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A Combined DPE/Epoxide Termination Strategy for Hydroxyl End-Functional Poly(2-vinylpyridine) and Amphiphilic AB_2-Miktoarm Stars

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S *Supporting Information*

Poly(vinylpyridine) (PVP) is a polymer with remarkable properties that plays an important role in complex polymer architectures, mainly due to its pH-responsive chain. There are numerous examples of block copolymers that contain at least one poly(2-vinylpyridine) (P2VP) block (diblock,[1] multiblock,[2] and miktoarm star polymers[3]). In a variety of elegant works the peculiar properties of PVP have been exploited, particularly with respect to its pH-sensitive[4,5] behavior, its interaction with transition metals salts,[6] and in the field of nanolithography.[7] Klingelhöfer et al.[8] have demonstrated the catalytic efficiency of colloidally dispersed palladium nanoparticles in block copolymer micelles of PS-*b*-P4VP and introduced the possibility of performing a Heck reaction in standard organic solvents with an increased catalyst stability compared to classical palladium complexes. On the basis of this work, P4VP- and P2VP-dispersed transition metals salts have been investigated, particularly with regard to their catalytic impact in coupling reactions such as Suzuki, Heck, and Stille.[9] Additionally, Ruokolainen et al. applied PS−P4VP block copolymers as temperature-sensitive electrical semiconductors by protonating the P4VP block quantitatively with methanesulfonic acid (MSA), building up hydrogen bonds to pentadecylphenol. These materials form reversible, temperature-dependent microphase separation that controls ionic conductivity.[10]

Although the living carbanionic polymerization represents a highly useful technique for the preparation of PVP with tailored chain length and narrow molecular weight distribution, there is a problematic issue: The carbanionic chain end of the living P2VP can attack the electron-poor pyridine ring of the backbone, leading to branched and cross-linked polymeric side products.[11] Characterization of this undesired process was achieved by Sigwalt and Tardi.[12] An established strategy to overcome the formation of high molecular weight side products is the addition of inorganic salts, such as lithium chloride to the reaction, followed by fast quenching.[13] In this case LiCl and the living P2VP are in equilibrium with the corresponding aggregates, which reduces the reactivity with simultaneous increase of the selectivity. However, this reaction route necessitates additional work-up and purification steps. Rapid termination of the living polymer with an appropriate compound to decrease the chain end reactivity could be an alternative strategy to suppress the side reactions. Commonly used termination reagents for PVP are chlorosilanes,[14] epoxides,[15] and diphenylethylene (DPE)[16] derivatives. In particular, DPE derivatives are prominent and have recently been employed to incorporate various functional groups at the polymer backbone[17] or in the terminal position.[18] Furthermore, DPE derivatives can be used to build up unusual macromolecular architectures.[19] The significant advantage of DPE is the absence of self-propagation due to its sterical hindrance and the decrease in nucleophilicity of the carbanionic chain end. Although DPE is frequently used to moderate the reactivity of living carbanionic polymers, it is surprising to note that DPE has rarely been employed for end-capping reactions of P2VP. Müller and co-workers used DPE-terminated P2VP to polymerize *tert*-butyl methacrylate (tBMA), preparing two different linear terpolymers (PS-*b*-P2VP-*b*-PtBMA and PB-*b*-P2VP-*b*-PtBMA).[20,21]

Epoxides represent another class of valuable end-capping reagents for carbanionic polymerization.[15,22] On the one hand, they can provide a large variety of functional groups combined with a high reactivity toward nucleophilic attack due to the pronounced ring strain.[23,24] On the other hand, the termination allows for facile transformation of a carbanionic chain end to an oxyanionic macroinitiator with a hydroxyl group.[25]

In the current work a two-step termination strategy for the preparation of hydroxyl end-functional P2VP has been developed. P2VP was end-capped successively with DPE and ethoxy ethyl glycidyl ether (EEGE) to introduce hydroxyl termini after hydrolysis. After removal of the acetal protecting group by acidic hydrolysis, the resulting end-functional P2VP-$(OH)_2$ has been utilized as a macroinitiator for the polymerization of ethylene oxide (EO) to afford a novel AB_2 miktoarm star polymer P2VP−(PEO_2). An overview of the synthetic strategy is shown in Scheme 1. It is an unusual feature of this strategy that P2VP is used as the first block for the synthesis of miktoarm star structures.

All polymers described in this contribution have been synthesized by high-vacuum techniques at low temperatures (−78 °C) and in a polar solvent (THF) to obtain a highly reactive chain end for the desired end-capping procedure. For the direct end-capping reaction of living P2VP with EEGE, it is necessary to increase the temperature after the addition; otherwise, there is no incorporation of the epoxide (see Figures S4 and S5). As shown in Scheme 1 (top, right side), even at higher temperatures subsequent to the addition of EEGE to the living P2VP chains the reddish color remained for several hours, indicating the noninstantaneous termination with EEGE. In this period there is a competition between the desired epoxide termination and the attack of the P2VP carbanions on

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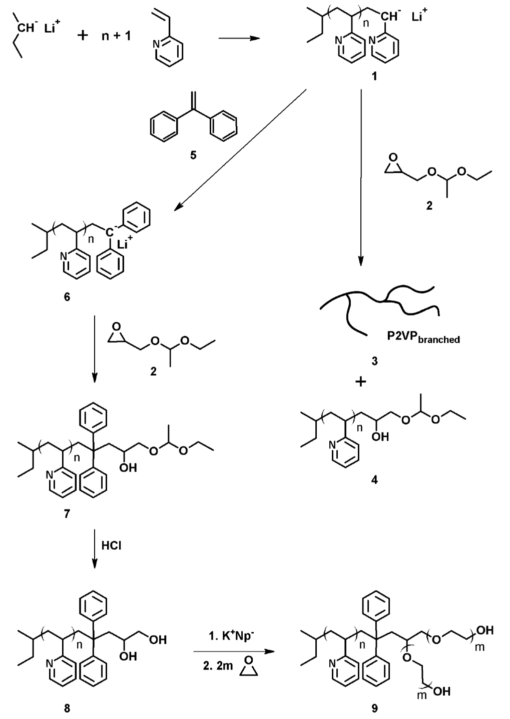
Scheme 1. Synthetic Strategy for P2VP−EEGE and Amphiphilic P2VP−(PEO)$_2$ Miktoarm Star



the electron-poor pyridine ring, resulting in the branched high molecular weight byproduct. Because of this competition, one obtains a bimodal, broad molecular weight distribution (MWD) with a high PDI of 13.51 (no. 1, Table 1) in direct end-capping experiments, containing a main polymer mode at 2300 g mol^{-1} and a large amount of branched P2VP, which can be identified at high molecular weight in the SEC trace (Figure 1, left). Additionally the branching reaction was observed by ^{13}C NMR spectroscopy (Figure S2). Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-Tof MS) (Figure S3) of the low molecular weight, linear polymer confirmed complete functionalization with EEGE, indicating no undesired proton termination.

Table 1. Molecular Characteristics of the Polymers Prepared

no.	polymer[a]	M_n[a]	PDI[b]
1	P2VP−EEGE	5400	13.51
2	P2VP−DPE−EEGE	2100	1.12
3	P2VP−DPE−EEGE	3200	1.10
4	P2VP−DPE−EEGE	5700	1.09
5	P2VP−DPE−EEGE$_d$[c]	3200	1.11
6	P2VP−(PEO)$_2$	20600	1.13

[a] Molecular weight in g mol^{-1}, calculated from ^{1}H NMR. [b] MWD characterized by SEC in DMF (PS standard). [c] Polymer 3 after acidic hydrolysis leading to a dihydroxyl end-functional P2VP.

In contrast to this direct epoxide termination, we were able to prevent the undesired branching reaction by precapping the living P2VP with DPE and subsequent addition of EEGE. This "double termination" procedure has been studied for molecular weights in the range 1500−5700 g mol^{-1} and resulted in a single narrow distribution mode (PDI = 1.09−1.12, Table 1) for all polymer samples.

Conclusive evidence for quantitative termination of the double-terminated polymer samples (nos. 2−4, Table 1) was gained from MALDI-ToF MS. Each signal of the resulting spectra can be assigned to EEGE-terminated polymer chains (Figure S13). Both spectra of Figure 2 contain only one distribution mode for the desired polymer, which demonstrates that all chain ends are double-terminated. Subsequently, all acetal groups of the P2VP−DPE−EEGE were cleaved by treating the polymers with hydrochloric acid, which is

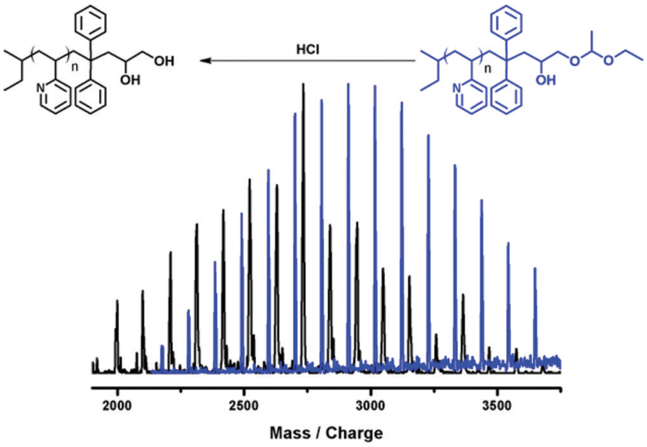


Figure 2. MALDI-ToF spectra of the cleavage of the protecting acetal by acidic hydrolysis (no. 3 → no. 5). Blue lines represent protected precursor compound.

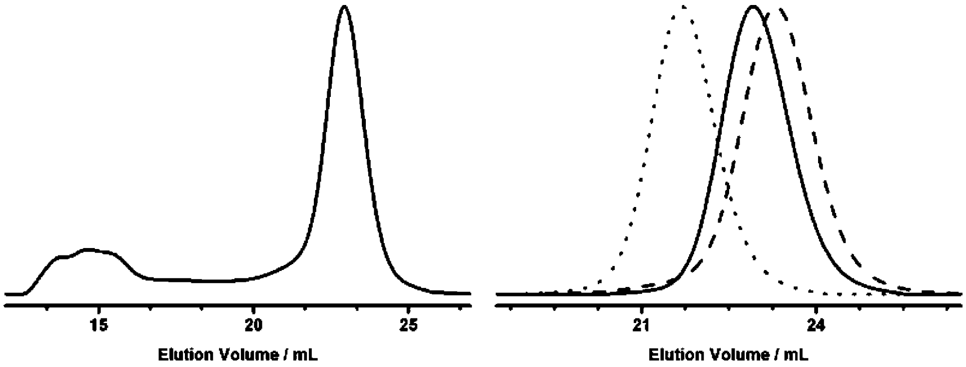


Figure 1. (left) SEC trace of P2VP−EEGE (no. 1) in case of direct EEGE termination. (right) Double termination resulting in P2VP−DPE−EEGE (nos. 2−4) (dotted line: no. 4; solid line: no. 3; dashed line: no. 2).

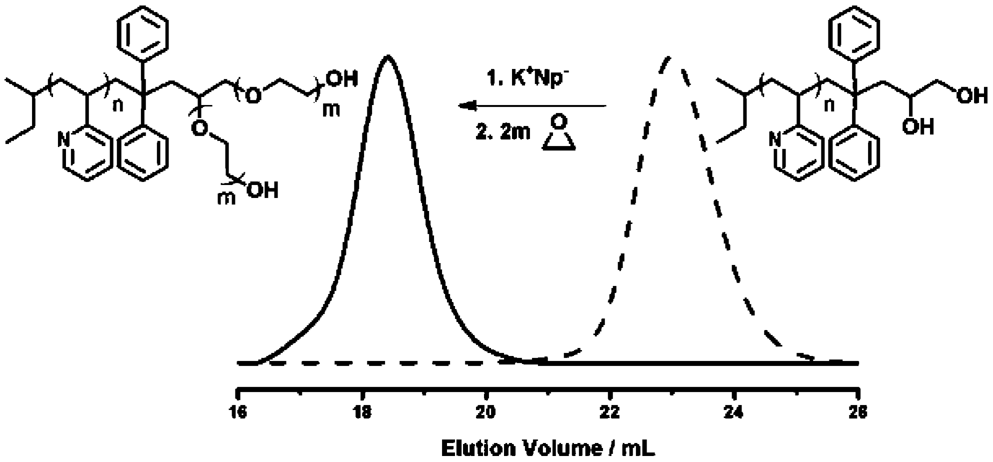


Figure 3. SEC curves of terminated precursor (P2VP–DPE–EEGE$_d$, right) and a miktoarm star polymer (P2VP–PEO$_2$, left) (no. 6) with two PEO chains.

confirmed by the calculated shift of the distribution by 72.11 Da (Figure 2).

In combination with the results of SEC characterization, it can be concluded that this procedure leads to quantitative end-functionalization of P2VP (**7**) without any side product. The potential of this strategy is emphasized, if one considers that the reaction mixture of the DPE-capped P2VP (**6**) and the glycidyl ether capping reagent had to be warmed up to room temperature to obtain quantitative conversion. The key step of the presented work is thus DPE-capping of P2VP that allows for the reaction with an epoxide termination reagent and suppression of the branching side reaction, most probably due to the steric hindrance at the active chain end. We presume that the double termination strategy is general for a broad range of functionalized epoxides with various functionalities, such as multiple hydroxyl, amino, allyl, and nitroxy groups.[15]

In order to demonstrate a possible application for the synthesized P2VP–DPE–EEGE$_d$ (**8**), we employed the polymer as a macroinitiator for the anionic ring-opening polymerization of ethylene oxide (EO), resulting in an AB$_2$-type miktoarm star polymer. Miktoarm star polymers with AB$_2$ structure have e.g., been prepared by Glaied et al.[26,27] Seminal work on miktoarm star polymers has been carried out by Hadjichristidis and co-workers.[28,29] Linear AB-block copolymers containing PVP and PEO segments have also been described in several works that capitalize on the pH sensitivity to achieve reversible assembly and disassembly of polymer micelles in aqueous solution.[4,5,30,31] However, to the best of our knowledge, miktoarm stars consisting of PVP and PEO have not been described yet.

We have prepared an amphiphilic, pH-sensitive AB$_2$-miktoarm star polymer consisting of one P2VP and two PEO arms (P2VP–PEO$_2$, no. 6; cf. Scheme 1, bottom). The hydroxyl groups of the P2VP–DPE–EEGE$_d$ (no. 5, Table 1) were deprotonated by potassium naphthalide, and subsequently polymerization of ethylene oxide has been carried out. Block copolymerization was monitored by SEC (see Figure 3; ^{1}H NMR: Figure S9), and the resulting materials have been analyzed by dynamic light scattering (DLS) at pH = 7 and pH = 1. Because of the PEO-*b*-P2VP structures, the micelles formed by the AB$_2$-miktoarm star polymer grow from 78.6 to 84.0 nm upon decreasing the pH value. This is a consequence of the protonation of the P2VP chain. Further, detailed studies on solution and bulk structures of the resulting amphiphilic AB$_2$-miktoarm stars with different chain length are in progress.

In summary, well-defined hydroxyl end-functional P2VP with narrow molecular weight distribution has been synthesized by carbanionic polymerization. Quantitative end-capping was achieved by a novel double termination process by successively adding DPE and EEGE to the living polymer chains. The key step is the reaction of the living P2VP with DPE prior to epoxide termination, which prevents the coupling side reaction of the living P2VP chains. In addition, a novel AB$_2$ miktoarm star polymer P2VP–(PEO$_2$) has been synthesized. Further studies on the aggregation behavior as well as other functionalization sequences with other glycidyl ethers are in progress, aiming at other PVP-*b*-polyether miktoarm stars.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

(1) Detailed experimental procedures and (2) analytical and spectral characterization data (Figures S1–S13). This material is available free of charge via the Internet at http://pubs.acs.org.

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