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# Reversible Addition–Fragmentation Chain Transfer Polymerization of Vinyl Chloride

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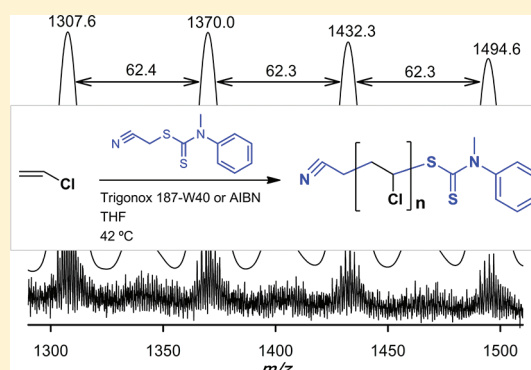
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## Supporting Information

**ABSTRACT:** Controlled/"living" radical polymerization (CLRP) of vinyl chloride (VC) via the reversible addition–fragmentation chain transfer (RAFT) process is reported for the first time. The cyanomethyl methyl(phenyl)carbamodithioate (CMPCD) was found to be an efficient RAFT agent enabling the CLRP polymerization of VC monomer under certain experimental conditions. Two different radical initiators, having very distinct half-life times at room temperature, were employed in this study. The kinetic studies of RAFT polymerization of VC show a linear increase of the molecular weight with the monomer conversion and the lowest polydispersity (PDI) ever reported for poly(vinyl chloride) (PVC) synthesized with CLRP method (PDI  $\sim$  1.4). The resulting PVC was fully characterized using the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), <sup>1</sup>H nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR), and gel permeation chromatography (GPC) techniques. The <sup>1</sup>H NMR and MALDI-TOF-MS analysis of PVC prepared via RAFT polymerization method have shown the absence of structural defects and the presence of chain-end functional groups. The "livingness" of the PVC was also confirmed by a successful reinitiation experiment. The suitability of the RAFT agent was also confirmed via high-level *ab initio* molecular orbital calculations.



## INTRODUCTION

Controlled/"living" radical polymerization (CLRP) methods provide unprecedented tools for the synthesis of polymers with controlled structures, architectures, chain-end fidelity, and narrow molecular weight distributions. The most widely used CLRP methods are transition metal catalyzed living radical polymerization, which is often called atom transfer radical polymerization (ATRP),<sup>1</sup> nitroxide mediated polymerization (NMP),<sup>2</sup> and reversible addition–fragmentation chain transfer (RAFT) polymerization.<sup>3,4</sup> The development of the next generation of CLRP methods for control of nonactivated vinyl monomers (such as vinyl acetate, *N*-vinylpyrrolidone, vinyl chloride, etc.) remains an important challenge. CLRP of vinyl chloride (VC) is of particular interest because poly(vinyl chloride) (PVC) is one of the most widely consumed polymers worldwide. Conventional free radical polymerization (FRP) of VC is the only available industrial process to produce the polymer in large scale. PVC made via conventional FRP process lacks the thermal stability due to the presence of structural

defects (allyl and tertiary chloride groups), which are the result of different unavoidable side reactions.<sup>5–9</sup>

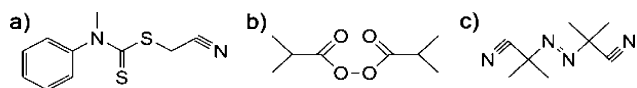
To date, the most successful CLRP of VC has been achieved by single electron transfer living radical polymerizations (SET-LRP)<sup>10</sup> or single electron transfer degenerative chain transfer living radical polymerizations (SET-DTLRP).<sup>7,11–20</sup> Since the development of these CLRP strategies for VC polymerization, several studies involving the homopolymerization, copolymerization, functionalization, and scaling-up have been published, and this topic summarized in a recent review paper by Rosen and Percec.<sup>21</sup> Despite these advances, it remains desirable to adapt other CLRP techniques to VC so as to broaden the scope of compatible monomers for block copolymer synthesis. To this end, in the present work we investigate the RAFT polymerization of VC in the presence of cyanomethyl methyl(phenyl)carbamodithioate (CMPCD),

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using 2,2'-azobis(isobutyronitrile) (AIBN) or a very fast peroxide initiator (Trigonox 187-W40) (see Figure 1 for structures).



**Figure 1.** Structures of (a) cyanomethyl methyl(phenyl)-carbamodithioate (CMPCD), (b) Trigonox 187-W40 (diisobutryl peroxide or DIBPO), and (c) 2,2'-azobis(isobutyronitrile) (AIBN).

## EXPERIMENTAL SECTION

**Materials.** VC (99%) was kindly supplied by CIREs Lda, Portugal. CMPCD (Sigma-Aldrich, 98%) and Trigonox 187-W40 (40% water and methanol emulsion of diisobutryl peroxide (DIBPO), AkzoNobel), deuterated tetrahydrofuran ( $d_8$ -THF) (Euriso-top, 99.5%), 2-(4-hydroxyphenylazo)benzoic acid (HABA) (Sigma-Aldrich, 99.5%),  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA) (Sigma-Aldrich, 99.5%), and methanol (Labsolve, 99.5%) were used as received. AIBN (Fluka, 98%) was recrystallized three times from ethanol before use. THF (Panreac, HPLC grade) was filtered (0.2  $\mu$ m filter) under reduced pressure before use. Cyclohexanone (Sigma-Aldrich, 99.8%) and dichloromethane (Fluka, 99.9%) were dried before use.

**Techniques.** The  $^1\text{H}$  NMR spectra of reaction mixture samples were recorded with a Varian VNMRs 600 MHz spectrometer, with a warm 3 mm PFG triple resonance indirect detection probe, in THF- $d_8$  with tetramethylsilane (TMS) as an internal standard.

The chromatographic parameters of the samples were determined using high performance gel permeation chromatography HPSEC; Viscotek (Viscotek TDAmx) with a differential viscometer (DV); right-angle laser-light scattering (RALLS, Viscotek); low-angle laser-light scattering (LALLS, Viscotek) and refractive index (RI) detectors. The column set consisted of a PL 10 mm guard column (50  $\times$  7.5 mm<sup>2</sup>) followed by one Viscotek T200 column (6  $\mu$ m), one MIXED-E PLgel column (3  $\mu$ m), and one MIXED-C PLgel column (5  $\mu$ m). HPLC dual piston pump was set with a flow rate of 1 mL/min. The eluent (THF) was previously filtered through a 0.2  $\mu$ m filter. The system was also equipped with an online degasser. The tests were done at 30  $^\circ\text{C}$  using an Elder CH-150 heater. Before the injection (100  $\mu$ L), the samples were filtered through a polytetrafluoroethylene (PTFE) membrane with 0.2  $\mu$ m pore. The system was calibrated with narrow polystyrene (PS) standards. The  $dn/dc$  was determined as 0.105 for PVC. Molecular weight ( $M_n^{\text{GPC}}$ ) and polydispersity (PDI) of synthesized polymers were determined by Universal Calibration (the viscosity was measured directly by the viscometer detector) using OmniSEC software version 4.6.1.354.

For the MALDI-TOF-MS analysis, the PVC samples were dissolved in THF at a concentration of 10 mg/mL. HABA and CHCA (0.05 M in THF) were used as matrix. The dried-droplet sample preparation technique was used to obtain 1:1 ratio (sample/matrix); an aliquot of 1  $\mu$ L of each sample was directly spotted on the MTP AnchorChip TM 600/384 TF MALDI target, Bruker Daltonik (Bremen Germany), and before the sample dry, 1  $\mu$ L of matrix solution in THF was added and allowed to dry at room temperature, to allow matrix crystallization. External mass calibration was performed with a peptide calibration standard (PSCII) for the range 700–3000 (9 mass calibration points); 0.5  $\mu$ L of the calibration solution and matrix previously mixed in an Eppendorf tube (1:2, v/v) were applied directly on the target and allowed to dry at room temperature. Mass spectra were recorded using an Autoflex III smartbeam1MALDI-TOF-MS mass spectrometer Bruker Daltonik (Bremen, Germany) operating in the linear and reflectron positive ion mode. Ions were formed upon irradiation by a smartbeam1 laser using a frequency of 200 Hz. Each mass spectrum was produced by averaging 2500 laser shots collected across the whole sample spot surface by screening in the range  $m/z$  400–8000. The laser irradiance was set to 35–40% (relative scale 0–100) arbitrary units according to the corresponding threshold required for the

applied matrix systems. The theoretical isotope distribution was obtained using the Isotope Distribution Calculator software.<sup>22</sup>

**Procedures.** The VC RAFT polymerization kinetic experiments were carried out in a 50 mL glass high-pressure tube equipped with a magnetic stir bar. In the kinetic studies each point represents a single experiment.

**Typical Procedure for the RAFT Polymerization of VC in THF at 42  $^\circ\text{C}$  with  $[\text{VC}]_0/[\text{CMPCD}]_0/[\text{Trigonox}]_0 = 250/1/0.2$ .** A 50 mL Ace Glass 8645#15 pressure tube, equipped with bushing and plunger valve, was charged with a mixture of CMPCD (64.8 mg, 0.291 mmol), Trigonox 187 W40 (25.4 mg), and THF (5.0 mL) (previously bubbled with nitrogen for about 5 min). The precondensed VC (5 mL, 73 mmol) was added to the tube. The exact amount of VC was determined gravimetrically. The tube was closed and degassed through the plunger valve by applying reduced pressure and filling the tube with  $\text{N}_2$  about 20 times, submerged in liquid nitrogen. The valve was closed, and the tube reactor was placed in a water bath at  $42 \pm 0.5$   $^\circ\text{C}$  with stirring (700 rpm). After 24 h, the reaction was stopped by plunging the tube into ice water. The tube was slowly opened, the excess VC was distilled, and the mixture was precipitated into 250 mL of methanol. The polymer was separated by filtration and dried in a vacuum oven until constant weight to produce 2.514 g (49.7%) of PVC,  $M_n^{\text{GPC}} = 6044$  g/mol,  $M_w/M_n = 1.43$ .

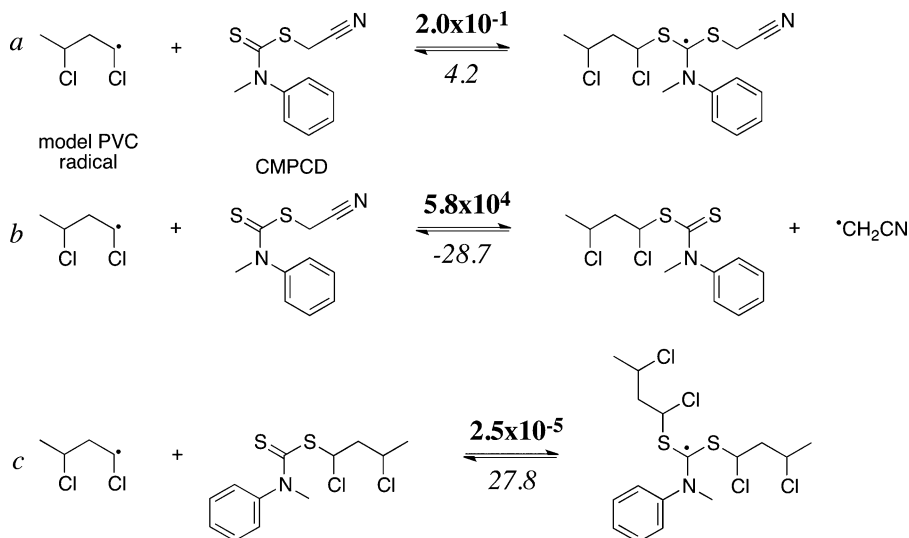
**Chain Extension Experiment.** The experiment was performed in a similar way to the typical polymerization, but using 46.8 mg of PVC-CTA (CTA: chain transfer agent) previously dissolved in THF ( $M_n^{\text{GPC}} = 3100$  g/mol,  $M_w/M_n = 1.44$ ) as macro-CTA, 3.3 mg of Trigonox 187 W40, a total 10 mL of THF (previously bubbled with nitrogen for about 5 min), and 5.0 mL (73 mmol) of precondensed VC were also charged into the reactor. The reaction proceeded for 72 h, and 2.19 g (42.6%) PVC was obtained.  $M_n^{\text{GPC}} = 10\,700$  g/mol,  $M_w/M_n = 1.42$ .

**Computational Procedures.** To assist in the selection of a suitable RAFT agent, standard *ab initio* molecular orbital theory and density functional theory calculations were carried out using Gaussian 09<sup>23</sup> and Molpro 2009.1<sup>24</sup> Calculations were performed at a high level of theory that was based on our previous assessment studies for RAFT reactions<sup>25</sup> and recently shown to reproduce experimental equilibrium constants to within chemical accuracy.<sup>26,27</sup> For all species, either full systematic conformational searches (at a resolution of 120 $^\circ$ ) or, for more complex systems, energy-directed tree searches<sup>28</sup> were carried out to ensure global, and not merely local minima were located. These were performed at the B3LYP/6-31G(d) level of theory in a THF solution at 25  $^\circ\text{C}$  to mimic experimental conditions. The PCM<sup>29</sup> solvent model was used in conjunction with UAKS model of spheres radii, and an electrostatic scaling factor was set equal to the recommended value of 1.2.<sup>30</sup> Geometries of the solution-phase lowest energy conformers of all species were then relaxed in the gas phase at the B3LYP/6-31G(d) level, and frequencies were also calculated at the same level and scaled by recommended scale factors.<sup>31</sup> Accurate gas-phase electronic energies were calculated using a three-layer ONIOM approach described previously.<sup>32,33</sup> The core layer was treated using the W1 procedure,<sup>34</sup> the G3(MP2)-RAD<sup>35</sup> method was applied to describe the effects of the primary substituents, and the full system was calculated using R(O)MP2/6-311+G(3df,2p) method. Gas-phase entropies and thermal corrections at 42  $^\circ\text{C}$  were calculated using standard textbook formulas<sup>36</sup> for the statistical thermodynamics of an ideal gas under the harmonic oscillator approximation in conjunction with the optimized geometries and scaled frequencies. Free energies of solvation for all species were calculated at the UAKS-PCM/B3LYP/6-31G(d) level of theory at 25  $^\circ\text{C}$  and corrected for the phase change correction term  $RT(\ln V)$ . Equilibrium constants were determined according to the equation

$$K(T) = (c^0)^{\Delta n} \exp\left(\frac{-\Delta G}{RT}\right)$$

where  $c^0$  is the standard concentration unit equal to 1 mol L<sup>-1</sup> in solution.

**Scheme 1. Equilibrium Constants (Bold; L mol<sup>-1</sup>) and Corresponding Gibbs Free Energies (Italics; kJ mol<sup>-1</sup>) of Addition (*a* and *c*) and Chain Transfer (*b*) Reactions in THF at 42 °C, Calculated Using Three-Layer ONIOM Approximation for Electronic Energies and UAKS-PCM/B3LYP/6-31G(d) Method for Solvation Free Energies**



**Table 1. RAFT Polymerizations of VC with CMPCD as a RAFT Agent under Different Conditions**

entry	[VC] <sub>0</sub> /[CMPCD] <sub>0</sub> /[Trigonox] <sub>0</sub>	[VC] <sub>0</sub> /[solvent] (v/v)	time (h)	T (°C)	conv (%)	M <sub>n</sub> <sup>th</sup> (g/mol)	M <sub>n</sub> <sup>GPC</sup> (g/mol)	M <sub>w</sub> /M <sub>n</sub>
1	250/1/0.2	1/1 (dichloromethane)	24	42	0			
2	250/1/0.2	1/1 (cyclohexanone)	24	42	36	6000	3500	1.88
	[VC] <sub>0</sub> /[CMPCD] <sub>0</sub> /[Trigonox] <sub>0</sub>	[VC] <sub>0</sub> /[THF] (v/v)						
3	250/1/0.2	1/1	24	42	50	8500	6000	1.43
4	250/1/0.2	1/1	24	30	34	7000	4200	1.68
5	250/1/0.2	1/1	24	60	30	6000	3400	1.76
6	250/1/0.1	1/1	24	42	42	9000	5800	1.68
7	250/1/0.5	1/1	24	42	49	9900	6000	1.55
8	100/1/0.2	1/1	24	42	43	3100	2400	1.69
9	500/1/0.2	1/1	24	42	39	14600	7400	1.50
10	250/1/0.2	1/1	48	42	54	9400	7300	1.43
11	250/1/0.2	1/3	48	42	86	15200	4400	1.78
12	250/1/0.2	1/5	48	42	91	18700	3200	1.84
	[VC] <sub>0</sub> /[CMPCD] <sub>0</sub> /[AIBN] <sub>0</sub>							
13	250/1/0.2	1/1	24	42	38	7100	4200	1.70
14	250/1/0.1	1/1	24	42	36	6800	3700	1.67
15	250/1/0.5	1/1	24	42	44	8200	4500	1.76

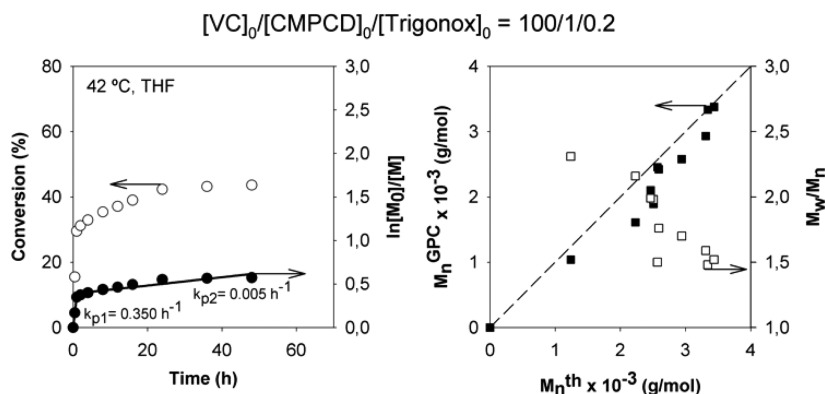
## RESULTS AND DISCUSSION

**Computational Results.** VC belongs to the so-called nonactivated (or less activated) vinyl monomer class, which is characterized by having propagating radicals with relatively low radical stabilities. For instance, based on its calculated radical stabilization energy of 27.0 kJ mol<sup>-1</sup> at the G3(MP2)-RAD level of theory, a unimeric VC propagating radical is only slightly more stabilized than the corresponding vinyl acetate derived unimeric propagating radical (24.4 kJ mol<sup>-1</sup>) and considerably less than corresponding values for such activated monomers as methyl acrylate (41.3 kJ mol<sup>-1</sup>), methyl methacrylate (54.9 kJ mol<sup>-1</sup>), or styrene (68.0 kJ mol<sup>-1</sup>).<sup>37</sup> Less activated monomers pose two key problems when selecting an appropriate RAFT agent. First, the relatively low stabilities of their propagating radicals render them poor leaving groups from standard dithioester-type RAFT agents, leading to significant inhibition or rate retardation effects. Second, many of the typical leaving groups in initial RAFT agents do not readily reinitiate polymerization of unactivated monomers.<sup>4</sup>

To address the first problem, one typically uses RAFT agents such as xanthates or dithiocarbamates in which the “Z-group” of the RAFT agent is a lone pair donor that can undergo resonance with the thiocarbonyl group. This resonance stabilizes the RAFT agent relative to the RAFT-adduct radical, helping to promote fragmentation. In the present work we have opted for a dithiocarbamate, cyanomethyl methyl(phenyl)carbamodithioate (CMPCD, see Figure 1 and the Supporting Information for the model thermodynamic measures), which has already found success in the control of other unactivated monomers.<sup>4</sup> Moreover, the •CH<sub>2</sub>CN leaving group of this RAFT agent is known to be an effective initiating species for VC (e.g., Fischer and Radom report a rate coefficient of 1.2 × 10<sup>4</sup> L mol<sup>-1</sup> s<sup>-1</sup> at 25 °C),<sup>38</sup> thereby simultaneously addressing the second problem. At the same time, based on previously published model calculations, this leaving group would be expected to undergo preferential fragmentation from intermediate radical.<sup>37,39</sup>

To confirm that this RAFT agent would be suitable, we calculated the equilibrium constant for the addition of a dimeric





**Figure 2.** Kinetic plots for RAFT polymerization of VC under the following conditions:  $[VC]_0/[CMPCD]_0/[Trigonox]_0 = 100/1/0.2$  at 42 °C in THF ( $[VC]_0/[THF]$  (v/v) = 1/1).

VC propagating radical to CMPCD (reaction *a* in Scheme 1) in THF solution at 42 °C and also to the corresponding “polyRAFT” agent where the  $CH_2CN$  leaving group is replaced by the VC dimer radical (reaction *c* in Scheme 1). In both cases, the equilibrium constants ( $2.0 \times 10^{-1}$  and  $2.5 \times 10^{-5} \text{ L mol}^{-1}$ , respectively) are much less than the values of  $10^6 \text{ L mol}^{-1}$  or more typically associated with rate retardation.<sup>40,41</sup> We also calculated the equilibrium constant of the chain transfer reaction in the pre-equilibrium (reaction *b* in Scheme 1) to confirm that fragmentation of the  $\bullet CH_2CN$  leaving group is strongly favored in the pre-equilibrium, as is required for efficient chain transfer. Hence, based on these results, CMPCD is expected to be a suitable RAFT agent for control of VC polymerization.

**Experimental Results.** Having selected CMPCD as our RAFT agent, we then tested it experimentally. Two different initiators—AIBN (with  $t_{1/2} = 1 \text{ h}$  at 82 °C)<sup>42</sup> and Trigonox 187-W40 (with  $t_{1/2} = 1 \text{ h}$  at 39 °C)<sup>42</sup>—were used as a free radical source during the polymerization (Figure 1). Since PVC is not soluble in its monomer, the RAFT polymerization was conducted in the presence of different solvents that dissolve both VC and PVC (THF, cyclohexanone, and dichloromethane). Results of the VC RAFT polymerization under different conditions, summarized in Table 1, suggest that the combination of Trigonox 187-W40 and THF is the most successful in providing fast, yet well-controlled RAFT polymerization of VC. No polymerization occurs in dichloromethane, while a polymer with high PDI is formed in cyclohexanone (entries 1 and 2, Table 1).

In order to find optimal conditions for a successful RAFT polymerization of VC, mediated by CMPCD as a chain transfer agent in THF solution, we have evaluated the effect of temperature and VC/THF and VC/CMPCD ratios on the polymerization process (Table 1). Reactions at different temperatures (entries 3–5, Table 1) were conducted under the following conditions:  $[VC]_0/[CMPCD]_0/[Trigonox]_0 = 250/1/0.2$  and  $[VC]_0/[THF]$  (v/v) = 1/1. Previous studies of SET-DTLRP of VC had shown that 42–43 °C is the maximum temperature of polymerization yielding PVC with minimized structural defects and well-defined chain-end functionalities.<sup>7,15</sup> Under the conditions of the present study, the optimum temperature of RAFT polymerization of VC was found to be equal to 42 °C (50% monomer conversion in 24 h). Only a limited monomer conversion was observed at 30 and 60 °C (34% and 30%, respectively); moreover, the obtained PVC exhibited a broad molecular weight distribution indicating

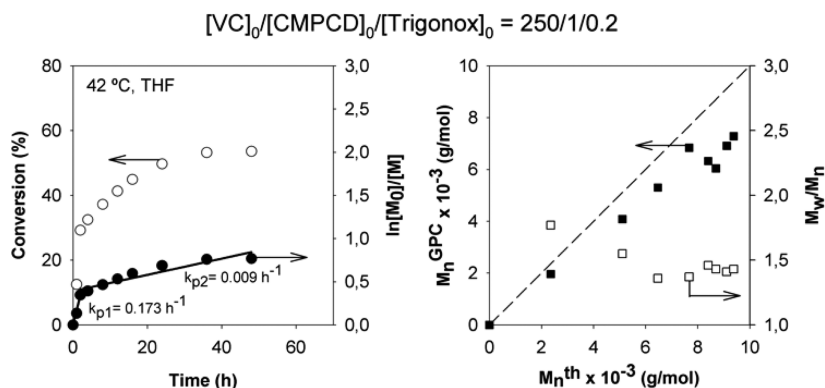
possible loss of control over the polymerization. At lower temperatures radical initiation is expected to be significantly slower, while at higher temperatures the chain transfer to VC competes with a chain transfer via RAFT mechanism.

The molar ratio  $[initiator]/[CTA]$  also has an important role in the control of the PVC molecular weight during the RAFT polymerization of VC. Results of VC RAFT polymerization at 42 °C with different  $[initiator]/[CTA]$  ratios given in Table 1 (entries 3, 6, and 7) indicate that the lowest PDI could be achieved when  $[initiator]/[CTA]$  is equal to 0.2/1.

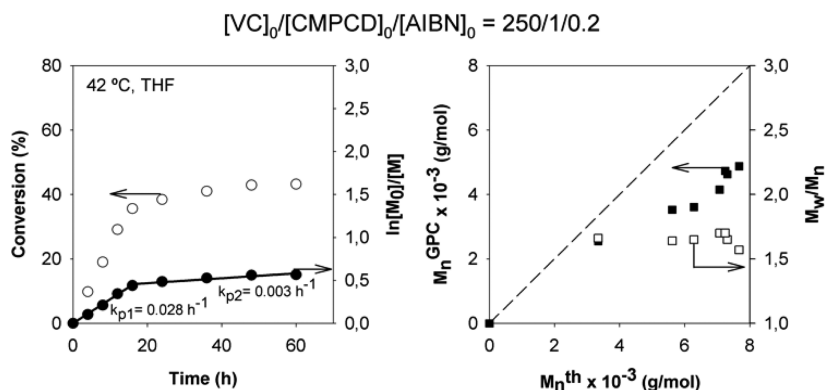
The entries 3, 8, and 9 in Table 1 correspond to the results of RAFT polymerizations conducted at 42 °C with different  $[monomer]_0/[CTA]_0$  ratios and constant  $[initiator]/[CTA]$  ratio (equal to 0.2). As expected for CLRP systems, the molecular weight of the polymers increases with the  $[monomer]_0/[CTA]_0$  value. Entries 10–12 in Table 1 reflect the effect of the  $[VC]_0/[THF]$  ratio on the RAFT polymerization of VC. Obtained results show that the conversion increases with the increase in the amount of solvent used. At the same time, however, control over the polymerization diminishes, since the obtained molecular weights of PVC decrease (rather than increase as expected) and the PDI values increase. Side reactions involving chain transfer from the growing macroradicals to the solvent are assumed to be responsible for this.

Finally, performance of Trigonox 187-W40 and AIBN initiators for RAFT polymerization of VC (entries 3, 6, 7, 13, 14, and 15 in Table 1) was evaluated. According to our results, Trigonox 187-W40 provides slightly higher monomer conversion and better control (lower PDI values and  $M_n^{th}$  are closer to  $M_n^{GPC}$  in case of Trigonox). These results may be explained by the fact that cyanoisopropyl radicals (formed by AIBN thermal decomposition) add slower to the VC monomers and RAFT agents when compared to the isopropyl radicals resulting from Trigonox. Also, addition of cyanoisopropyl radicals to RAFT agent is a reversible process. On the other hand, isopropyl radical (formed from  $(CH_3)_2CH-C(O)-O-O-C(O)-CH(CH_3)_2$ ) should add much faster to both RAFT agent and VC monomer. Addition of isopropyl radical to RAFT agent is irreversible. Thus, in case of Trigonox any induction period should be eliminated, polymerization is expected to be faster (higher  $M_n$  at given monomer conversion) and the initiation efficiency is higher.

**Kinetic Experiments.** Figures 2–4 show typical kinetic experiments for the RAFT polymerization of VC in solution. Remarkably, in all cases the  $\ln([M]_0/[M])$  exhibits two linear



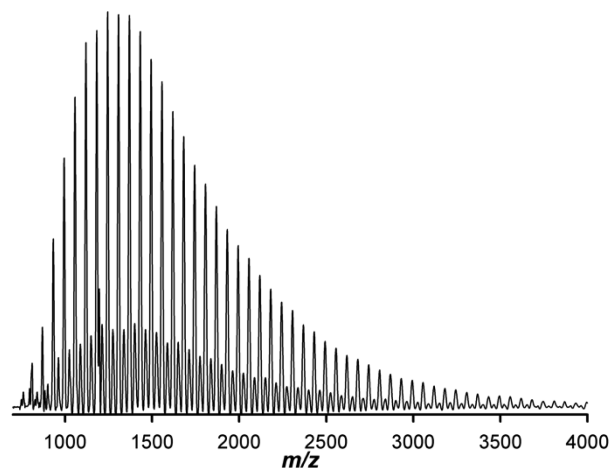
**Figure 3.** Kinetic plots for RAFT polymerization of VC under the following conditions:  $[VC]_0/[CMPCD]_0/[Trigonox]_0 = 250/1/0.2$  at 42 °C in THF ( $[VC]_0/[THF]$  (v/v) = 1/1).



**Figure 4.** Kinetic plots for RAFT polymerization of VC under the following conditions:  $[VC]_0/[CMPCD]_0/[AIBN]_0 = 250/1/0.2$  at 42 °C in THF ( $[VC]_0/[THF]$  (v/v) = 1/1).

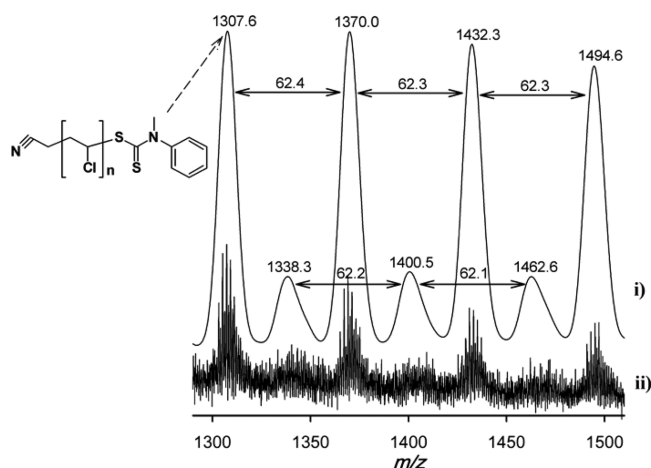
dependencies on the polymerization time. Similar behavior was observed during SET-DTLRP of VC in water/THF mixtures.<sup>11,12,43</sup> The linear dependencies of  $\ln([M]_0/[M])$  vs time indicate constant concentration of growing radicals throughout the polymerization. The presence of two different linear regions, a phenomenon known as hybrid behavior, is most likely caused by the differences in the initiation and reinitiation rates (by the leaving  $^{\bullet}CH_2CN$  radical in the pre-equilibrium). In all experiments  $M_n^{GPC}$  agrees with the theoretical molecular weight ( $M_n^{th}$ ), and PDI is decreasing with the monomer conversion.

**PVC Structure Determination.** The chemical structure of the PVC synthesized by RAFT polymerization was determined with MALDI-TOF-MS and  $^1H$  NMR techniques. In MALDI-TOF-MS experiments, two types of matrices, HABA and CHCA (Figure S1, Supporting Information), were tested, but only the former gave a clearly resolved spectrum (Figures 5–7). The MALDI-TOF-MS of RAFT-PVC in the linear mode with  $m/z$  ranging from 700 to 4000 is shown in Figure 5. Enlargement of the 1300–1500 range in the linear and reflectron modes is shown in Figure 6. Importantly, two series of main peaks (for linear mode) are separated by an interval corresponding to a VC repeating unit (62.5 mass units). The highest main series is attributed to a polymer chain R-PVC-Z' (species 5, Scheme 2) where R-Z' is the RAFT agent:  $R = -CH_2-CN$  and  $Z' = -S-C(S)-N(Me)Ph$  ( $1307.6 = 40.02 + 17 \times 62.5 + 182.2 + 23$ , where 40.02, 62.5, 182.2, and 23 correspond to the molecular weight of R, VC, Z', and  $Na^+$ , respectively). This particular structure was confirmed by comparing the results with a theoretical distribution shown in



**Figure 5.** MALDI-TOF-MS in the linear mode of RAFT-PVC ( $M_n^{GPC} = 3300$  g/mol,  $M_w/M_n = 1.48$ ) mediated by CMPCD.

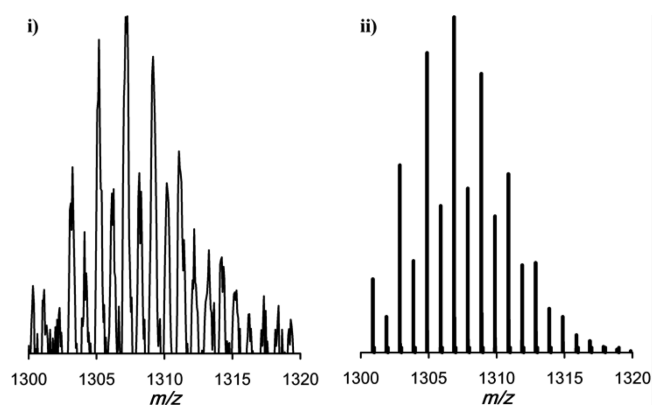
Figure 7. The enlarged spectrum (reflectron mode) from  $m/z$  1300 to 1320 (DP = 17) shows that the isotope distribution of the polymer chain match the isotope distribution calculated for  $R-(PVC)_{17}-Z' + Na^+$  using Isotope Distribution Calculator software<sup>22</sup> (from  $m/z$  925 to 945 or DP = 11; see Figure S2 in the Supporting Information). Therefore, obtained RAFT-PVC has a well-defined structure (i.e., without any detectable structural defects). The presence of possible structural defects would cause a deviation of  $m/z$  values and a different pattern of the isotope distribution. The series of less intensive peaks



**Figure 6.** Enlargement of the MALDI-TOF-MS from  $m/z$  1300 to 1500 of RAFT-PVC ( $M_n^{GPC} = 3300$  g/mol,  $M_w/M_n = 1.48$ ) mediated by CMPCD in the (i) linear and (ii) reflectron mode.

(Figure 6i) cannot be ascribed to any chain-end structures expected from the RAFT polymerization. The presence of these peaks is probably due to the occurrence of the fragmentation of dithiocarbamate moieties during ionization in the MALDI-TOF-MS analysis, as reported by other authors.<sup>44–47</sup>

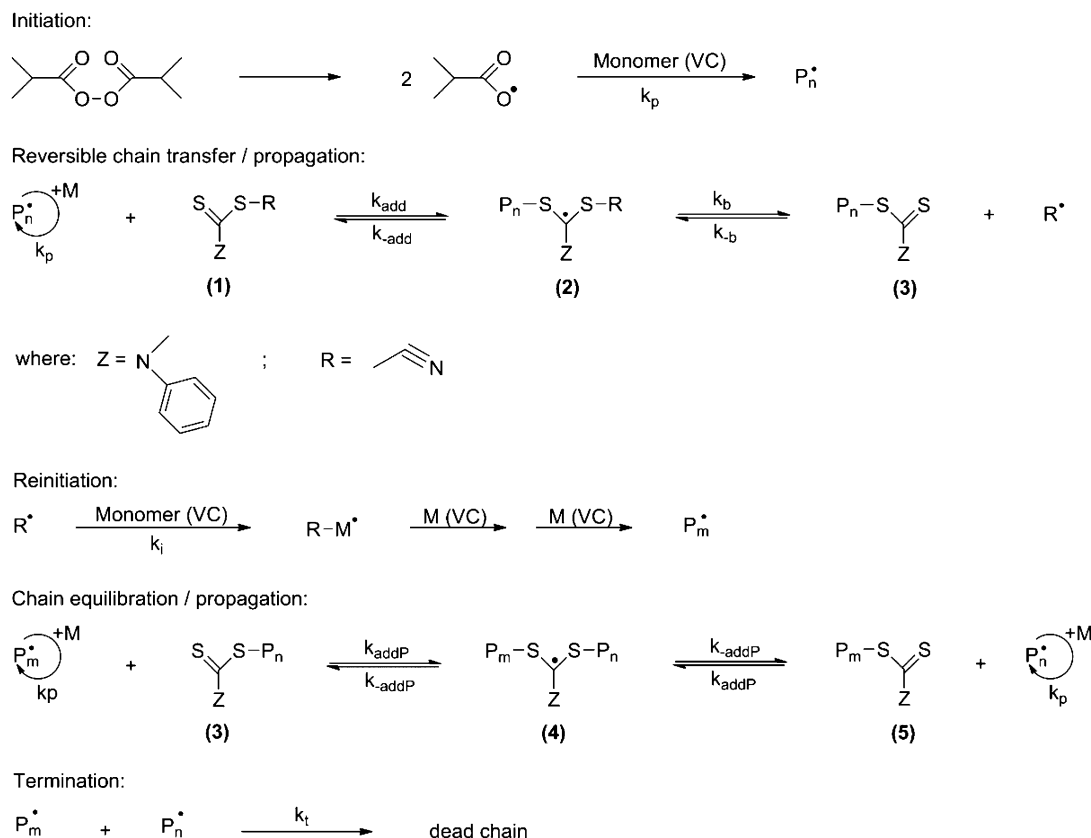
The  $^1\text{H}$  NMR spectrum of the PVC sample used in MALDI-TOF-MS analysis is shown in Figure 8. This spectrum confirms the main structure suggested based on the results of the MALDI-TOF-MS analysis.  $^1\text{H}$  NMR spectra of the initiator (top) and the RAFT agent (in the middle) are also given in

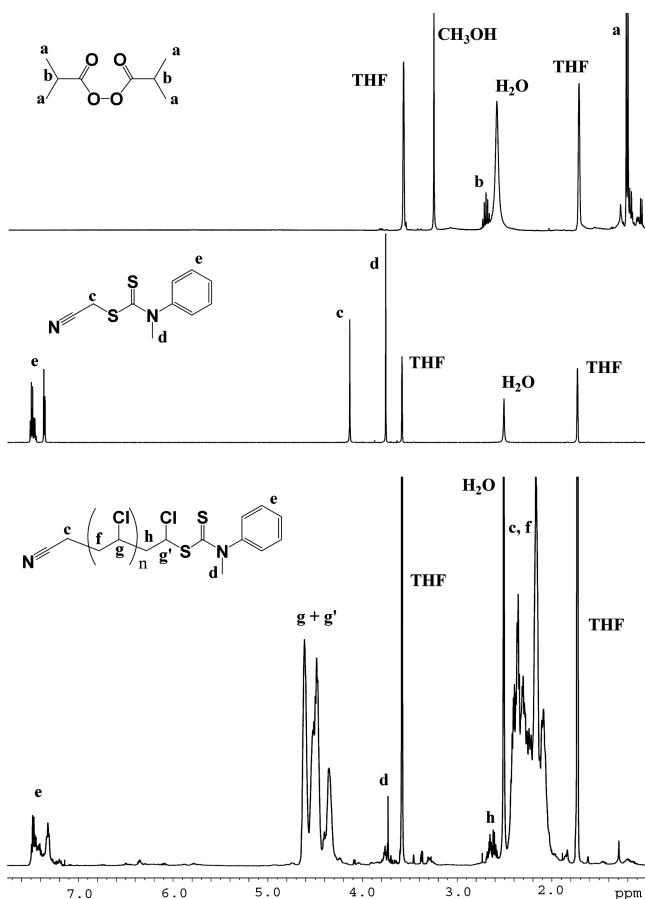


**Figure 7.** (i) Enlargement of the MALDI-TOF-MS in the reflectron mode of Figure 6 from  $m/z$  1300 to 1320 and (ii) theoretical isotope distribution of the  $m/z$  1300–1320 region ( $DP = 17$ ,  $\text{C}_{44}\text{H}_{61}\text{Cl}_{17}\text{N}_2\text{S}_2\text{Na}$ ) using Isotope Distribution Calculator software.

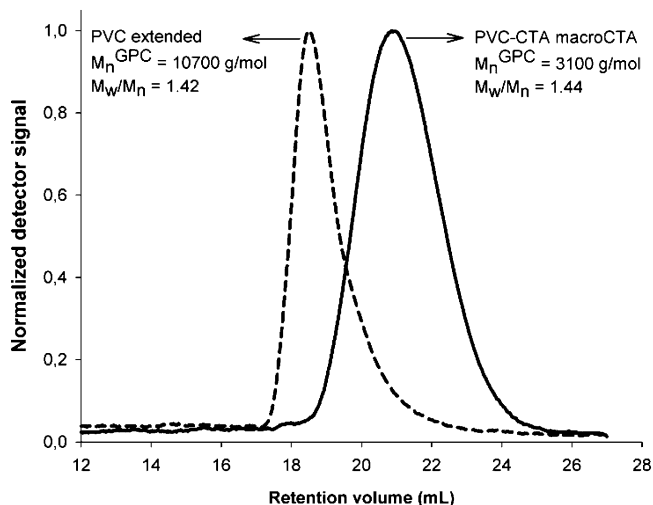
Figure 8. The spectrum of the RAFT-PVC reveals the resonances of the repeat unit  $\text{CH}_2\text{—CHCl}$ : **f** (1.9–2.7 ppm) and **g** (4.2–4.7 ppm), respectively. The terminal  $\text{—CH}_2\text{—CHCl—S—}$  (**h** and **g'**) group resonates at 2.65 and  $\sim 4.7$  ppm, respectively. The spectrum of the RAFT-PVC also reveals the resonances of the RAFT agent (**e**, **d**). Phenyl protons **e** resonate at 7.2–7.4 ppm and N-Me protons **d** signal at 3.75 ppm. The signal of  $\text{NC—CH}_2$  group **c** is probably hidden in the resonance of the main chain methylene group **f** at 1.9–2.7 ppm. The initiator fragments (containing protons **a** and **b**) reveal no noticeable signals. Additionally, there is no significant amount

## Scheme 2. Mechanism of the RAFT Polymerization of VC Initiated by Trigonox 187-W40 Using CMPCD as Chain Transfer Agent





**Figure 8.**  $^1\text{H}$  NMR spectra of Trigonox 187-W40 initiator (top), CMPCD RAFT agent (middle), and RAFT-PVC obtained ( $M_n^{\text{GPC}} = 3300$  g/mol,  $M_w/M_n = 1.48$ ) in  $d_8$ -THF.



**Figure 9.** Normalized GPC traces of PVC-CTA samples before (on the right) and after chain extension experiment (on the left).

of vinyl protons (resonances at 5.8 and 5.9 ppm are usual for free radical PVC<sup>7</sup>), consistent with the vanishingly small concentrations of structural defects observed in PVC species obtained via SET-DTLRP process.<sup>7,15</sup>

**Chain Extension Experiment.** To prove the “living” nature of the VC RAFT polymerization, a reinitiation experiment was performed. As shown in Figure 9, a complete

shift of the GPC trace of the PVC sample during the chain extension experiment was observed. Molecular weight of the starting PVC ( $M_n^{\text{GPC}} = 3100$  g/mol,  $M_w/M_n = 1.44$ ) has shifted toward higher molecular weight ( $M_n^{\text{GPC}} = 10700$  g/mol,  $M_w/M_n = 1.42$ ), which proves the “living” character of the PVC obtained via RAFT polymerization mediated by a CMPCD agent.

## CONCLUSIONS

To conclude, for the first time PVC with well-defined structure was successfully synthesized via RAFT polymerization using the RAFT agent cyanomethyl methyl(phenyl)-carbamodithioate (CMPCD). Careful choice of reaction conditions (initiator type and concentration, solvent type and concentration, temperature) is required to achieve low polydispersities. The structural analysis performed via  $^1\text{H}$  NMR and MALDI-TOF-MS experiments revealed that PVC chains had well preserved functional groups and no structural defects. The “living” nature of the PVC synthesized via RAFT polymerization method was confirmed by a successful chain extension experiment. *Ab initio* MO calculations confirmed the suitability of CMPCD as a good RAFT agent for VC polymerization.

## ASSOCIATED CONTENT

### Supporting Information

Details of the ONIOM layers, optimized geometries in the form of GAUSSIAN archive entries, corresponding total energies, thermal corrections, zero-point vibrational energies, entropies, free energies and free energies of solvation, calculated thermodynamic and kinetic parameters of investigated reactions in gas and solution phases; MALDI-TOF-MS in the linear mode (using  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA) as matrix) of RAFT-PVC; enlargement of the MALDI-TOF-MS in the reflectron mode and theoretical isotope distribution of the  $m/z$  925–945 region ( $\text{DP} = 11$ ,  $\text{C}_{32}\text{H}_{43}\text{Cl}_{11}\text{N}_2\text{S}_2\text{Na}$ ). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614–5615.
- (2) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987–2988.
- (3) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559–5562.
- (4) Moad, G.; Rizzardo, E.; Thang, S. H. *Acc. Chem. Res.* **2008**, *41*, 1133–1142.
- (5) Starnes, W. H. Jr.; Zaikov, V. G.; Chung, H. T.; Wojciechowski, B. J.; Tran, H. V.; Saylor, K.; Benedikt, G. M. *Macromolecules* **1998**, *31*, 1508–1517.
- (6) Starnes, W. H. *Prog. Polym. Sci.* **2002**, *27*, 2133–2170.
- (7) Percec, V.; Popov, A. V.; Ramirez-Castillo, E.; Coelho, J. F. J.; Hinojosa-Falcon, L. A. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6267–6282.
- (8) Starnes, W. H. Jr.; Ge, X. *Macromolecules* **2004**, *37*, 352–359.
- (9) Starnes, W. H. Jr. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2451–2467.
- (10) Percec, V.; Guliasvili, T.; Ladislav, J. S.; Wistrand, A.; Stjern Dahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. *J. Am. Chem. Soc.* **2006**, *128*, 14156–14165.
- (11) Percec, V.; Popov, A. V.; Ramirez-Castillo, E.; Monteiro, M.; Barboiu, B.; Weichold, O.; Asandei, A. D.; Mitchell, C. M. *J. Am. Chem. Soc.* **2002**, *124*, 4940–4941.
- (12) Percec, V.; Popov, A. V.; Ramirez-Castillo, E.; Weichold, O. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3283–3299.
- (13) Percec, V.; Guliasvili, T.; Popov, A. V. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1948–1954.
- (14) Percec, V.; Popov, A. V.; Ramirez-Castillo, E.; Coelho, J. F. J.; Hinojosa-Falcon, L. A. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 779–788.
- (15) Percec, V.; Ramirez-Castillo, E.; Popov, A. V.; Hinojosa-Falcon, L. A.; Guliasvili, T. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2178–2184.
- (16) Coelho, J. F. J.; Carreira, M.; Goncalves, P. M. O. F.; Popov, A. V.; Gil, M. H. *J. Vinyl Addit. Technol.* **2006**, *12*, 156–165.
- (17) Coelho, J. F. J.; Mendonça, P. V.; Popov, A. V.; Percec, V.; Goncalves, P. M. O. F.; Gil, M. H. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 7021–7031.
- (18) Coelho, J. F. J.; Fonseca, A. C.; Gois, J. R.; Goncalves, P. M. O. F.; Popov, A. V.; Gil, M. H. *Chem. Eng. J.* **2011**, *169*, 399–413.
- (19) Coelho, J. F. J.; Fonseca, A. C.; Goncalves, P. M. F. O.; Popov, A. V.; Gil, M. H. *Polymer* **2011**, *52*, 2998–3010.
- (20) Coelho, J. F. J.; Fonseca, A. C.; Goncalves, P. M. O. F.; Popov, A. V.; Gil, M. H. *Chem. Eng. Sci.* **2012**, *69*, 122–128.
- (21) Rosen, B. M.; Percec, V. *Chem. Rev.* **2009**, *109*, 5069–5119.
- (22) IDCalc - Isotope Distribution Calculator, written by Michael J. MacCoss, Department of Genome Sciences, University of Washington: <http://proteome.gs.washington.edu/software/IDCalc/> (accessed Feb 10, 2012).
- (23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision B.01 ed., Wallingford, CT, 2009.
- (24) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Mitrushenkov, A.; Rauhut, G.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hetzer, G.; Hrenar, T.; Knizia, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklaß, A.; Palmieri, P.; Pflüger, K.; Pitzer, R.; Reiher, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; Wolf, A. *MOLPRO* **2009**.
- (25) Izgorodina, E. I.; Coote, M. L. *J. Phys. Chem. A* **2006**, *110*, 2486–2492.
- (26) Lin, C. Y.; Coote, M. L. *Aust. J. Chem.* **2009**, *62*, 1479–1483.
- (27) Chernikova, E.; Golubev, V.; Filippov, A.; Lin, C. Y.; Coote, M. L. *Polym. Chem.* **2010**, *1*, 1437–1440.
- (28) Izgorodina, E. I.; Lin, C. Y.; Coote, M. L. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2507–2516.
- (29) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999–3093.
- (30) Brinck, T.; Larsen, A. G.; Madsen, K. M.; Daasbjerg, K. *J. Phys. Chem. B* **2000**, *104*, 9887–9893.
- (31) Merrick, J. P.; Moran, D.; Radom, L. *J. Phys. Chem. A* **2007**, *111*, 11683–11700.
- (32) Izgorodina, E. I.; Brittain, D. R. B.; Hodgson, J. L.; Krenke, E. H.; Lin, C. Y.; Namazian, M.; Coote, M. L. *J. Phys. Chem. A* **2007**, *111*, 10754–10768.
- (33) Lin, C. Y.; Hodgson, J. L.; Namazian, M.; Coote, M. L. *J. Phys. Chem. A* **2009**, *113*, 3690–3697.
- (34) Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843–1856.
- (35) Henry, D. J.; Sullivan, M. B.; Radom, L. *J. Chem. Phys.* **2003**, *118*, 4849–4860.
- (36) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice Hall: Englewood Cliffs, NJ, 1989.
- (37) Krenke, E. H.; Izgorodina, E. I.; Coote, M. L. In *Controlled/Living Radical Polymerization: From Synthesis to Materials*; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 2006; Vol. 944, pp 406–420.
- (38) Fischer, H.; Radom, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1340–1371.
- (39) Based on the data in Table 2 of ref 37, the chain transfer reaction  $\cdot\text{CH}_2\text{CN} + \text{S}=\text{C}(\text{CH}_3)\text{S}-\text{CH}(\text{CH}_3)\text{Cl} \rightarrow \cdot\text{CH}(\text{CH}_3)\text{Cl} + \text{S}=\text{C}(\text{CH}_3)\text{S}-\text{CH}_2\text{CN}$  would be exothermic by 27.1 kJ mol<sup>-1</sup>; it would be reasonable to assume similar qualitative results would be obtained for other RAFT-agent Z-groups.
- (40) Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Macromol. Theory Simul.* **2002**, *11*, 823–835.
- (41) Coote, M. L.; Krenke, E. H.; Izgorodina, E. I. *Macromol. Rapid Commun.* **2006**, *27*, 473–497.
- (42) Akzo Nobel: Initiators and Reactor Additives for Thermoplastics, [http://www.akzonobel.com/polymer/system/images/AkzoNobel\\_Initiators\\_and\\_Reactor\\_Additives\\_for\\_Thermoplastics\\_Low-res\\_protected\\_July%202010\\_tcm96-39468.pdf](http://www.akzonobel.com/polymer/system/images/AkzoNobel_Initiators_and_Reactor_Additives_for_Thermoplastics_Low-res_protected_July%202010_tcm96-39468.pdf) (accessed Feb 10, 2012).
- (43) Percec, V.; Popov, A. V.; Ramirez-Castillo, E.; Weichold, O. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6364–6374.
- (44) Beyou, E.; Chaumont, P.; Chauvin, F.; Devaux, C.; Zydowicz, N. *Macromolecules* **1998**, *31*, 6828–6835.

- (45) Schilli, C.; Lanzendörfer, M. G.; Müller, A. H. E. *Macromolecules* **2002**, *35*, 6819–6827.
- (46) Pound, G.; Aguesse, F.; McLeary, J. B.; Lange, R. F. M.; Klumperman, B. *Macromolecules* **2007**, *40*, 8861–8871.
- (47) Yan, Y. F.; Zhang, W.; Qiu, Y. S.; Zhang, Z. B.; Zhu, J. A.; Cheng, Z. P.; Zhang, W. D.; Zhu, X. L. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, S206–S214.