# Solid-Supported MADIX Polymerization of Vinyl Acetate

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ABSTRACT: A simple, one-pot synthesis of a surface-tethered MADIX agent was established via the reaction of 1,1′-thiocarbonyl diimidazole (TCDI) with a thiol, followed by reaction with the hydroxyl groups of a Wang resin. The supported RAFT agent was used to control the polymerization of vinyl acetate in toluene. The amount of surface-bound polymer was found to greatly increase with increasing content of solid MADIX agent, reaching values of almost 80%. The grafted PVAc chains were cleaved from the Wang resin support via radical reaction with *tert*-amyl peroxy acetate (TAPA), and the molecular weight distributions exhibited the typical shape of polymers formed via a well-controlled living radical polymerization (LRP), with the free polymers showing a slightly higher molecular weight than the living fraction. The $M_n$ values of both living polymer fraction (surface-bound polymer) and dead polymer (free polymer) increased steadily with monomer conversion—as expected for a well controlled MADIX polymerization—and were in good agreement with the theoretical molecular weights. PDI values of both polymer fractions scatter around 1.5, with a slight tendency of narrower molecular weight distributions of the living polymer, which shows a minimum value of 1.43. Addition of free MADIX agent to the solution phase led to a decrease in PDI values of both free and bound polymer, and the experimental molar masses were in very good agreement with theoretical predictions.

## Introduction

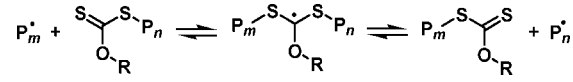
The advent of living radical polymerization (LRP) made possible the generation of synthetic polymeric material with preassigned and narrowly distributed molecular weights, distinct end-group functionalities, and complex topologies while retaining the versatility and robustness of radical polymerization. The methods based on degenerative chain-transfer, e.g., reversible addition−fragmentation chain transfer (RAFT) polymerization[1−5] and macromolecular design via the interchange of xanthates (MADIX) polymerization,[6,7] are arguably the most versatile representatives of LRP with respect to monomer type and reaction conditions. RAFT and MADIX polymerization rely on the same mechanistic principle of reversible transfer of thiocarbonyl thio compounds to macroradicals, P•, which leads to chain equilibration and imparts controlled polymerization behavior. This accepted mechanism is depicted in Scheme 1 for MADIX polymerization. The characteristic feature of MADIX is that the stabilizing Z-group of the associated mediating agent is an −OR group, i.e., xanthates are used as controlling compounds.

MADIX is especially advantageous for controlling polymerizations in which highly reactive propagating radicals, such as in vinyl acetate polymerization, occur. When using xanthates as mediating agents, two effects counterbalance this high reactivity, which constitute an obstacle for an effective RAFT equilibrium: First, an enhanced electron density on the central carbon decreases the stability of the intermediate radical (central species in Scheme 1), hence facilitating the fragmentation reaction, and second, the addition rates of the propagating radicals toward the xanthate are reduced, due to resonance stabilization that lowers the double-bond character of the S═C-bond.[8] These effects make MADIX an ideal technique for controlling vinyl acetate (VAc) polymerization, which proceeds via highly reactive propagating radicals.[9−11]

The advent of LRP had a significant impact on the fast growing field of surface-confined polymerizations, which leads to terminally grafted polymers on solid surfaces. Covalently bound polymer films offer an efficient and convenient way of modifying physicochemical characteristics of material surfaces, and thus play an important role in many areas of science.[12,13] Synthetic polymers serve as excellent candidates for surface modification because of their tunable mechanical properties as well as the variability of film thickness and degree of functionality. Surface-initiated grafting from LRP, using mediating agents that are immobilized at the surface, is a powerful method for controlling with great precision the functionality, density, and thickness of polymer films.[14−18]

There are surprisingly few reports on the application of RAFT/MADIX techniques to modify surfaces, although these methods offer the greatest versatility with respect to monomer and solvent. In addition, the specific mechanistic principles of these techniques allow for various synthetic strategies of performing surface-confined LRP: (i) The initiating radicals may be generated directly on the surface, e.g., via surface-confined initiators,[19−21] or by radiation-induced surface radical formation.[22] The radical growth may subsequently be controlled by a controlling agent that has been added to the solution phase. Following this approach, the surface-confined polymer originates from continuous initiation and will hence not be narrowly distributed. (ii) The mediating agent may be tethered to the solid substrate via its reinitiating R-group.[23−33] During the polym-

**Scheme 1. Main Equilibrium Reactions of MADIX Polymerization**



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erization, the propagating radicals are thus positioned at the terminal end of the surface-bound polymer and the mediating thiocarbonylthio-moieties are departing from the surface. This approach allows for the formation of dense polymer brushes, as the active end-group is well accessible on the outside of the polymer film. (iii) The RAFT/MADIX agent may be connected to the solid substrate via its stabilizing Z-group.[34−40] This strategy implies that the mediating thiocarbonylthio moiety is permanently fixed to the surface and propagating radicals occur unattached in the interstitial solution phase.

The Z-group approach is mechanistically unique when compared to other LRP methods. This strategy was exploited—first by Perrier and co-workers[34,39] and shortly after by Vana and co-workers[35]—for designing solid-supported RAFT agents that may effectively be separated and recovered after the polymerization process. Merrifield-resin-supported[41] and silica-supported *S*-methoxycarbonylphenylmethyl dithiobenzoate were probed in methyl acrylate polymerization,[34] silica-supported cumyl dithiobenzoate was used for controlling styrene and methyl methacrylate polymerization,[35] and silica-supported 3-(methoxycarbonylphenylmethylsulfanylthiocarbonylsulfanyl) propionic acid—a trithiocarbonate-type RAFT agent—was used to mediate polymerization of methyl acrylate, methyl methacrylate, butyl acrylate, and styrene.[39] All these studies revealed that such Z-supported RAFT polymerizations lead to well-controlled polymers and that the supported nature of the mediating agent allows its easy recovery after reaction. It was also found that the addition of free controlling agent to the solution helps to increase the control over the molecular weight and polydispersity of the product. In Z-supported RAFT polymerization, nonreactive (dead) polymeric chains, which only form in the interstitial solution phase, can be separated from the living chains by simple filtration. This scenario has been exploited to reduce the amount of homopolymer that is generated during a surface-confined RAFT block copolymerization.[39]

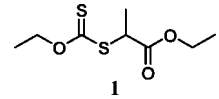
This work aims to expand the concept of surface-confined LRP using Z-group immobilized mediating agents to the field of MADIX polymerization. To the best of our knowledge, there is no report for a solid-supported MADIX system for controlling VAc polymerization. We systematically probed the variables that govern the ability of the solid-supported MADIX agent for controlling radical polymerization of VAc. Wang resin, which is hydroxyl-functionalized cross-linked polystyrene, was employed as the solid support. This choice was motivated by the relative ease of generating xanthates that are tethered to this resin as well as by the fact that cross-linked polystyrene particles were found to serve well as solid support for Z-group immobilized RAFT polymerizations.[34] The newly developed solid MADIX agent may find its application as an easily recoverable controlling agent in large scale processes.

## Experimental Section

**Materials.** Wang resin ([4-(hydroxymethyl)phenoxymethyl]polystyrene cross-linked with 1% of divinylbenzene) was purchased from Fluka and had a particle size of 100−200 mesh and an OH-group loading of 1.1 mmol per gram resin. Toluene was dried over 4 Å molecular sieves. Vinyl acetate (VAc) was passed through a basic alumina column to remove the inhibitor. 2,2′-Azobisisobutyronitrile (AIBN, 99%, AKZO) was recrystallized from methanol. The radical initiator *tert*-amyl peroxy acetate (TAPA, 97%, AKZO) was used as received. All other chemicals were purchased from Aldrich or Fluka at the highest purity available unless otherwise stated.

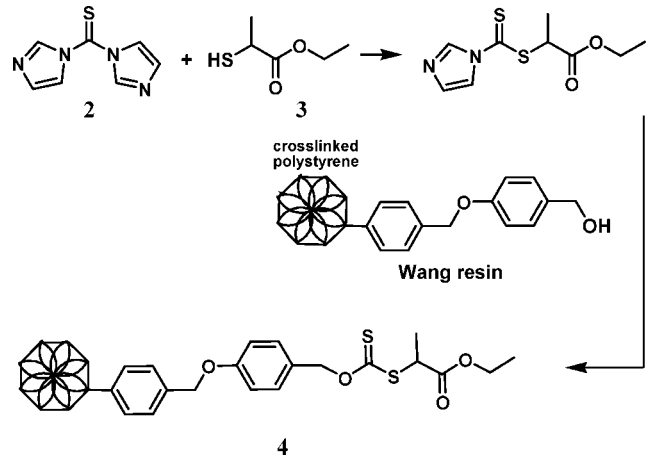
**MADIX Agents.** The MADIX agent 2-ethoxythiocarbonylsulfanyl propionic acid ethyl ester **1** (see Scheme 2) was synthesized according to a previously reported method.[42] 1,1′-Thiocarbonyl diimidazol **2** (TCDI, 1.78 g, 10.0 mmol) were dissolved in dry toluene (60 mL) under nitrogen atmosphere. Ethanol (0.46 g, 10.0 mmol) was then added dropwise. The mixture was heated at 60 °C for 6 h and then stirred at room temperature overnight. Ethyl 2-mercaptopropionate **3** (1.34 g, 10.0 mmol) was added, and the resulting suspension was again heated at 60 °C for 6 h. After removing the residual solvent under reduced pressure, the crude product was purified via column chromatography (silica, pentane: ethyl acetate = 9: 1, *Rf* = 0.57). **1** was obtained as light yellow liquid (1.3 g, 5.8 mmol, 58%).

**Scheme 2. 2-Ethoxythiocarbonylsulfanyl-propionic Acid Ethyl Ester, Used as the Free Xanthate-Type MADIX Agent**



**1**

**Scheme 3. Synthesis of Wang-Resin-Supported MADIX Agent**




**2** **3** **4**

$^1$H NMR (300 MHz, $CDCl_3$), $\delta$ (ppm): 1.3 (t, 3H, $-CH_3$), 1.4 (t, 3H, $-CH_3$), 1.6 (d, 3H, $-CH_3$), 4.2 (q, 2H, $-O-CH_2-CH_3$), 4.8 (q, 1H, $-S-CH_1-CH_3$), 5.7 (q, 2H, $-O-CH_2-CH_3$).

$^{13}$C NMR (300 MHz, $CDCl_3$), $\delta$ (ppm): 14.4 and 17.2 ($CH_2-CH_3$), 31.1 ($CH_1-CH_3$), 48.8 and 51.8 ($CH_2-CH_3$), 62.1 ($CH_1-CH_3$), 172.3 (C(=O)O), 213.7 (C=S).

The synthesis of the immobilized xanthate upon Wang resin **4** was achieved by a one-pot synthesis using the TCDI approach,[42] which is outlined in Scheme 3. TCDI **2** (3.60 g, 19.2 mmol) was added to dry toluene (60 mL) under nitrogen atmosphere. Ethyl 2-mercaptopropionate **3** (2.71 g, 19.2 mmol) was added to this solution dropwise. The mixture was stirred at 60 °C for 6 h. After cooling to room temperature, Wang resin (5 g, 5.5 mmol of OH-groups) was added under nitrogen to the stirred solution. The mixture was heated at 60 °C for 6 h and then left for cooling to room temperature. The suspension was filtered, and the resulting modified Wang resin was intensively washed consecutively with toluene, acetone, THF, and dichloromethane and then dried under vacuum at room temperature overnight. Elemental analysis: S, 1.3% (loading of 0.20 mmol per gram of modified resin, i.e., 18% of functional groups are substituted). FT-IR: 3430 (broad, O−H), 3024 (C−H, phenyl), 2920 (C−H), 1727 (C=O), 1600 (C=C) $cm^{-1}$.

**Polymerizations.** A mixture of VAc and toluene was thoroughly degassed via three freeze−pump−thaw cycles and mixed inside an argon-filled glovebox with AIBN, giving concentrations of 3.3 $mmol \cdot L^{-1}$, and with free MADIX agent **1** when indicated. The solution was then portioned to glass vials that contained weighed amounts of the modified Wang resin **4**. The glass vials were sealed with Teflon/rubber septa and subsequently heated at 60 °C under intensive stirring in an oil bath. The reactions were stopped by putting the glass vials into ice water after distinct time periods. A small amount of polymerization solution was drawn to measure the monomer conversion in the solution phase by $^1$H NMR. The residual monomer and toluene were removed by evaporation, and the overall monomer conversion was determined by gravimetry.

The mixture of polymer and modified Wang resin were washed in a Soxhlet apparatus for 12 h using dichloromethane to remove residual AIBN and to isolate the free polymer. The filtrate was analyzed by SEC, and the poly(VAc)-coated resin particles were dried under vacuum.

**Cleavage of the Surface-Bound Polymer.** The polymer-coated Wang resin was extensively washed (12 h with dichloromethane, 1 h with THF) and then dispersed inside an argon-filled glovebox in a solution of 0.5 mol·L$^{-1}$ TAPA in toluene, which had been degassed via three freeze−pump−thaw cycles prior to use. The dispersion was then heated to 130 °C for 2 h inside glass vials. After the reaction the particles were filtered off and the filtrate was analyzed by SEC.

**Instrumentation.** *SEC:* Molecular weight distributions were determined by size-exclusion chromatography (SEC) using a JASCO AS-2055-plus autosampler, a Waters 515 HPLC pump, three PSS-SDV columns with nominal 5 $\mu$m particle size and pore sizes of $10^5$, $10^3$ and $10^2$ Å, a Waters 2410 refractive index detector, and THF at 35 °C as the eluent at a flow rate of 1 mL·min$^{-1}$. The SEC setup was calibrated with polystyrene standards of narrow polydispersity ($M_p$ = 410 to 2 000 000 g·mol$^{-1}$) from Polymer Standards Service. Mark−Houwink parameters for poly(VAc) in THF ($K = 2.24 \times 10^{-2}$ mL·g$^{-1}$, $a = 0.674$)[43] provided access to absolute molecular weights according to the principles of universal calibration. *IR:* Fourier transform infrared (FT-IR) spectra were recorded on a Bruker IFS 66/S using a single reflection horizontal attenuated total reflection (ATR) accessory (Harrick MVPStar). *TGA:* Thermogravimetry analyses (TGA) were carried out under a nitrogen atmosphere using a TA Instruments TGA 2050 going from ambient temperature to 500 °C at a rate of 10 K·min$^{-1}$. Prior to analysis, the samples were carefully freed from residual solvents by applying vacuum at 40 °C for 24 h. *Elemental analysis:* Determination of the sulfur content was carried out by the Schoeniger oxygen flask combustion method followed by titration. *NMR:* $^1$H NMR spectra were recorded on a Bruker 400 UltraShield spectrometer at 25 °C using $CDCl_3$ as a solvent.

## Results and Discussion

The synthesis strategy for preparing the MADIX agents used in this study is based on a method using 1,1′-thiocarbonyl diimidazole (TCDI), which has been introduced by Perrier and co-workers.[42] TCDI undergoes controlled monosubstitution when reacted with primary alcohols, and the intermediate ester of imidazole-*N*-thionocarboxylic acid subsequently reacts efficiently with a secondary thiol to form a xanthate that is suitable for MADIX polymerization. This one-pot reaction presents clear advantages in terms of yield, reaction time, and simplicity, when compared to alternative protocols, and was therefore employed for obtaining compound **1** (see Scheme 2), which was used as free MADIX agent. Immobilizing the attacking hydroxyl groups on a solid support opens up the reverse order strategy, that is, adding the thiol first and then the alcohol, for surface-confined xanthate formation (see Scheme 3). This approach seems beneficial for obtaining surface-tethered MADIX agents, because the number of reaction steps proceeding at the surface is thus minimized. Indeed, a precursor is initially formed in solution and subsequently linked to the surface via a single reaction step. This offers good yields and high purity of the immobilized MADIX agent.

Great care has to be taken when choosing a solvent for the MADIX polymerization of VAc mediated by a xanthate-loaded Wang resin. Indeed, the relatively polar VAc is not capable of swelling the apolar polystyrene-based resin to a sufficient extent, thus preventing the access to the controlling xanthate groups that are bound to the inner surface of the porous resin. As the internal xanthate groups constitute the major part of the immobilized MADIX agent, swelling of the particles by a nonpolar solvent is mandatory. Furthermore, the large internal surface of a Wang resin makes the supported MADIX polymerization occur mostly within the swollen particles. The addition of solvent helps to maintain a sufficient diffusivity of macromolecular species within the pores, at least up to intermediate monomer conversion.

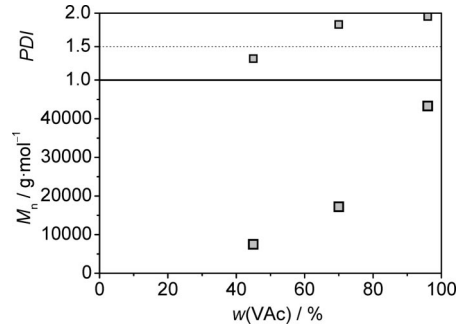



**Figure 1.** Number average molecular weight, $M_n$, and polydispersity index, PDI, of free polymer vs initial weight fraction of monomer in the liquid phase, $w$(VAc) (= $m$(VAc)/($m$(VAc) + $m$(toluene))), in **4**-mediated solid-supported vinyl acetate polymerization at 60 °C, initiated by 3.3 mmol·L$^{-1}$ AIBN and using a mass ratio $\mu$(**4**) (= $m$(**4**)/($m$(VAc) + $m$(toluene))) of modified Wang resin **4** of about 0.05. The reaction time was 24 h.

Toluene was identified as a suitable solvent for Wang-resin-supported MADIX polymerization of VAc at 60 °C. Figure 1 illustrates the influence of the toluene content on the number average molecular weight, $M_n$, and polydispersity, PDI, of the polymer formed in the interstitial solution phase of solid-supported MADIX polymerization of VAc for a fixed time of 24 h.

Earlier computer simulations[35] of styrene polymerizations have demonstrated that the free polymer formed via termination during Z-supported RAFT polymerization may be a suitable representative of the living polymer fraction that is tethered to the surface. Theoretically, these two polymer fractions show similar $M_n$ values. It should, however, be noted that this theoretical consideration is based on the assumption that the system is equally well controlled as a homogeneous RAFT polymerization. Long distances between particles where no polymerization control occurs and very fast propagating monomers, such as methyl acrylate,[34] may, however, lead to increased chain lengths of the dead polymer formed in the interstitial solution phase. Good agreement between the dead and living polymer fractions, as observed in this study (see below), is thus an indication for close to homogeneous conditions. As predicted from simulations,[35] the PDI of dead polymer, is naturally higher than that of living polymer and ranges between 1.35 and 1.45 for a typical RAFT process in which termination via combination is dominant. Inspection of Figure 1 indicates that PDI values of the dead polymer of around 1.4, which are characteristic for a successful MADIX polymerization, are found for intermediate toluene contents only. At higher VAc concentrations, the mandatory swelling of the resin particles did not occur and the surface-bound MADIX agent is thus not capable of imparting LRP behavior to the system. This scenario is indicated by the PDI values of around 2, which are typical for a conventional polymerization process. The assumption that a successful MADIX polymerization occurs at around 50 wt % of VAc in toluene is supported by the largely decreased $M_n$ values when compared to high VAc contents, which indicates that molecular weight control is operative. Decreasing the VAc content further is not desirable, because of an unacceptable deceleration of the polymerization without significantly improving the process, which appears to be very well controlled at intermediate VAc concentration (see below). In addition, transfer to solvent may potentially occur at very high toluene concentrations, which may deteriorate the quality of molecular weight control. Conse-

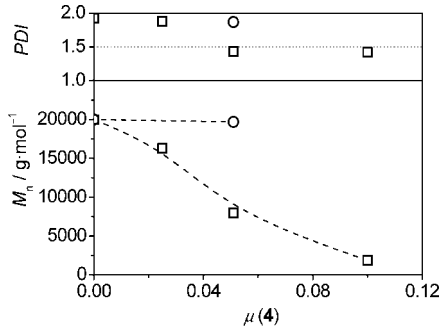



**Figure 2.** Number average molecular weight, $M_n$, and polydispersity index, PDI, of free polymer vs the mass ratio $\mu$(**4**) (= $m$(**4**)/($m$(VAc) + $m$(toluene))) of (circles) pure Wang resin (control experiment), and of (squares) xanthate-loaded Wang resin **4** in solid-supported vinyl acetate polymerization at 60 °C initiated by 3.3 mmol·L$^{-1}$ AIBN. The reaction time was 24 h.

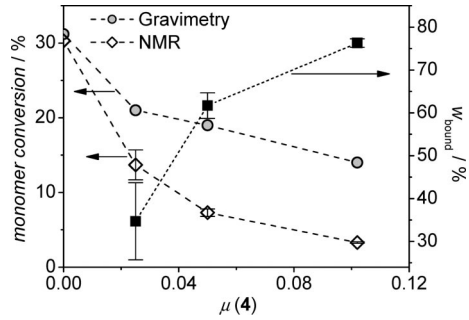



**Figure 3.** Monomer conversion determined via gravimetry and NMR spectroscopy, respectively (left ordinate), and weight fraction $w_{bound}$ of poly(VAc) that is tethered to the surface (right ordinate) after a reaction time of 24 h vs mass ratio $\mu$(**4**) (= $m$(**4**)/($m$(VAc) + $m$(toluene))) of xanthate-loaded Wang resin **4** in solid-supported vinyl acetate polymerization at 60 °C initiated by 3.3 mmol·L$^{-1}$ AIBN. The error bars indicate the systematic error of the evaluation procedure; for details see text.

quently, the MADIX polymerizations in this study were carried out with a weight fraction of monomer of 50%. The concentration of AIBN was chosen to be 3.3 mmol·L$^{-1}$, i.e., the molar ratio of monomer:AIBN was 1000:0.55.

A distinct feature of LRP is that the molar mass of the produced polymer can be controlled by varying the concentration of the mediating agent. Ideally, the $M_n$ value is inversely proportional to the MADIX agent concentration after identical monomer conversion. The influence of an increasing amount of modified Wang resin **4**—which is depicted as the mass ratio $\mu$ between solid and liquid phase—on average molar mass and polydispersity is illustrated in Figure 2. It can be clearly seen that the $M_n$ value decreases with an increasing resin particle content in the system. The addition of pure Wang resin as a blank sample did not change the polymerization behavior at all. This finding is in agreement with the expectation that a higher MADIX agent concentration induces a lower molar mass of the produced polymer. It should however be stressed that the drop in $M_n$ is not solely due to an increased MADIX agent concentration, but also due to variations in the monomer conversion. Indeed, monomer conversions after a constant reaction time of 24 h are not identical (see Figure 3), but higher MADIX agent concentrations result in smaller monomer conversions. This finding implies that rate retardation is operative and/or that an induction period occurs. These kinetic effects have frequently been observed in MADIX polymerization of VAc;[10,11,44] a discussion of rate retardation and initialization in RAFT/MADIX polymerization, however, is beyond the scope of this article, but can be found in ref 45 on the example of dithiobenzoate-mediated polymerization.

The drop in $M_n$ with increasing amounts of xanthate-loaded particles is accompanied by decreasing PDI values (see Figure 2). A mass ratio $\mu$ of 0.025 is not sufficient to induce well-controlled behavior in VAc polymerization, as indicated by the relatively high PDI. At a mass ratio of around 0.05 and above, however, the PDI of the free (dead) polymer is slightly below 1.5, which is in agreement with well-controlled MADIX polymerizations of VAc. In order to exclude that free MADIX agent was present in the resin particles—which also could have induced such well-controlled polymerization behavior—the modified Wang resin was subject to extensive washing cycles before use. It is gratifying to see that a relatively low amount of **4** can induce good molecular weight control, which is of relevance for a potential technical process in terms of cost-effectiveness. It was for this reason that the following polymerizations were mediated by a mass ratio of modified Wang resin **4** of about 0.05. On the basis of the xanthate density upon the modified Wang resin, i.e., 0.20 mmol·g$^{-1}$, the overall xanthate concentration in this system was estimated to be 11.1 mmol·L$^{-1}$. The molar ratio of monomer:bound xanthate:AIBN was therefore 1000:2.0:0.55.

In order to adequately characterize the solid-supported MADIX polymerization, monomer conversions were determined via gravimetry and NMR spectroscopy (see Figure 3).

Gravimetry allows the determination of the overall monomer conversion, that is, both the polymer generated upon the surface and the free polymer produced in the interstitial solution phase. On the other hand, the NMR method detects selectively the yield of unbound polymer, as no signal intensity arises from the Wang resin scaffold and from the polymer that is immobilized on these particles, due to the extremely restricted motion of polymer chains in cross-linked polymer.[46] Indeed, $^1$H NMR spectroscopy relies on the measurement of the signal intensity of the vinylic protons of the residual monomer in relation to that of the protons of the acetate moiety of monomeric units, which remain constant throughout the polymerization.[47] It must be noted that this approach is beset with a systematic error, since the reference signal of the acetate moiety is constantly lowered due to polymerization upon the surface. This error, however, becomes significant especially at higher monomer conversions; the impact on the results of the present study—as indicated by the error bars in Figure 3—are only minor. In combination with the data from gravimetry, the weight fraction $w_{bound}$, which represents the fraction of generated poly(VAc) that is tethered to the surface, can be estimated via eq 1.

$$w_{bound} = \frac{m_{bound}}{m_{bound} + m_{free}} = 1 - \frac{X_{NMR}}{X_{gravi}} \quad (1)$$

$m_{bound}$ and $m_{free}$ are the masses of bound and free polymer, respectively, $X_{gravi}$ is the overall monomer conversion measured by gravimetry, and $X_{NMR}$ is the monomer conversion obtained from NMR spectroscopy. It can be seen in Figure 3, which also depicts the weight fraction $w_{bound}$ of tethered (living) polymer, that the amount of surface-bound polymer is greatly increasing with increasing content of solid MADIX agent, reaching values of almost 80% in the case of $\mu$ = 0.01. This finding can easily be explained by the steady increase of the ratio between MADIX agent and initiator, when increasing the content of **4**, whereby the impact of initiator-derived dead polymer is lowered. This observation is again in agreement with a well-controlled MADIX polymerization. Interestingly, the proportion of up to 80 wt % of tethered living polymer is substantially higher than the values of around 50 wt % that were observed earlier in immobilized dithiobenzoate-mediated polymerization of styrene, methyl methacrylate and methyl acrylate using Merrifield resin and silica as solid support.[34,35]

The process of **4**-mediated MADIX polymerization of VAc was followed by ATR-FTIR spectroscopy. Figure 4 depicts the

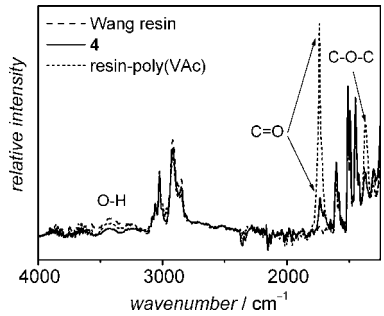



**Figure 4.** ATR-FTIR spectra of the original Wang resin, the modified Wang resin **4**, and the poly(VAc) ($M_n$ = 1800 g·mol$^{-1}$) loaded Wang resin after the polymerization.

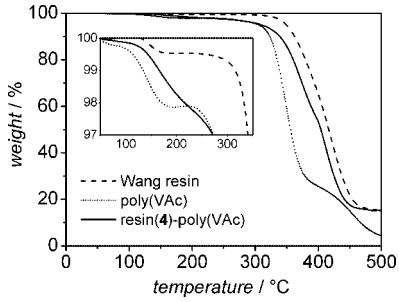



**Figure 5.** TGA curves of Wang resin, of pure poly(VAc) ($M_n$ = 10000 g·mol$^{-1}$; generated from **1**-mediated MADIX polymerization), and of the poly(VAc)-covered resin particles (molar mass of tethered polymer: $M_n$ = 1800 g·mol$^{-1}$).

ATR-FTIR spectra of pure Wang resin before and after its loading with the xanthate, and that of the polymer-coated resin after the polymerization. The organic resin itself exhibits a multitude of IR peaks, which complicates the characterization of the surface-confined species. The spectrum of the modified Wang resin **4**, however, shows a distinct peak at 1727 cm$^{-1}$, which is characteristic for the C═O bonding of the xanthate leaving group moiety, indicating that the MADIX agent loading process was successful. The broad OH valence vibration peak at around 3200 cm$^{-1}$ is accordingly slightly decreasing, due to the reaction of hydroxyl groups; the tendency, however, is hardly significant, as only a few percent of the hydroxyl groups are actually converted. In the spectrum of the poly(VAc)-covered resin particles, which were extensively washed prior to the analysis, the C═O bonding peak is greatly increased, due to the carbonyl bonds in the VAc repeat units. Additionally, a C−O−C valence vibration peak at 1370 cm$^{-1}$ occurs, which is characteristic for the ester bonding of the VAc units. The intensity of this peak is much smaller than that of the carbonyl peak, so that it cannot be discerned for the ester moiety of the xanthate leaving group. The findings from the IR spectroscopy clearly indicate that the resin particles are indeed well covered by poly(VAc).

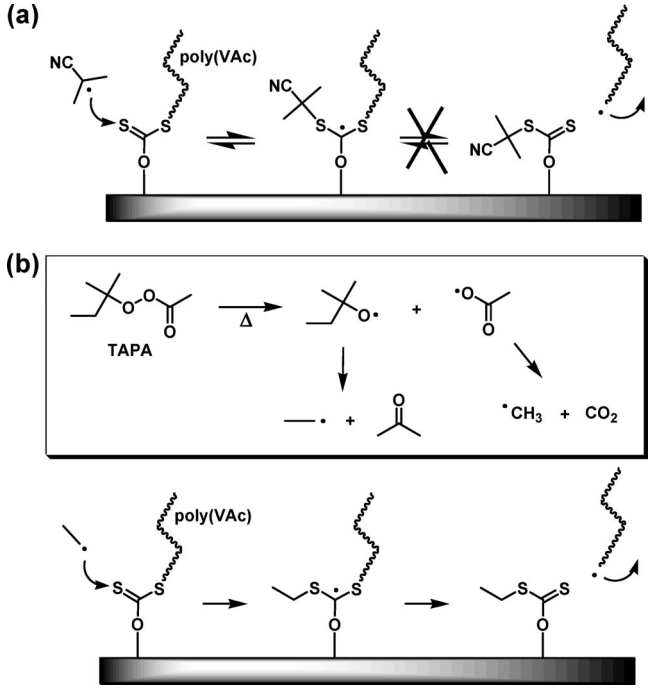
The polymer-covered particles were further characterized by thermogravimetry analysis (TGA) (see Figure 5). As a reference, the pure Wang resin was analyzed first (dashed line). The TGA trace indicates a decomposition starting at around 300 °C, which is typical for polystyrene. The small drop in mass at around 120 °C is most likely due to residual volatiles, which could not quantitatively be removed prior to analysis. The thermogravimetrical behavior of poly(VAc) from homogeneous MADIX polymerization using **1** as the mediating agent is indicated by the dotted line. The mass loss starting at ca. 120 °C can be assigned to the cleavage of the loosely bound xanthate end-groups. This relatively low fragmentation temperature of MADIX end-groups when compared to dithioester- and trithiocarbonate end-groups from RAFT polymerization that start to cleave off at $T$ < 180 °C[48,49] is in line with the earlier finding that MADIX agents show a much lower decomposition temperature than typical RAFT agents.[50] The poly(VAc) backbone itself decomposes at temperatures above 250 °C.

The poly(VAc)-coated Wang resin, generated by the solid-supported MADIX polymerization, in essence resembles a block copolymer made from polystyrene and poly(VAc), with the blocks being separated by the xanthate group. The features associated with this structure are clearly observable in the respective TGA trace (full line in Figure 5): First, the cleave-off of the xanthate groups starts at 130 °C, followed by the decomposition of the tethered poly(VAc), which is apparently occurring at higher temperatures than that of the pure poly(VAc), due to the strong overlap of the individual components. A transition from the decomposition of poly(VAc) to that of the cross-linked polystyrene, however, can clearly be observed at around 400 °C. This trace is thus in full agreement with the assumption that surface-tethered resin particles were formed via the solid-supported MADIX polymerization of VAc.

In order to characterize the solid-supported MADIX polymerization more directly, the tethered polymer was cleaved from the solid support. The particles were extensively washed before this cleavage procedure in order to guarantee that no free polymer was retained inside the pores. In the case that the MADIX agent is linked to the surface via its Z-group, the cleavage process may be achieved via flushing the system with small initiator-derived radicals in the absence of monomer. This approach, which first was introduced by Perrier and co-workers for the end-group modification of polymer,[51] releases the surface-tethered chain via a single addition−fragmentation chain transfer step and recovers the mediating agent.[34,35] The released macroradicals are in turn terminated by further small radicals yielding sulfur-free polymeric material. This termination reaction is not altering the average chain length of the living material—independent of the termination mode—since only small radicals are involved as terminating partners. Termination between two macroradicals giving polymer of double the chain length can safely be neglected, because of the vast abundance of initiator-derived radicals.

In order to design a technical process in which the solid MADIX agent may efficiently be recovered via this cleavage process, an initiator-derived small radical is desired, which generates a good leaving group. AIBN-derived 2-cyanoisopropyl radicals, which are known to exhibit good leaving group characteristics in many RAFT polymerization systems, were thus employed in earlier studies. This cyano-stabilized tertiary radical, however, is not capable of releasing the highly reactive secondary poly(VAc) radical (see Scheme 4a). Indeed, the intermediate radical that is formed via 2-cyanoisopropyl radical attack is quantitatively yielding back the educts and does not undergo a transfer reaction. It became thus necessary to employ more reactive small radicals for cleaving off the surface-bound poly(VAc). Consequently, *tert*-amyl peroxy acetate (TAPA), which yields ethyl and methyl radicals after thermally induced fragmentation (see box in Scheme 4b),[52] was used to harvest the tethered polymer.[53] The attacking primary alkyl radicals are more unstable than the poly(VAc) macroradical, which guarantees that the single addition−fragmentation chain transfer step proceeds selectively into the desired direction (see Scheme 4b). The surface-bound xanthate that is generated by these sequential reactions, however, is carrying a primary ester moiety, which is not a suitable leaving group for MADIX polymerization of VAc. Therefore an efficient recovery process of solid MADIX agent is admittedly impeded when using TAPA as the cleaving reagent. When targeting the optimization of such a recovery for technical processes, small radicals that have similar energies to the poly(VAc) macroradicals have to be used. The selective

**Scheme 4. Reaction of Surface-Bound Poly(VAc) That Has Been Generated via Z-Supported MADIX Polymerization with (a) AIBN-Derived and (b) TAPA-Derived Radicals**




formation of such radicals is not easily achieved by commercially available initiators and is therefore the subject of ongoing work, which aims at paving the way for industrial application of the herein proposed solid-supported MADIX polymerization.

The free and surface-bound polymers of a typical **4**-mediated Z-supported MADIX polymerization of VAc are depicted in Figure 6. It can be seen that the molecular weight distributions do not show any unexpected components, but exhibit the typical shape of polymer from well-controlled LRP.

The free polymer is slightly higher in molecular weight than the living fraction, which can also be seen from inspection of Figure 7, in which the molecular weight evolution with monomer conversion is presented. The $M_n$ values of both the living polymer fraction (surface-bound polymer) and the dead polymer (free polymer) increase steadily with monomer conversion—as expected for a well controlled MADIX polymerization—and are in good agreement with the theoretical molecular weights, $M_n^{theo}$, which have been calculated via eq 2, which accounts for the increase of the number of chains in the system due to continuous initiation.[49]

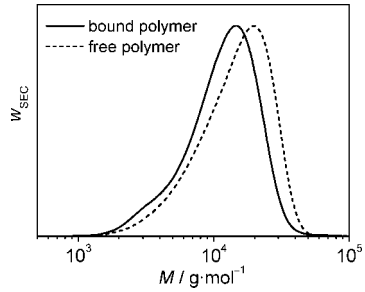



**Figure 6.** Molecular weight distributions (SEC-curves) of polymer after 19% of monomer conversion in **4**-mediated solid-supported vinyl acetate polymerization at 60 °C, initiated by 3.3 mmol·L$^{-1}$ AIBN and using a mass ratio $\mu(\mathbf{4}) = 0.05$; (—) surface-bound polymer cleaved from particles after treatment with TAPA, (- - -) free polymer formed in the interstitial solution phase.

$$M_n^{theo} = \frac{m_{VAc} X_{gravi}}{n_{bound} + n_{free} + \frac{1}{2} n_{I\cdot}} \quad (2)$$

$m_{VAc}$ represents the monomer mass, $n_{bound}$ and $n_{free}$ are the molar amounts of bound and free MADIX agent, and $n_{I\cdot}$ is the molar amount of initiator-derived radicals that have been released to the system until $X_{gravi}$ have reached. Equation 2 assumes that termination occurs via combination. This assumption is in agreement with the fact that the molecular weight of the terminated polymer is slightly higher than the living surface-bound polymer. The PDI values of both polymer fractions scatter around 1.5, with a slight tendency of narrower molecular weight distributions of the living polymer, which shows a minimum value of 1.43. The fact that the PDI values of the living polymer are relatively high for a well-controlled polymerization can be understood by the decreased accessibility of MADIX agents within the resin particles, whereby the effective addition rate of macroradicals toward the controlling thiocarbonylthio compound is substantially reduced. In an earlier study into RAFT polymerization kinetics using PREDICI simulations[54] it has been found that a reduction in the addition rate induces increased values of the polydispersity. The absolute PDI values of the living polymer fractions are slightly higher than found for Merrifield resin-supported RAFT polymerizations of methyl acrylate and styrene using trithiocarbonate-type RAFT agents,[41] which is easily understood in the face of the smaller transfer activity of xanthates.[10] When, however, compared to other solid-supported RAFT polymerizations using silica particles,[34,35] the quality of the molecular weight control is exceptionally high. This finding suggests that the major part of the polymerization proceeds inside the resin particles, where the MADIX agent concentration is high, and only a minor part in the solution phase between the particles, where no mediating agent is present. Such a beneficial situation possibly points toward an increased concentration of AIBN within the resin when compared to the interstitial solution phase, which may be due to a preferential solubility effect.

When adding free MADIX agent **1** to the solution phase, the molecular weight control increases in quality with respect to the polydispersity of the generated living polymer. Figure 8 depicts the evolution of molecular weight and polydispersity of a system that is identical to that described above, but to which 4.9 mmol·L$^{-1}$ of unbound MADIX agent **1** has been added. It can be clearly seen that the PDI values both of the free and of the bound polymer is largely decreased and reaches minimal values of 1.15 after 16% of monomer conversion. The molar masses are very well described by the theoretical predictions, which were calculated by eq 2. The free xanthate induces LRP in the interstitial solution phase to a level of quality that is expected for a homogeneous MADIX polymerization. The chain

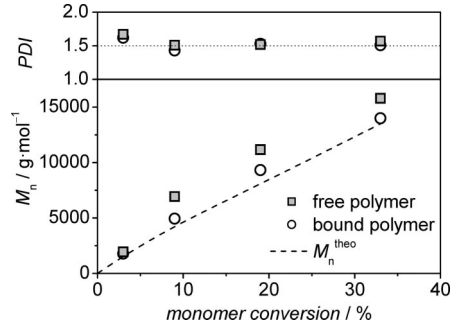



**Figure 7.** Number average molecular weight, $M_n$, and PDI of both free and surface-bound polymer vs overall monomer conversion in **4**-mediated solid-supported vinyl acetate polymerization at 60 °C, initiated by 3.3 mmol·L$^{-1}$ AIBN and using a mass ratio $\mu(\mathbf{4}) = 0.05$.

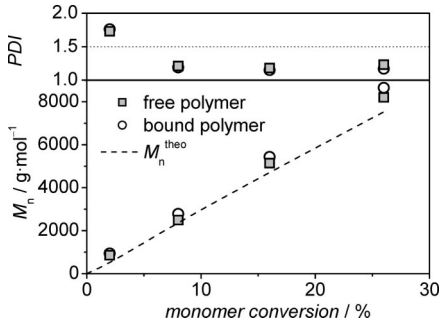



**Figure 8.** Number average molecular weight, $M_n$, and PDI both of free and surface-bound polymer vs overall monomer conversion in vinyl acetate polymerization at 60 °C, using a mixture of solid-supported MADIX agent **4** ($\mu$(**4**) = 0.05) and free MADIX agent **1** ($c_1$ = 4.9 mmol·L$^{-1}$), initiated by 3.3 mmol·L$^{-1}$ AIBN; mol ratio of $n$(VAc):$n$(**4**):$n$(**1**):$n$(AIBN) = 1000:2.0:0.88:0.55.

equilibrium, which encompasses reaction with all xanthates, that is, free and tethered ones, leads to the formation of perfectly controlled polymer upon the resin support. It should be noted that the surface-tethered polymer still constitutes a pure living fraction of the system; the free polymer in the interstitial solution phase, however, is a mixture of living and dead polymer, such as in a classical homogeneous MADIX polymerization. This is in agreement with the PDI values of the surface-tethered material being again slightly smaller than that of the free polymer. The beauty of only employing solid-supported MADIX agent is somewhat lost by such an approach. This strategy, however, becomes advantageous for the formation of block copolymers of greater purity,[39] because pure living polymer upon the solid support having very narrow polydispersities becomes accessible.

## Conclusion

The one-pot reaction of 1,1′-thiocarbonyl diimidazole (TCDI) with a thiol, followed by reaction with the hydroxyl groups of a Wang resin, led to the production of a surface-immobilized MADIX agent. The supported RAFT agent was used to control the polymerization of vinyl acetate in toluene, with a ratio monomer-to-solvent optimized at 50 wt %. $M_n$ and PDI values were found to decrease with an increase in resin particle content in the system, thus agreeing with the expectation that a higher MADIX agent concentration induces a lower molar mass of the produced polymer. The amount of surface-bound polymer was found to greatly increase with increasing content of solid MADIX agent, reaching values of almost 80%. FT-IR spectroscopy and thermal analyses confirmed the successful grafting of PVAc to Wang resin. The grafted PVAc chains were cleaved from the Wang resin support via radical reaction with *tert*-amyl peroxy acetate (TAPA) and the molecular weight distributions exhibited the typical shape of polymers formed via a well controlled LRP, with the free polymers showing a slightly higher molecular weight than the living fraction. The $M_n$ values of both living polymer fraction (surface-bound polymer) and dead polymer (free polymer) increased steadily with monomer conversion—as expected for a well controlled MADIX polymerization—and were in good agreement with the theoretical molecular weights. PDI values of both polymer fractions scatter around 1.5, with a slight tendency of narrower molecular weight distributions of the living polymer, which shows a minimum value of 1.43. Addition of free MADIX agent to the solution phase led to a decrease in PDI values of both free and bound polymer, and the experimental molar masses were in very good agreement with theoretical predictions.

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