

ARTICLE

Controlling molar mass and dispersity in polymers through deuteration: the case of poly(phenyl D₃-vinyl sulfide)

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Polymer properties can be defined by functionalizing the monomer and tuned by modifying key properties, such as, molar mass and dispersity. Typically, these modification approaches require significant alterations to the synthesis process, or even re-optimization of the whole process. In this study, we demonstrate that deuteration, a mainly overlooked method, can significantly influence the properties without altering the chemical structure of the monomer or the synthesis procedure. For the poly(phenyl vinyl sulfide), we introduce a technique for integrating deuterium into a monomer, providing a novel way to adjust the properties of the resulting polymer without changing its chemical nature. This method is both accessible and cost-effective, adhering to the principles of green chemistry. Quantum chemical analysis revealed that this control over properties is due to a reduction in the rate of the polymerization deactivation, which proceeds through the chain transfer mechanism. The opportunity highlighted in the present study may be well-applicable for a number of other polymers, leading to a new approach to practical tuning of polymer properties and developing materials with enhanced properties

Introduction

Radical polymerization provides a wide range of materials with desired properties.^{1–4} Molecular weight (M_w) and dispersity (\mathcal{D} , polydispersity index, PDI) significantly determined the properties of polymeric materials.^{5–13} However, modifying polymer properties obtained according to controlled radical polymerization (CRP) may be challenging. A vast majority of current approaches results in tailoring polymer characteristics, including adjustments to temperature, solvent, and initiator. Additionally, altering reagent concentrations,^{14, 15} their addition rates,¹⁶ and modifying the activation process^{17–24} of the polymerization yields polymers with an appropriate molecular-mass values (Figure 1a).

Anastasaki and colleagues developed a powerful approach for aqueous ATRP polymerization of both homopolymer and block copolymers, achieving control over dispersity ($1.08 < \mathcal{D} < 1.60$) by varying the deactivator concentration (Figure 1a).²⁵ Matyjaszewski's group reported a method for dynamically controlling dispersity through radical polymerization with electrochemical atom transfer utilizing the Cu(II)/Cu(I) redox

reaction controlled by an external current to produce polymers with M_w values close to those theoretically predicted and low \mathcal{D} .²⁶ Further diversification of CRP methodologies included blending polymers of different molecular weights,^{27–29} combining RAFT^{30–33} and ATRP³⁴ initiators/agents, incorporating chain coupling/terminating agents,^{35–38} utilizing organic catalysis,^{39–43} changing the degree of polymerization^{44–46} (Figure 1a) and employing flow chemistry.^{47–49} These techniques have led to extensive opportunities for monomer polymerization using CRP. However, in these approaches, the monomer structure generally remains unaltered.

In general, changing the nature of the monomer should change the desired polymer's properties (Figure 1b).⁵⁰ Changing the properties of the final polymer material while keeping the nature of the monomer unit unchanged would be a great way to fine-tune the material. Accordingly, incorporating isotopes into a monomer unit can be a promising approach. On the one hand, the nature of the polymer unit is still the same, and the final properties of the polymer material should be similar. On the other hand, isotope incorporation can modify the crucial values (M_w and \mathcal{D}), providing a more efficient tool for fine-tuning valuable properties. D-labeling is the best choice for evaluating the isotope effect due to the significant difference in the weight of H/D isotopes. As a result, the free energies of C-H and C-D bond formation are different, and the C-D bond is stronger. If the cleavage of the C-H/D covalent bond is a rate-limiting step in the polymerization or deactivation processes, using D-labeled monomers could vary M_w and \mathcal{D} through a more efficient chain growth process. This approach not only preserves the nature of the monomer but also provides additional control of the reaction, thereby leading to polymers with distinct properties. Deuteration was previously applied to

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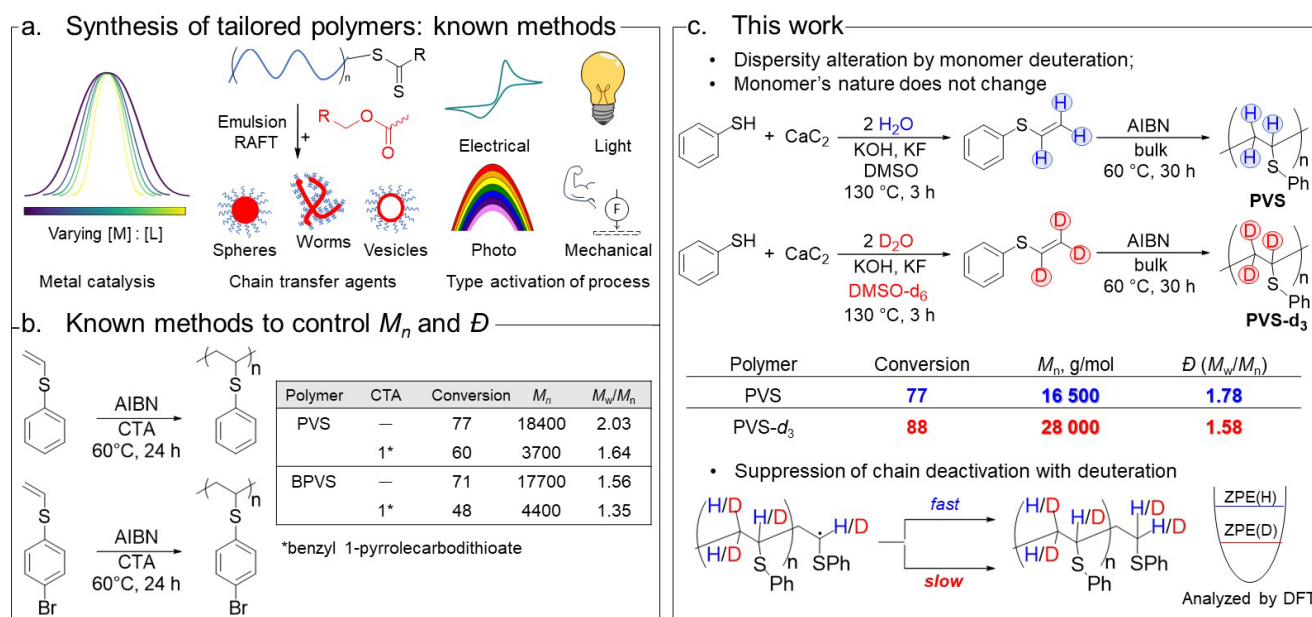


Figure 1. Methods for fine-tuning the structure of polymers by influencing their mass characteristics (a) Various tools for the precision synthesis of tailored polymers: control of polymer dispersity by varying the ratio of [CuBr]/L; changing the degree of polymerization to obtain various self-organizing structures; different type activation of process. See references in the text. (b) Known methods for tuning the monomer structure. See references in the text. (c) This work.

polymers to achieve desirable characteristics.^{51–57} However, the specific impact of deuteration on polymer dispersity was not extensively explored.⁵⁸

This work was carried out to modulate polymer properties using deuterium incorporation into a monomer unit (Figure 1c). It was found that deuteration reduced the polymer dispersity from 1.78 to 1.58 and doubled its molecular weight. Quantum chemical analysis corroborated these experimental findings, highlighting the role of the kinetic isotope effect in altering the polymerization kinetics. This synthetic route provided enhanced dispersity under free-radical polymerization conditions.

A systematic study of the effect of deuteration on polymerization kinetics is highlighted here for the first time. In addition, deuterated monomers were efficiently synthesized on a gram scale for detailed mechanistic investigations, providing facile access to these valuable compounds using calcium carbide as a source of vinyl unit and D_2O as the deuteration agent.

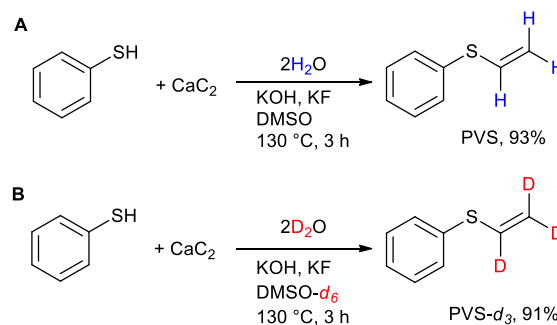
Results and discussion

The synthesis of the monomer

Initially, an appropriate monomer should be selected to evaluate the effect of deuterium. A monomer should be easily polymerizable, according to the radical polymerization technique. At the same time, deuterium labels can be introduced into monomer structures according to a well-described procedure at the gram scale. Therefore, phenyl vinyl sulfide (PVS) was selected due to its polymerizable nature^{50, 59} and access to the deuterated substrate.⁶⁰ Gram-scale synthesis of both deuterated and nondeuterated monomers was carried out using calcium carbide as a source of acetylene (Scheme 1, A and B). Recently, calcium carbide has been efficiently used as a source of C_2 units in synthetic chemistry^{61–70} and various

applications.^{71–76} In the case of the deuterated substrate, deuterium oxide was used to hydrolyze calcium carbide instead of water (Scheme 1, B).

Both monomers were synthesized in 10 g amounts due to the straightforward and scalable synthetic procedure, as well as due to the low price of deuterium oxide, which is the cheapest industrially produced source of deuterium. Then, the monomers were distilled under vacuum over calcium hydride. As a result, two anhydrous and highly pure monomers were obtained and used in further polymerization studies.

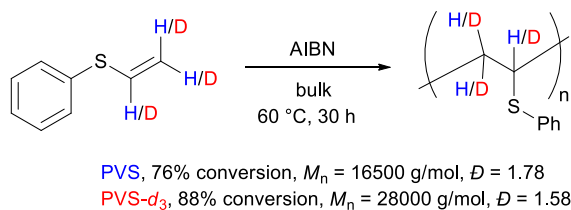


Scheme 1. Synthesis of the monomer using calcium carbide as an acetylene source: A) phenyl vinyl sulfide (PVS) and B) deuterated phenyl vinyl sulfide (PVS- d_3).

Free-radical polymerization of the vinyl sulfides

The monomers readily polymerized following the standard polymerization procedure using AIBN as an initiator in bulk (Scheme 2). The polymerization products were reprecipitated three times in a toluene-methanol solvent system, dried at 40 °C for two days, and analyzed. The conversion of the monomers was nearly the same ($\approx 80\%$); however, the average molecular mass and dispersity were markedly different. Thus, deuterium atoms affected the crucial features of the polymers,

and deuteration improved both the average molecular mass and dispersity.



Scheme 2. Polymerization of PVS and PVS- d_3 under free radical conditions.

The kinetics of polymerization for both monomers were similar (Figure 2), so the nature of the deuterium effect can hardly be associated with the kinetics of polymerization. A blank experiment was carried out. Two monomers (deuterated and nondeuterated) were mixed at a nearly 1:1 ratio. The mixture was analyzed using GC-MS before and after polymerization without preprocessing. As a result, we could hardly separate these two monomers from each other after optimization of the GC conditions (see the ESI): before polymerization, PVS- d_3 :PVS = 51.21%:48.79%; after polymerization, PVS- d_3 :PVS = 47.91%:52.79%. If the deuterated monomer had been more reactive in the polymerization reaction, the final mixture would have contained significantly less nondeuterated monomer, resulting in a polymer with a higher proportion of the deuterated unit. However, the ratio of the monomers was similar in both mixtures: before and after the polymerization. Therefore, similar rates of polymerization may be assumed for PVS- d_3 and PVS.

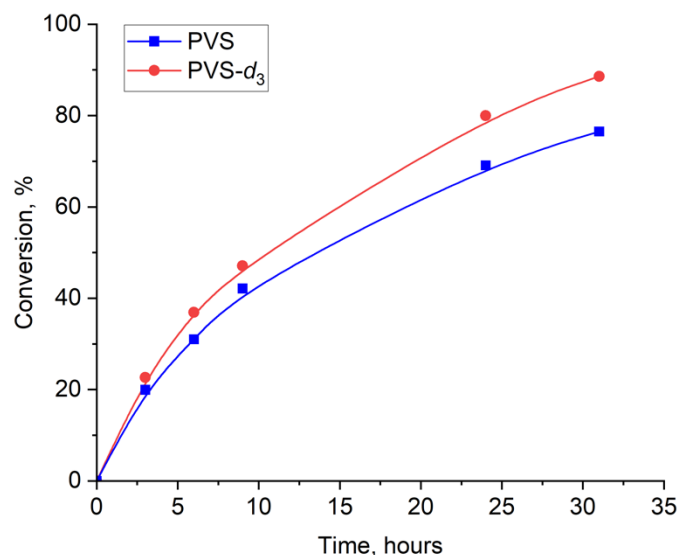
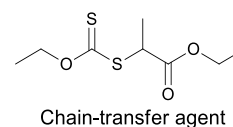


Figure 2. The kinetics of polymerization of vinyl thioethers: PVS- d_3 (upper curve, red) and PVS (lower curve, blue).

RAFT polymerization of the vinyl thioethers

We carried out RAFT polymerization of the same monomers in the presence of the chain transfer agent O-ethyl-S-(1-ethoxycarbonyl)-ethylthiocarbonate to better understand the nature of the deuterium effect (Table 1).

Table 1. RAFT polymerization of phenyl vinyl sulfide.

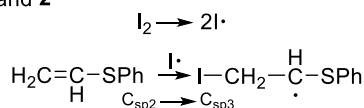


Monomer	RAFT polymerization		
	Conversion, %	M_n	\mathcal{D}
PVS	73	5100	1.42
PVS- d_3	87	5500	1.40

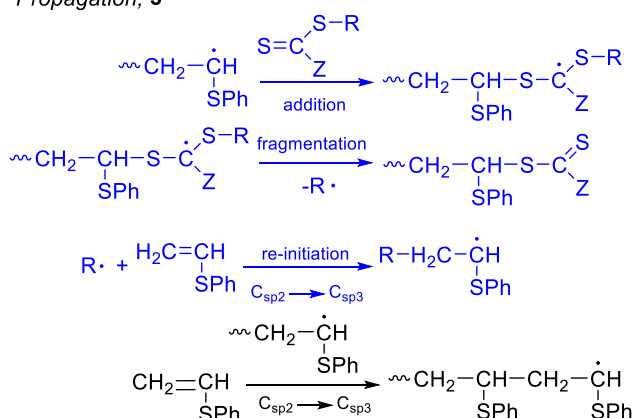
In the case of controlled chain termination, i.e., under RAFT conditions, the polymerization of both labeled and nonlabeled monomers resulted in polymers with the same features. Therefore, deuterium incorporation resulted in increased molecular weights and improved \mathcal{D} only in the case of free radical polymerization. Presumably, the isotope effect is achieved because of differences in the deactivation rate during free radical polymerization. At the same time, the kinetics were similar in both cases: the deuterated monomer polymerized faster and better under free-radical and RAFT conditions.

The possible reactions for both free radical and RAFT mechanisms in the bulk polymerization of phenyl vinyl sulfide are given in Scheme 3. Reactions 2, 3, 4, 7, and 8 can be influenced by the substitution of hydrogen with deuterium. Suppose that the chain propagation reaction constants (3) are measured for both deuterated and nondeuterated monomers. Therefore, it can be determined whether the environment of the radicaloid carbon atom affects the rate of change in its hybridization. The influence of deuterium on the initiator addition to the monomer (2) may be negligible, given the fewer acts of the addition compared to the chain propagation reactions and because the rate-determining step in initiation is the decomposition of the initiator into radicals (1). Reaction (4) is atypical for monosubstituted vinyl monomers such as styrene, where 95% termination occurs due to recombination. Typically, radical recombination is realized via the chain termination mechanism (5). Generally, chain transfer reactions (6-9) do not impact the kinetics of polymerization if rapid reinitiation occurs; they primarily affect the molecular weight and polydispersity. If reinitiation proceeds slowly, the reaction rate decreases, and inhibition may be observed. Deuterium could influence the chain-transfer reactions on both the monomer (7) and polymer (8) since proton transfer is possible in both scenarios.

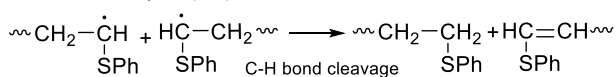
Initiation, 1 and 2



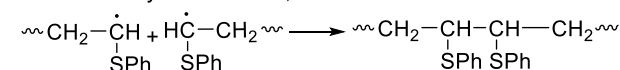
Propagation, 3



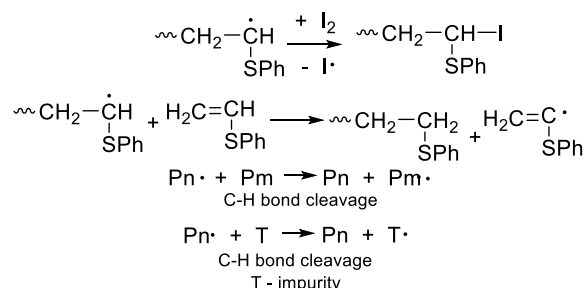
Termination by disproportionation, 4



Termination by combination, 5



Chain transfer, 6-9

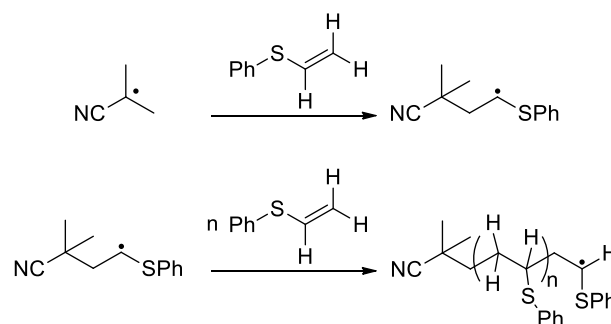


Scheme 3. Polymerization of phenyl vinyl sulfide under free radical and RAFT conditions. The additional steps in RAFT polymerization are marked in blue.

Computational analysis of monomer reactivity

Quantum chemical modeling of chain initiation, propagation ($n = 1-5$ in Scheme 4), and deactivation was carried out to gain insight into the divergent reactivity of the regular and deuterated monomers. The corresponding Gibbs free energies, ΔG_{rxn} , and activation free energies, ΔG^\ddagger , are plotted for $n = 1-5$ in Figure 3. Although ΔG_{rxn} values indicated systematically higher exothermicity of chain initiation and chain propagation in the case of PVS- d_3 , the difference was very small, 0.4 kcal/mol on average (Figure 3, top; see also Table S2 for values). The calculated free energies of activation for $n = 1-5$ also showed no significant difference. In particular, the barriers ΔG^\ddagger for chain initiation and growth involving PVS- d_3 were systematically lower by 0.2 kcal/mol (Figure 3, bottom and Table S3). For both PVS and PVS- d_3 , the oscillatory behavior of ΔG^\ddagger and ΔG_{rxn} was observed. On average, the free energy of PVS radical addition to the chain was -10.2 kcal/mol ($n = 1-5$). The corresponding

barriers were equal to 17.3 kcal/mol. Therefore, the radical polymerization is facile at 60 °C, which was experimentally observed.



Scheme 4. Modeled chain initiation and propagation for the case of PVS. The same processes were modeled with PVS- d_3 .

We compared the relative kinetic constants of the chain growth with PVS and PVS- d_3 according to the Eyring equation ($t = 60$ °C). Given that the difference in ΔG^\ddagger is 0.2 kcal/mol, the kinetic constants for PVS and PVS- d_3 are 1 to 1.35, respectively. This result qualitatively agrees with the experimentally observed reaction rates (Figure 2). If we take the increase in the conversion from 9 to 31 hours in Figure 2, the relative rates (kinetic constants) are 1 to 1.2, which is slightly lower than the computational estimation.

In Section S2, we compare the free activation energies of the chain growth reactions for both head-to-tail and head-to-head oligomerization, concluding that only head-to-tail polymerization is kinetically feasible. Upon closer examination, the analysis of the oligomer chain structures formed in the modeled process shows that the formation of the syndiotactic polymer is the most kinetically and thermodynamically feasible outcome. The structure of the model tetramer is depicted in Figure 4.

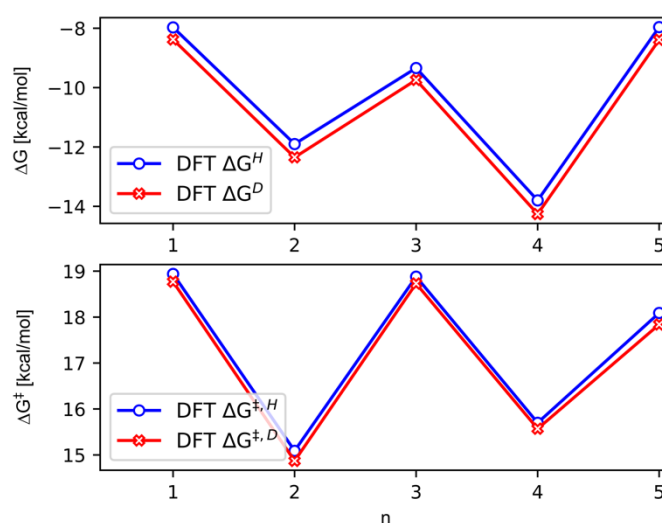
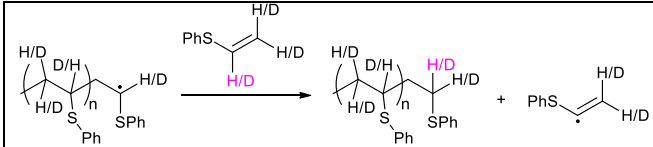


Figure 3. Gibbs free energies and free activation energies of chain growth ($n = 1-5$) in kcal/mol.

Table 2. Computed Gibbs free energies and free activation energies of chain transfer to the monomer, in kcal/mol. The model mechanism for the case of PVS is shown.



n	ΔG^H	ΔG^D	$\Delta\Delta G$
2	9.2	8.5	-0.7
3	8.3	8.1	-0.2
4	12.5	12.4	-0.1
	$\Delta G^{\ddagger,H}$	$\Delta G^{\ddagger,D}$	$\Delta\Delta G^{\ddagger}$
2	26.6	27.4	0.8
3	27.5	28.3	0.8
4	25.4	26.2	0.8

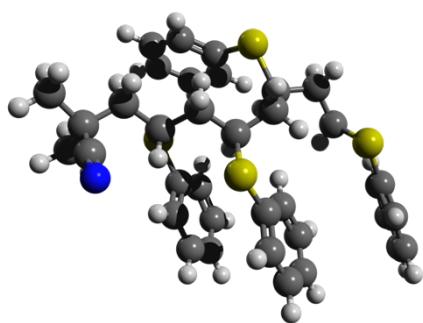


Figure 4. Optimized structure of the tetramer showing the arrangement of substituents in the main chain.

Next, the kinetics and thermodynamics of the deactivation by chain transfer to the monomer are discussed. We consider chain transfer the primary deactivation mechanism during the radical polymerization of PVS and PVS- d_3 under selected conditions since the polymerization is conducted neat, and the monomer is present in high excess and readily available for chain transfer. Moreover, the comparison of RAFT polymerization revealed a difference in the kinetics of PVS and PVS- d_3 polymerization, which agrees with the deactivation by chain transfer (see the previous subsection).

The computed Gibbs free energies and free activation energies of chain transfer are presented in Table 2. Chain transfer is an endergonic process in both cases, PVS and PVS- d_3 . The corresponding $\Delta\Delta G_{rxn}$ values are small and change from -0.7 to -0.1 kcal/mol as n changes from 2 to 4. The activation barriers in PVS- d_3 oligomerization are systematically greater than those in PVS oligomerization, decreasing from 27.4 to 26.2 kcal/mol when changing $n = 2$ to $n = 4$. $\Delta\Delta G^{\ddagger}$ remains at a constant value of 0.8 kcal/mol from $n = 2$ to $n = 4$.

The isotope effect on the radical polymerization of PVS- d_3 was attributed to this difference in barriers to chain transfer. First, according to the Eyring equation, the relative kinetic constant of the chain transfer at 60 °C is 3.35 times lower than that in the case of PVS if the computed $\Delta\Delta G^{\ddagger}$ value is used. Second, if the first order for the monomer was assumed in the kinetic equation, the value of the kinetic constant of 1 (mol·hour)⁻¹

corresponded to ΔG^{\ddagger} equal to 25.0 kcal/mol. The values of ΔG^{\ddagger} for both PVS and PVS- d_3 were close to this threshold. It should be noted that DFT methods have limited accuracy, just as using the Eyring equation may lead to some inaccuracies. However, given that the activation barrier for chain transfer tended to decrease with increasing n and that the barrier for PVS was systematically lower, we can assume that chain transfer to PVS may proceed well below a certain threshold value, after which this unwanted process significantly decreases the amount of M_n observed in the nondeuterated polymer.

Conclusions

A novel method for improving the polymer dispersity index under radical polymerization conditions was developed. The method, tested for a deuterated monomer, utilized the isotope effect of PVS- d_3 , which was synthesized through a simple, inexpensive, and scalable procedure. For the first time, poly(phenyl D_3 -vinyl sulfide) with a high M_n of 28000 g/mol was obtained. DFT modeling and analysis of the RAFT polymerization showed that the isotope effect in the radical polymerization process could be associated with the decreased kinetic feasibility of deactivation via the chain transfer mechanism. The modeling indicated that the formation of the stereoregular head-to-tail syndiotactic polymer is the most favorable.

D-labeled monomers can be efficiently employed in applications such as elucidating polymerization mechanisms, kinetic studies, synthesizing polymers with modified mechanical properties, and polymer tracking in the environment. The reaction of calcium carbide and deuterium oxide is an effective method for synthesizing D-labeled monomers because of the unsaturated acetylene unit in calcium carbide. The acetylene unit from calcium carbide can be converted through straightforward hydrolysis into a polymerizable D-labeled vinyl unit. Many deuterated monomers can be isolated on more than gram scales using established procedures with calcium carbide. Notably, other D-labeling methods typically rely on multistep reaction sequences or require expensive and explosive D-labeled acetylene gas.

Given that calcium carbide is an inexpensive and readily available chemical and that D_2O is the most cost-effective deuterium source, the procedure described here represents an unparalleled way to synthesize D-labeled polymers on a batch scale. Incorporating deuterium into the polymeric chain can also be considered a strategy to modify or enhance polymer properties while preserving the type of polymerization (specifically, radical polymerization) and the chemical properties of the monomer/polymer. Therefore, we propose further research on monomer and polymer deuteration via synthesis based on the interaction of CaC_2 with D_2O .

A central question concerns the extent to which the properties of polymeric materials intrinsically change upon deuteration. It is well-established that C-D bonds are stronger than their C-H counterparts, enabling new potential applications where enhanced stability is required. Some may argue about the increased costs associated with deuteration, even using the

most economical agent, D₂O. Beyond materials with improved properties, as discussed previously, the synthesis of tagged materials represents a high-value application for D-polymers. We have outlined a promising methodology and the mechanistic basis for changes in reactivity. Further research is essential to explore the properties and potential applications of these materials more thoroughly.

Experimental and Computational Details

General information and detailed experimental procedures are described in the ESI. The RAFT polymerization procedure and the synthesis of the chain transfer agent were described elsewhere.⁵⁰

Synthesis of monomers

A pressure vessel with a screw cap was charged with 30 mL of DMSO, followed by thiophenol (9.82 mmol, 1 mL), KOH (11.78 mmol, 0.661 g), KF (10.8 mmol, 0.626 g), and CaC₂ (39.3 mmol, 2.52 g). Then, H₂O (58.9 mmol, 1.06 mL) was added. The vessel was immediately sealed and stirred at 100 °C for 3 h. After completion of the reaction, the mixture was cooled to room temperature and then extracted with Et₂O. The organic layer was washed with brine and dried over Na₂SO₄, and the solvent was evaporated. The monomer was purified *via* vacuum distillation.

For the synthesis and isolation of the deuterated monomer, a mixture of DMSO-*d*₆/dioxane 1:4 should be used as a solvent, *t*BuOK as a base, PhSK instead of thiophenol, and D₂O instead of water.

DFT Calculations

Low-energy conformers of the oligomer chains were obtained with molecular dynamics simulations using the GFN2-xTB Hamiltonian and the original xtb program.^{77, 78} In GFN2-xTB calculations, the ALPB solvent model was used.⁷⁹ 50 equitemporal snapshot structures from every trajectory were subjected to semiempirical geometry optimizations using the ORCA 5.0.1 computational package.⁸⁰ So-obtained lowest-energy conformers were used in subsequent DFT modeling.

Spin-unrestricted DFT computations were performed in ORCA 5.0.1. B97-3c method⁸¹ was used for initial geometry optimizations and vibrational frequency calculations. Final single-point energy evaluations were performed at the ωB97X-V/def2-TZVP level.^{82, 83} Thermochemical corrections were calculated at 333.15 K. C-PCM⁸⁴ was used to simulate the reaction medium. Further computational details are given in the ESI.

Conflicts of interest

There are no conflicts to declare.

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