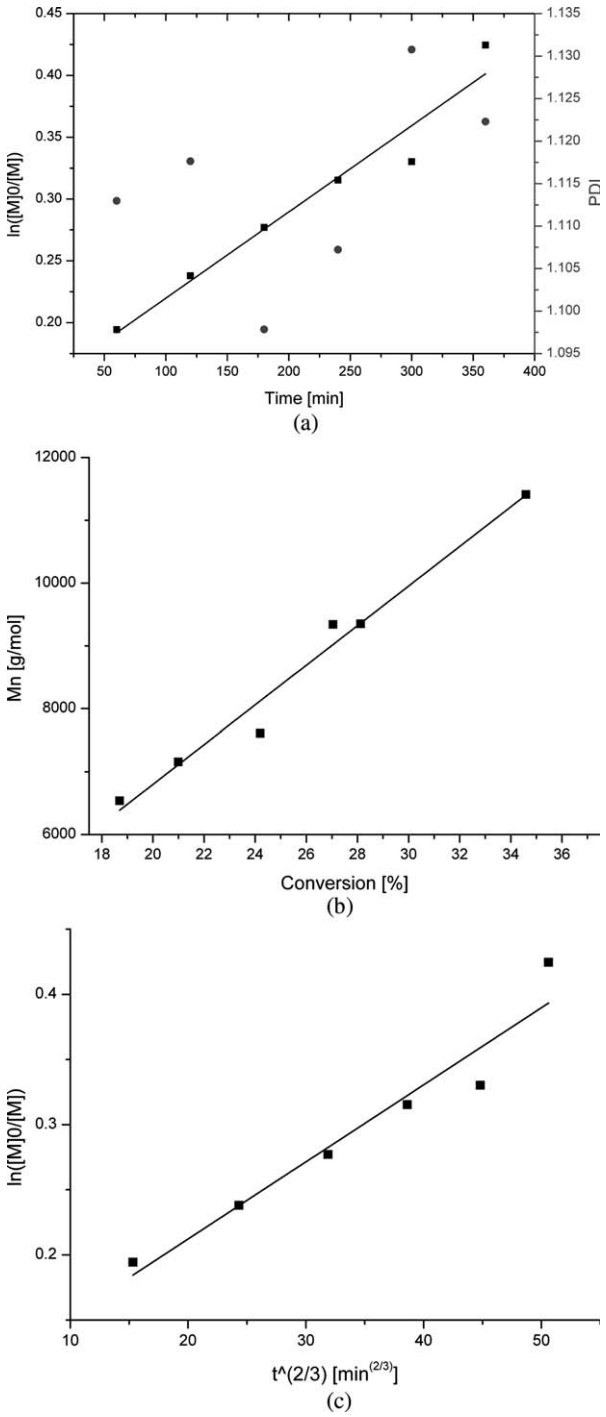


FIGURE 7 (a) Monomer conversion versus time and PDI evolution versus time (PVK in benzene, 100°C, 0.5 mol % **1**, 0.025 mol % free nitroxide **2**; triangles = PDI; squares = $\ln([M]_0/[M])$. (b) Molecular weight versus monomer conversion (PVK in benzene, 100°C, 0.5 mol % **1**, 0.025 mol % free nitroxide **2**). (c) Molecular weight versus $t^{2/3}$ (PVK in benzene, 100°C, 0.5 mol % **1**, 0.025 mol % free nitroxide **2**).

All oligomers identified showed as first reaction in the gas phase the homolytic C—O bond cleavage liberating nitroxide 2 and the corresponding macroradical. The macroradical then further reacted via two different pathways:

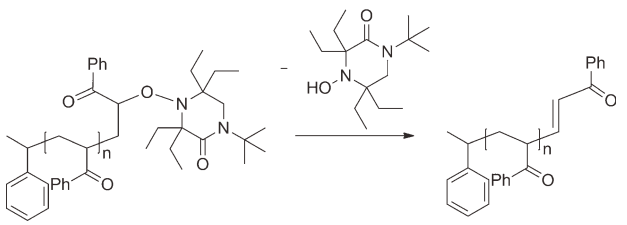
a. Gas-phase depolymerization by PVK fragmentation to form the corresponding macroradicals (Scheme 3) identified as Na^+-adducts (m/z = 1316, 1184, 1052, 920, 788, 656, 524; in Figure 8 the corresponding peaks are marked with ★), and
b. 1,5-H transfer to give the corresponding tertiary radicals which can further react via two pathways (Scheme 4). Fragmentation according to pathway 1 affords a macroradical, along with a trimer with m/z = 419 designated as ● in Figure 8. Fragmentation via pathway 2 provides an olefin terminated polymer designated as ■ with m/z = 1065, 933, 801, 669, 537 (see Scheme 4).

We assume that the chemistry which occurs in the gas phase is also occurring in solution. Hence, these gas-phase experiments gave important hints regarding possible competing reactions. Besides the disproportionation of the nitroxide with the macroradical we believe that the 1,5-H transfer in the macroradical occurs in the NMP of PVK as a major side reaction. We found that the larger the polymer the more intensive the corresponding follow-up product peaks appeared in the corresponding MS–MS spectra [compare Fig. 8(a–c)]. Since the rate for the 1,5-H transfer should not heavily depend on the size of the oligomer, we believe that the 1,5-H transfer likely already occurred during polymerization in solution leading after nitroxide trapping to tertiary alkoxyamines. In the MS analysis during mass selection, we cannot distinguish between two alkoxyamines of the same mass where the nitroxide moiety is terminally or internally located. Internal alkoxyamines will lead to the same gas-phase MS-analysis (Scheme 5). Tertiary alkoxyamines are more prone to undergo hydroxylamine elimination leading to dead polymer chains.

EXPERIMENTAL

Materials

All reactions were carried out in heat-gun-dried glassware under an argon atmosphere and were performed by using standard Schlenk techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), a Varian Inova 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz), or Varian Unity plus 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz). Chemical shifts δ in ppm are referenced to the solvent residual peak. Thin-layer chromatography was carried out on Merck silica gel 60 F_{254} plates; detection by UV or dipping into a solution of $KMnO_4$ (1.5 g), $NaHCO_3$ (5.0 g) in H_2O (400 mL) followed by heating. Flash chromatography (FC) was carried



SCHEME 2 Possible hydroxylamine elimination which leads to dead polymer chain ends.

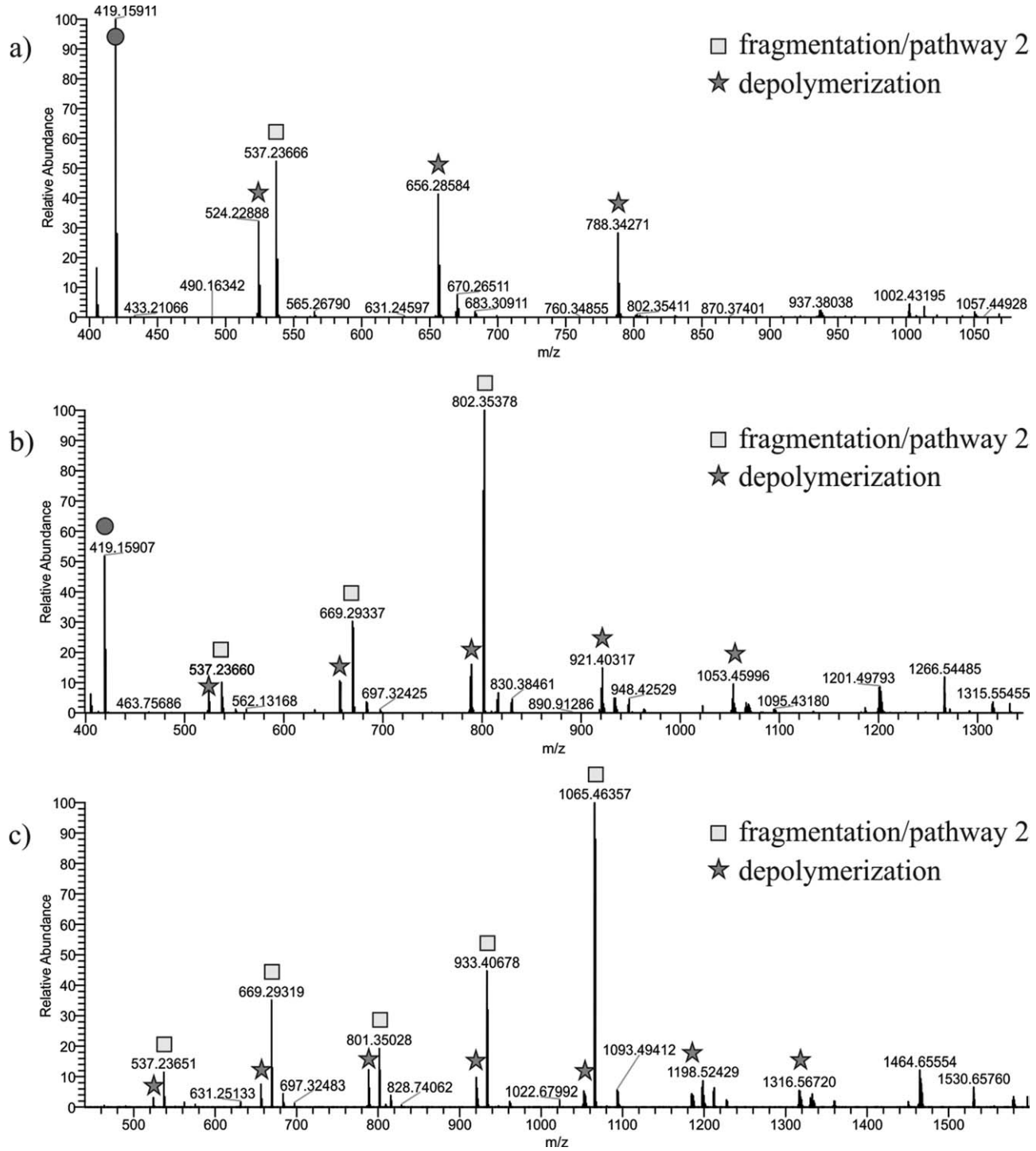
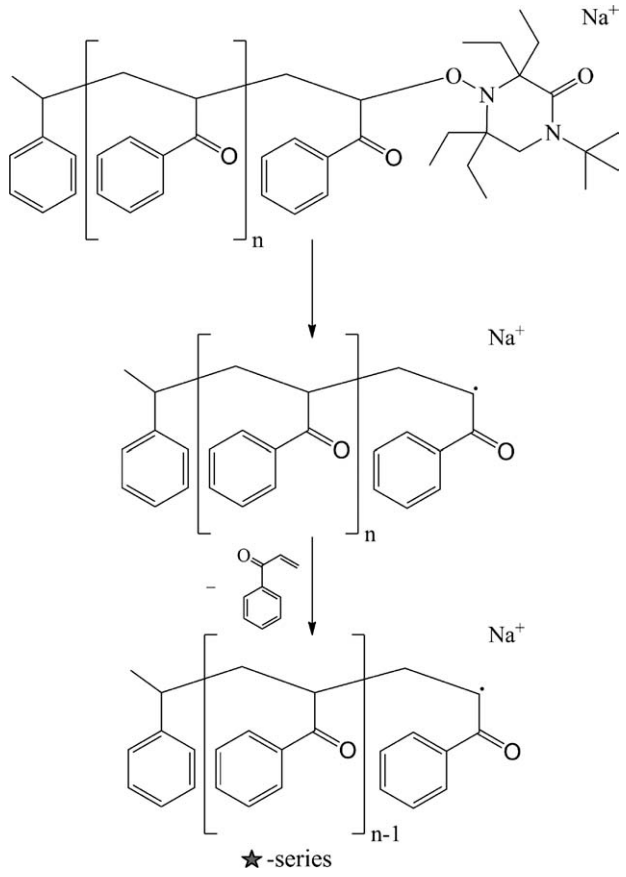


FIGURE 8 MS–MS spectra of a low molecular weight PVK oligomer. CID fragmentations of a PPVK oligomer (a) m/z = 1071 Na^+-addition, (b) m/z = 1336 Na^+-addition, and (c) m/z 1601 Na^+-addition (stars = depolymerization; squares = 1,5-H transfers; circles = 1,5-H transfer followed by elimination of the initiating styrene moiety).

out on Merck or Fluka silica gel 60 (40–63 μm) at about 1.5 bar. IR spectra were recorded on a Varian 3100 FT-IR equipped with a MKII Golden Gate Single Reflection ATR unit. ESI–MS (m/z) and HRMS (m/z) were performed using a Bruker MicroTof (loop injection; resolution: 10,000), a LTQ Orbitrap XL (nanospray inlet, 1.1 KV, resolution: 30,000), and an Autoflex Speed TOF-MS (Bruker Daltonics). SEC was carried out with degassed THF as eluent at a flow rate of 1.0 mL/min at room temperature on a system consisting of a Smartline Pump 1000 (Knauer), a set of two PLgel 5 μm MIXED-C columns (300 × 7.5 mm, Polymer Laboratories) and a Knauer RI differential refractometer detector. Data



SCHEME 3 C—O bond homolysis and depolymerization.

were analyzed with PSS WinGPC Compact V.7.20 software (Polymer Standards Service) based on calibration curves built upon poly(methyl methacrylate) standards (Polymer Laboratories Poly(methyl methacrylate) Medium MW Calibration Kit M-M-10 to determine the molecular weight of polyketones) with peak molecular weights ranging from 1660 to 1,000,000 g/mol. The following chemicals were purchased and used as received: acetic acid (Acros, 99.8%), ammonia solution (Acros, 25% in water), (1-bromoethyl)benzene (Alfa Aesar, 97%), 3-bromopentane (Sigma–Aldrich, 95%) chloroform (Fisher Scientific, $\geq$99%), copper powder (Sigma–Aldrich, $<$10 microns, 99%), copper(II) trifluoromethanesulfonate (Alfa Aesar, 98%), dimethyl sulfoxide (Acros, 99.8%), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (Sigma–Aldrich, 98%), ethyl acetate (Acros, 99.6%), formaldehyde (Acros, 37% solution in water, stabilized with 10–15% methanol), 4-heptanone (Acros, 98%), 3-pentanone (Sigma–Aldrich, 98%), peroxyacetic acid (Acros, 35% solution in diluted acetic acid), potassium hydroxide (Fluka, powder, $\geq$90%), 3-nitropropane (Acros, 96%), sodium nitrate (Acros, $\geq$98.5%), *tert*-butylamine (Acros, 99%), zinc powder (Acros, 99.99%, 40 mesh), 3-chlorophenylpropanone (Fluka, $\geq$97%).

MVK (Alfa Aesar, tech. 90%, stabilized with 0.5% hydrochinone) was distilled under reduced pressure to remove the stabilizer. THF was freshly distilled from K, Et_2O was freshly distilled from K/Na, benzene was freshly distilled from Na and CH_2Cl_2 was distilled from P_2O_5.

Mass Spectrometry

ESI spectra to prove livingness of the polymerization were recorded on a LTQ Orbitrap XL (Thermo Scientific) with CID and HCD capabilities. The resolution of the Orbitrap was R = 30,000 routinely, 100,000 if necessarily. Spectra are averaged to improve the signal to noise ratio. Samples (0.2 mg) were dissolved in 1 mL methanol or chloroform/methanol (1:1). To improve the sodiation, 10 μL of a saturated methanolic $NaBF_4$ solution was added. All samples were introduced by static nanospray with internal electrical contact. The capillary voltage was adjusted to provide a stable spray (0.8–1.4 kV). MALDI spectra were recorded with an Autoflex Speed TOF-MS (Bruker Daltonics) in linear mode. Samples were prepared with 2,5-DHB containing $NaBF_4$ to promote sodiation. The resolution in this mode is not sufficient to separate isotopes. Therefore, m/z is calculated with stoichiometric values and peak intensities were used to calculate the distribution.

1-*tert*-Butyl-3,3,5,5-tetraethyl-4-(1-phenylethoxy)-piperazin-2-on (1)

Alkoxyamine **1** and the corresponding nitroxide **2** were prepared according to our recently published procedure.[13a]

1-Phenylpropenone (2)

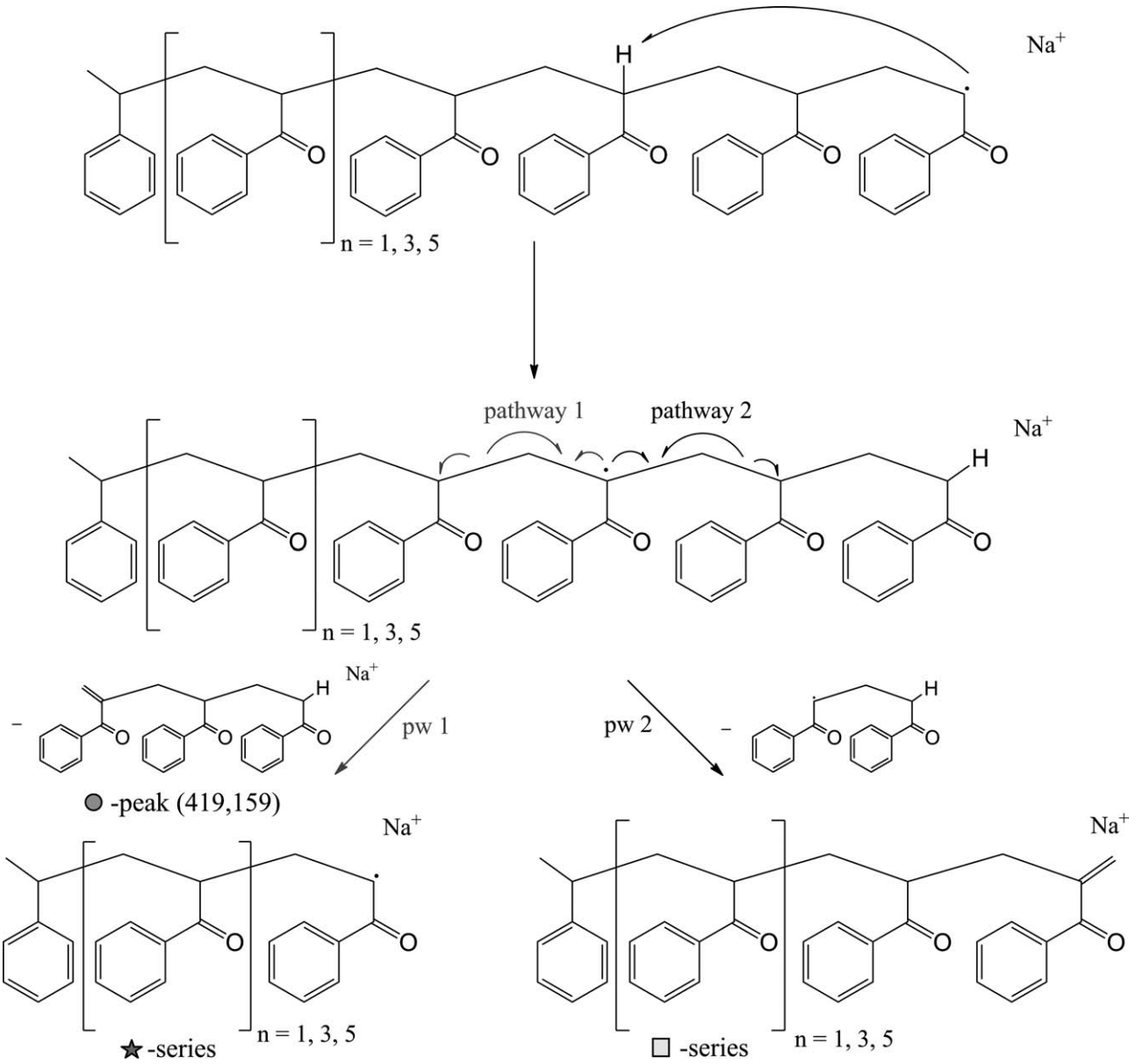
According to Martín-Matute et al.,[18] a mixture of 3-chloro-1-phenyl-1-propanone (10 g, 59 mmol) and potassium acetate (6.41 g, 65 mmol) in ethanol (500 mL) was stirred under reflux for 3 h. After cooling to room temperature, ethanol was removed under reduced pressure. The residue was dissolved in EtOAc (200 mL) and washed with H_2O (3 $\times$ 150 mL). The organic phase was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. Purification by FC on silica gel (pentane:EtOAc: 20:1) afforded a slightly yellow oil (5.4 g, 69%). The physical data are in agreement with those reported in the literature: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, J = 7.0 Hz 2 H), 7.42–7.27 (m, 3 H), 6.99 (dd, J = 17.1, 10.6 Hz, 1 H), 6.26 (d, J = 17.1, H), 5.75 (d, J = 10.6, H).[19]

Typical Procedure for the Polymerization of MVK

A heat-gun dried Schlenk tube was charged with initiator **1**, MVK, and benzene. The tube was subjected to three freeze–thaw cycles and then sealed. The polymerization was carried out under argon at 100°C for 1 h to 24 h. The resulting mixture was cooled to room temperature and dissolved in CH_2Cl_2 (1 mL). Solvent and residual monomer were removed under reduced pressure to afford the polymer. Conversion was determined gravimetrically; molecular weight and PDI were determined by SEC.

Typical Procedure for the Polymerization of PVK

A heat-gun dried Schlenk tube was charged with initiator **1**, nitroxide **2**, PVK, and benzene. The tube was subjected to three freeze–thaw cycles and then sealed. The polymerization was carried out under argon at 100°C for 1 to 8 h. After the reaction mixture was allowed to cool to room



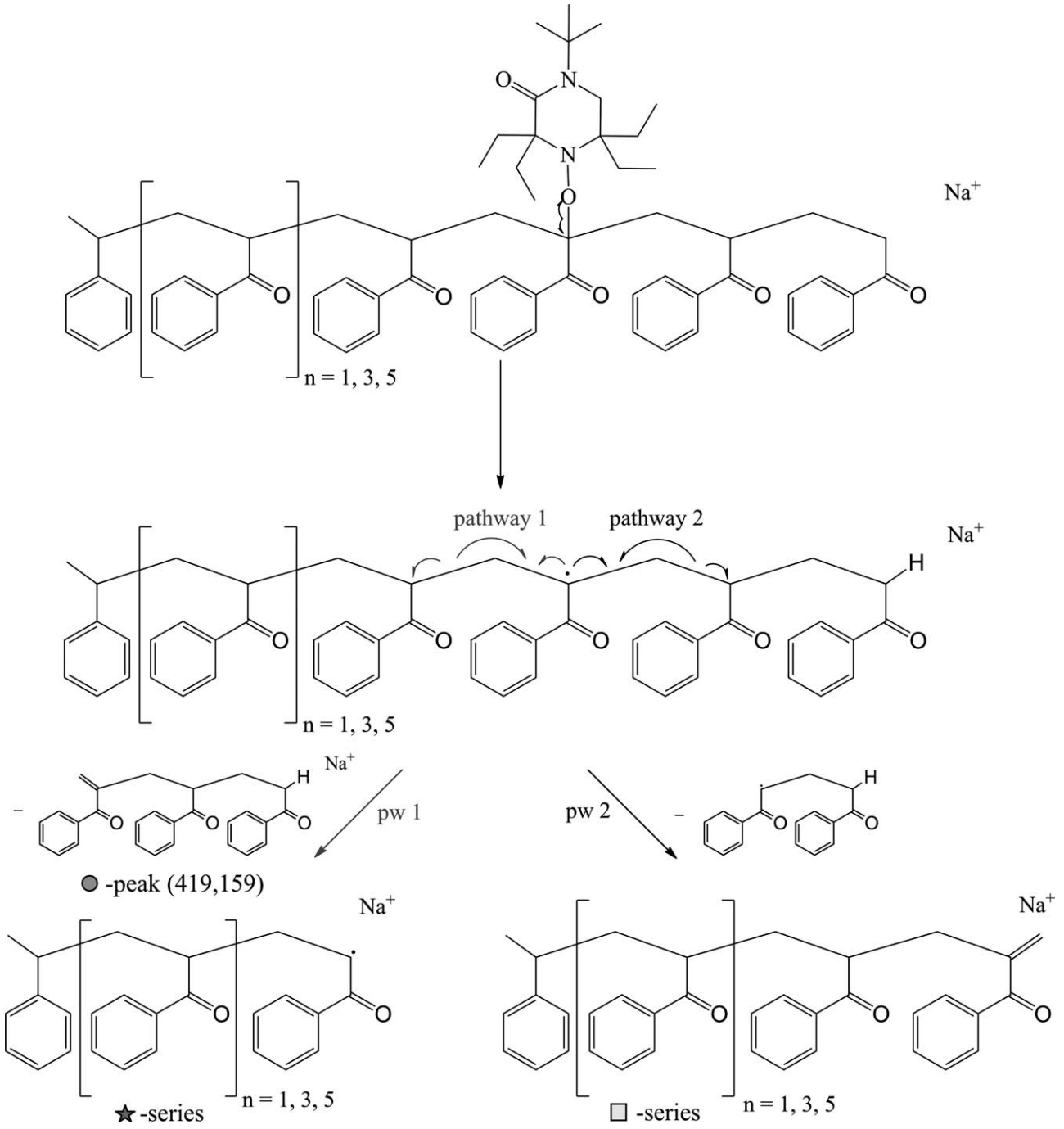
SCHEME 4 1,5-H transfer and follow up gas-phase chemistry by two different pathways investigated by MS-MS analysis (in pathway 1 both fragments can appear as sodiated ions in equal probabilities).

temperature, the residue was dissolved in dichloromethane (1 mL). The polymer was precipitated three times on addition of a 4:1 mixture of pentane/DCM (5 mL) to afford polyphenyl vinyl ketone as a white solid. Molecular weight and PDI were determined by SEC; conversion was determined gravimetrically.

CONCLUSIONS

We showed for the first time that controlled NMP of MVKs is possible using alkoxyamine **1** as an intiator/regulator. This alkoxyamine is readily prepared in a large scale.[13a] Polymerizations occurred well controlled delivering PMVKs with narrow PDIs. ESI–MS spectrometry provided evidence for a living radical polymerization process of MVK. Peak series in the mass spectrum showed that all polymers identified are dormant and bear a nitroxide moiety. Moreover, successful use of such a PMVK polymer as macroinitiator for the formation of block copolymers further supported the high degree of livingness of the polymerization.

Polymerization of PVK was far more difficult to control. Acceptable results were achieved only on adding free nitroxide **2** (0.025 mol %) and 5 mol % of styrene. Using these additives, it was possible to obtain polyphenyl vinyl ketone in a yield of 56% with a narrow PDI. Conversion and yield were not increased upon increasing the reaction time. ESI–MS and MS–MS studies revealed that hydroxylamine elimination



SCHEME 5 C—O-bond homolysis of the tertiary alkoxyamine and follow up gas-phase chemistry by two different pathways investigated by MS–MS analysis (in pathway 1 both fragments can appear as sodiated ions in equal probabilities).

leading to dead polymers is a problem in NMP of PVK. In contrast to MVK, the α,β-unsaturated ketones formed on hydroxylamine elimination are further stabilized by conjugation into the phenyl substituent. MS-studies also revealed that 1,5-H transfer in the macroradical is a competing reaction. That H-transfer can lead to chain termination as investigated by MS–MS experiments.

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