Engineering solvation in initiated Chemical Vapor Deposition (iCVD) for process-property control

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Abstract

Organic solvents are widely used in polymer synthesis, despite their use lengthening purification steps and generating chemical waste. All-dry synthesis techniques, such as initiated Chemical Vapour Deposition (iCVD) polymerization, eliminate the use of solvents, however, only a narrow palette of material properties is accessible. Inspired by the principles of solvent engineering in solution synthesis, we report a strategy to broaden this palette by vapour-phase complexing (namely, vapour-phase solvation) mediated by hydrogen-bonding. Broad ranges of polymer chain length, as well as the mechanical strength and variety of film surface morphology are demonstrating using this strategy. We further achieve an unprecedented solvation modality; more specifically, interfacial solvation. The molecular interactions, locations of solvation, and kinetics of the coupled solvation-adsorption-polymerization process are investigated using molecular dynamic simulations and experimental validation of a theoretical kinetic model. The strategy can be applied to various methacrylate and vinyl monomers. Solvation in all-dry polymerization offers a new degree of freedom in polymer design and synthesis with improved environmental benignness, pointing to accelerated discovery of polymer thin films by simply introducing active solvents in the vapour phase.

Introduction

Organic solvents are often considered a necessity in polymerization as they can improve molecular mobility and stabilize reaction intermediates[1,2]. Beyond serving the basic function of a liquid medium, new lights have been shed on solvents in the past decade, with recent research pointing to their influence on polymer properties, such as molecular weight and stereoregularity[3], hence enabling new control modalities via solvent engineering. Nevertheless, the profuse use of organic solvents in polymer synthesis made lengthy purification steps unavoidable, generating large amounts of toxic waste while rendering the production of plastics unsustainable[4]. Furthermore, the usage of organic solvents itself could pose constraints on materials design. For example, a cosolvent may not exist for monomers with contrasting solubility[5], which has hindered the development of amphiphilic copolymers that present desirable antifouling properties[6].

To address the drawbacks of conventional solution-based polymerization, all-dry polymerization techniques have been developed, such as initiated Chemical Vapor Deposition (iCVD), Plasma-Enhanced Chemical Vapor Deposition (PECVD)[7], and parylene deposition[8]. These all-dry processes enable one-step synthesis, processing, and application of polymers as a high-purity coating without the need for solvent removal or other purification steps, hence reducing the environmental impact of polymer synthesis. Furthermore, all-dry synthesis has enabled novel materials properties, such as superhydrophobicity and statistical amphiphilicity, which could revolutionize a broad cross-section of existing and future technologies, ranging from advanced fouling-resistant membranes and efficient energy storage devices to soft microrobots with novel mechanisms for sensing and actuation[9-14].

All-dry polymerization techniques afford powerful in-situ and real-time monitoring of the synthesis process, such as the continuous control of the reactant feed with picomole-precision and film thickness control on the nanoscale[7]. However, the material properties of the resultant polymer are largely determined by the choice of monomer(s). For example, mechanical strength is improved by increasing crosslinker content, which inevitably modifies the nature of

the resultant polymer thin film[15,16]. Although there have been examples of controlling polymer properties via deposition conditions[17], success of such control methods is highly variable. For example, increasing the surface monomer concentration in iCVD could lead to higher molecular weight for butylacrylate[18], but not for 4-vinylpyridine (4VP, as shown below).

To address the critical need for novel mechanisms to enable facile control of polymer properties in all-dry polymerization, we drew inspiration from the principles of solvent engineering. As a demonstration of this strategy, we focused on the effect of hydrogen bonding between a solvent and a monomer and demonstrated the generalizability of this approach using a variety of solvent-monomer combinations. This focus is motivated by the recent discovery that the hydrogen bonding between hexafluoroisopropanol (HFIP) and 4VP can affect the molecular weight of poly(4VP) (p4VP) during the Cu(0)-catalyzed controlled radical polymerization in solution[3]. While liquid solvents have been used in past iCVD studies, e.g., to anneal a polymer thin film[19] or to serve as porogens[20] or liquid substrate[21], monomer-solvent interactions have not been explored in the context of manipulating polymer properties or polymerization kinetics.

We showed that "solvation" of 4VP by HFIP occurred in the vapor phase, which greatly accelerated the deposition rate (DR), increased the upper bound of p4VP molecular weight, and enabled facile film morphology control. We then extended the concept of solvation to acetic acid (AcOH), whose effects are not well understood, and revealed an unprecedented interfacial solvation mechanism. We demonstrated the generalizability of this approach using a variety of monomers including methyl methacrylate (MMA), cyclohexyl methacrylate (CHMA), hydroxyethyl methacrylate (HEMA) and dimethylaminoethyl acrylate (DMAEMA) and acrylic acid (AA). Therefore, the solvation approach represents a novel degree of freedom in materials design and synthesis for all-dry polymerization, enabling new control modalities over polymer properties. It points to an exciting new direction for the discovery of novel CVD polymers, in which polymer thin film properties that were previously inaccessible can be achieved by simply introducing vaporized solvents[7].

Results and Discussion

Broadened polymer film properties by vapor-phase solvation

We chose 4VP as the monomer and HFIP as the vapor-phase solvent (Fig. 1 (a)) for investigating all-dry solvation based on their reported strong interactions in solution polymerization[22,23]. This selection also simplifies the stoichiometry of complexing in our subsequent modeling of the solvation-adsorption-polymerization process as 4VP and HFIP each presents a single site for hydrogen bonding[24-26].

We first confirmed their hydrogen bonding in solution using nuclear magnetic resonance (NMR, Extended Data Fig. 1 (a)). HFIP was subsequently used to replace the common inert patch flow (e.g., Ar) during iCVD polymerization of 4VP (Fig. 1 (a)), which led to a growth rate of p4VP film that was 409% that obtained when using Ar under identical conditions (Fig. 1 (b)). (Note the "conditions" here and below refer to deposition parameters that could be independently controlled, including flow rate for each chemical, stage temperature, filament temperature, and total pressure.) As discussed in detail in the section below, that increased deposition rate was likely a result of the vapor-phase hydrogen bonding, which enhanced

surface adsorption of 4VP, the rate-limiting step in iCVD, and increased its reactivity. According to the current mechanistic framework, first established by Lau and Gleason[18,27], surface adsorption of monomer dominates the overall kinetics of polymer growth under the conditions used here.

The p4VP films deposited in the presence of HFIP maintained high purity without detectable presence of HFIP, as demonstrated using Fourier transform infrared spectroscopy (FTIR, Extended Data Fig. 1 (b)). Nearly identical FTIR spectra were observed for the p4VP films deposited using Ar or HFIP, where no C-F signals were observed (e.g., at 1100 cm^{-1}). That high purity was further corroborated using X-ray photoelectron spectroscopy (XPS), which showed no detectable fluorine signal on p4VP films deposited with HFIP or Ar (Extended Data Fig. 1 (c)). As such, the strategy of vapor-phase solvation led to high-purity polymer thin films with much faster growth kinetics[7].

The vapor-phase solvation also greatly expanded the range of attainable molecular weights (Fig. 1 (c)). The molecular weight of conventionally vapor-deposited p4VP, measured with gel-permeation chromatography (GPC), varied in a narrow range of 6 – 8 kDa; whereas replacing Ar with HFIP increased the molecular weights, under otherwise identical conditions, to as high as 44 kDa, representing a 550% increase. The polydispersity index (PDI) fell in the range of 1.5 – 3.0 (Extended Data Fig. 1 (d)), comparable to the previously reported PDI for iCVD polymers[18,28]. We attributed the much-increased molecular weight to (i) the enhanced adsorption and increased surface concentration of 4VP (as discussed above), leading to a greater kinetic chain length[29] (monomer surface concentration has been shown to be proportional to the vapor-phase fractional saturation pressure, i.e., $P_{monomer}/P_{sat}$ (the x-axis in Fig. 1 (c)), as described by the Brunauer–Emmett–Teller (BET) theory[30]); (ii) the electron-withdrawing effect of HFIP[31], hence increasing the reactivity of 4VP. While vapor-phase solvation likely enhanced the adsorption of 4VP, we note that simply increasing the $P_{monomer}/P_{sat}$ (without HFIP) would not achieve the same effect. In an extreme case, we performed conventional iCVD at $P_{monomer}/P_{sat}$ of 1.01 (i.e., under supersaturation conditions) and achieved an overall deposition rate of 18.8 nm/min and a M_n of 27.5 kDa (with a PDI of 2.3). Despite that high monomer concentration (which led to condensation as shown in Extended Data Fig. 2 (a) and (b)), compared to a solvated deposition performed at a similar DR, i.e., 20.4 nm/min, the M_n without solvation was merely 62.5% that with solvation. Furthermore, a visual examination of the wafer coated via the solvated deposition (Figure S6) clearly illustrates that no condensation has occurred, pointing to even higher attainable deposition rates.

To further demonstrate the effect of vapor-phase solvation on the materials properties, we used mechanical strength (measured using nanoindentation) and surface morphology as two examples. First, by replacing Ar with HFIP without changing other deposition conditions, the indentation modulus of p4VP thin films increased from 5.1 GPa to 7.0 GPa, whereas the hardness increased from 0.15 GPa to 0.21 GPa (Fig. 1 (d)). The greater mechanical strength was likely a result of the higher molecular weight, and thus a greater degree of chain entanglement. It is worth noting that this enhancement of mechanical strength was achieved, for the first time, without having to increase the $P_{monomer}/P_{sat}$[17] or to introduce crosslinkers[26]. Second, by increasing the partial pressure of HFIP (P_{HFIP}) without changing the deposition conditions otherwise, the morphology of the film can be tuned from an ultra-smooth surface (with a root-mean-square roughness of 0.26±0.04 nm) to undulations of ~100 nm (Extended

Data Fig. 2 (c)) (although SEM images showed texture-free thin films with and without HFIP, Extended Data Fig. 2 (d) and (e)). That increase of film roughness upon increasing P_{HFIP} is likely a result of solvent-assisted dewetting, which has been well-documented in past reports[19,32,33].

Below, we unravel the fundamental effects of the vapor-phase solvation on surface adsorption and the thermodynamics and kinetics of all-dry polymerization, using a combination of experimental, theoretical, and computational approaches.

Rapid equilibration of the vapor-phase solvation

To capture the vapor-phase complexing in real-time, we monitored the pressure change as 4VP and Ar or HFIP were co-delivered into a vacuum chamber (while keeping the chamber temperature constant). Under the experimental conditions, non-interacting vapor species follow the ideal gas law (Extended Data Fig. 3), deviations from which thus indicate vapor-phase complexing.

While delivering 4VP alone, Ar alone, HFIP alone, or co-delivering 4VP and Ar led to linear increases of the chamber pressure over time (and the chamber pressure under the co-flow corresponded to the sum of the pressures of Ar and 4VP when they were delivered individually into the chamber), co-delivering 4VP and HFIP led to considerable deviations of the measured chamber pressures (P_{real}) from the predictions made based on the idea gas law (P_{idea}) (Fig. 2 (a)), indicating strong interactions between HFIP and 4VP despite the low densities of molecules under the vacuum condition[34,35]. To understand this non-ideal behavior, we defined $\Delta P = P_{ideal} - P_{real}$, and monitored the evolution of ΔP as a function of the vapor-phase composition (Fig. 2 (b)). Interestingly, we observed a linear correlation between ΔP and $P_{4VP} \cdot P_{HFIP}$ (Fig. 2(b)), where $P_{4VP} = P_{4VP,feed} - \Delta P$ and $P_{HFIP} = P_{HFIP,feed} - \Delta P$. That correlation held constant for all flowrates of 4VP and HFIP used. We interpreted that total overlap of $\Delta P - P_{4VP} \cdot P_{HFIP}$ correlations by viewing the vapor-phase solvation as a second-order reaction:

$$4VP(g) + HFIP(g) \rightarrow [4VP \cdots HFIP](g) \quad (1)$$

the equilibrium of which can be described as:

$$\Delta P = P_{4VP \cdots HFIP} = KP_{4VP} \cdot P_{HFIP} \quad (2)$$

where K is the equilibrium constant; $P_{4VP \cdots HFIP}$ is the partial pressure of the 4VP-HFIP vapor complex. Thus, the overlapping $\Delta P - P_{4VP} \cdot P_{HFIP}$ correlation was a result of the rapidly equilibrium of the vapor-phase solvation and the regression slope corresponded to the equilibrium constant, K, estimated as 0.926±0.032 Torr^{-1}. To account for the fractional conversion of 4VP to 4VP-HFIP complex, we define $\xi = \frac{P_{4VP \cdots HFIP}}{P_{4VP}}$. Considering equation (2), ξ becomes: $\xi = \frac{P_{4VP \cdots HFIP}}{P_{4VP}} = KP_{HFIP}$, which is estimated to fall in the range of 4% - 26% under the deposition conditions.

Unprecedented rate laws of polymerization with solvation

That rapid vapor-phase equilibrium in turn led to an unprecedented linear correlation between the rate of polymerization and flow rate of HFIP (F_{HFIP}) (when F_{4VP} was held constant, Fig. 2 (c)). This correlation seemed surprising at first because HFIP does not participate in the polymerization reaction (which is known to occur at the vapor-solid interface[18]). In fact, we

estimated (using the BET isotherm) that the concentration of HFIP at that interface was ~2% that of 4VP due to its high volatility, thus further reducing the likelihood of HFIP's participation in the polymerization.

To understand that unique rate law, we performed a separate series of kinetic studies, where the total flowrate of monomer and solvent was kept constant (F_{total} = 3 sccm) while varying the individual flowrates of 4VP and HFIP or Ar (Fig. 2 (d)). When Ar was used, the DR demonstrated a linear correlation with F_{4VP} (which approximates P_{4VP}/P_{sat}) (Extended Data Fig. 4 (a)), consistent with previously reported results[30]. In contrast, when HFIP was used, the deposition rate demonstrated a non-linear behavior with respect to F_{4VP} or F_P, due to the simultaneous variation of 4VP and HFIP flowrates as both affect deposition kinetics.

To decouple those effects, we defined an acceleration rate (AR): $AR = DR_{HFIP}/DR_{Ar}$, which compares the DR in the presence of HFIP versus Ar under otherwise identical conditions (Fig. 2 (e)). AR exhibited a linear correlation with P_{HFIP} ($AR = 11.98 \times P_{HFIP} + 1$, R^2=0.998), with an identical regression slope for the two disparate sets of data (from Fig. 2 (c) and Fig. 2 (d), respectively). That linear dependence of AR on P_{HFIP} can be understood by treating the aforementioned 4VP-HFIP as a third species, as detailed in "Theoretical derivation of acceleration rate" in supplementary materials. According to that theoretical framework we constructed for the coupled complexing-adsorption-polymerization process, the AR is predicted to linearly depend on P_{HFIP}:

$$AR = 1 + K' P_{HFIP} \quad (3)$$

where K' contains multiple temperature-dependent parameters that are independent of P_{HFIP}. As such, the linear dependence of DR on P_{HFIP} under constant P_{4VP} and T_s and that of AR on P_{HFIP} at varying P_{4VP} and constant T_s became evident. The experimental results in turn validated our theoretical model. Note that equation (3) is applicable to P_M/P_{sat} values up to 0.4, at which the experimentally obtained AR value (i.e., 2.4 using P_{HFIP} of 200 mTorr) closely matched the linear prediction (i.e., AR = 2.4). Higher P_M/P_{sat} values are not feasible because those conditions lead to condensation in the presence of HFIP.

Generalization of vapor-phase solvation to other solvents

The vapor-phase solvation effect was likely generalizable to other hydrogen bond donating solvents, such as alcohols and acids. To elucidate the structure-property relations in solvent selection, we investigated several volatile solvents with molecular dynamics (MD) simulations and with experiments, as detailed below.

The MD simulations of 4VP with three different solvents clearly illustrated the formation of molecular clusters (Fig. 3 (a) to (d), with their cluster formation energy summarized in Fig. 3 (e)). In the absence of solvents, clusters of 4VP emerged (Fig. 3 (a)) with a formation energy of −50.0±10.0 kcal/mol, which was likely a result of combined polar and van der Waals interactions. Substituting half of the 4VP molecules with Ar reduced the cluster formation energy to −0.6±0.7 kcal/mol (Extended Data Fig. 4 (b)). A similar substitution with HFIP led to a cluster formation energy of −104.4±12.1 kcal/mol, corroborating the experimentally observed strong vapor-phase solvation. Replacing HFIP with ethanol (EtOH), a weak Lewis acid, led to a 4VP cluster and excluded EtOH molecules (with the cluster outlined by a red dotted circle in Fig. 3 (b)). The cluster formation energy (−53.9±9.8 kcal/mol) was comparable

to that of 4VP alone (Fig. 3 (e)). Interestingly, solvation of 4VP by a stronger Lewis acid, i.e., AcOH, was only mild (with a cluster formation energy of −62.9±12.9 kcal/mol) as some AcOH molecules failed to participate in solvation and formed dimers instead (highlighted by the red dotted circle in Fig. 3 (c)). Indeed, the dimerization of AcOH is energetically favorable (with an enthalpy of −63.4 kJ/mol[36,37]) compared to solvation (with a hydrogen bonding formation energy of −32.7 kJ/mol[37]). While EtOH, AcOH, and HFIP are all good solvents for 4VP in the liquid phase, their vapor-phase solvation behaviors were disparate.

Guided by the MD simulation results, we explored their solvation behaviors experimentally by measuring ΔP and DR (Fig. 3 (f)). The ΔP values increase from Ar (9 mTorr), to EtOH (38 mTorr), to AcOH (150 mTorr), and to HFIP (188 mTorr) (with total pressure up to ~1 Torr, see Experimental Section for details), thus confirming the trend predicted by the MD simulations. That trend correlated well with their *AR* (Fig. 3 (g)). AcOH and HFIP led to the most significant acceleration (397±19% and 409±9% that of Ar, respectively); whereas the *AR* using EtOH was 108±6%. High-purity films were obtained with undetectable presence of HFIP, AcOH, or EtOH, as demonstrated using FTIR (Extended Data Fig. 1 (b)).

Building upon the strong solvation achieved using AcOH, we performed detailed kinetics studies, like those for HFIP, to reveal its effect on the surface adsorption and polymerization. The deposition kinetics demonstrated a linear dependence on P_{AcOH} (when P_{4VP} was kept unchanged, (Fig. 3 (h)), indicating rapid complexing equilibrium. When varying the flowrates of AcOH and 4VP simultaneously while keeping the total flowrate constant, DR demonstrated non-linearity (Fig. 3 (i)), whereas *AR* scaled linearly with P_{AcOH}, yielding a unifying linear correlation with respect to P_{AcOH} (Fig. 3 (j)): $AR = 14.53 \times P_{AcOH} + 1$ ($R^2 = 0.996$, at the T_s of 23°C). Despite the smaller cluster formation energy of AcOH than HFIP, as the simulations predicted, the *AR* of HFIP and AcOH was nearly identical. To unravel the fundamental mechanisms that led to this discrepancy, we performed additional studies that pointed to their different locations of solvation, as detailed in the section below.

Vapor-phase versus interface solvation

To identify the surface-bound steps during the coupled solvation-adsorption-polymerization process, we measured the apparent (total) activation energy of the surface-bound steps, $E_{a,apparent}$, by performing depositions as T_s was varied. The $E_{a,apparent}$ was then regressed using the Arrhenius Law (see Fig. 4 (a) and the "Definition of apparent activation energy" section in supplementary materials). As such, if a surface-bound solvation process exists, it would lead to a more negative $E_{a,apparent}$ (because of the exothermic solvation step).

The $E_{a,apparent}$ for the iCVD polymerization of 4VP, using Ar as the patch flow, was measured to be ~ −65.0±3.4 kJ/mol (Fig. 4 (b)), consistent with the values reported (61 kJ/mol[38]) for the enthalpy of desorption for styrene (a common surrogate for 4VP). This result also confirmed that the surface adsorption of 4VP was the rate-limiting step. The $E_{a,apparent}$ in the presence of HFIP was measured to be 20.5 kJ/mol greater than that obtained using Ar (Fig. 4 (b)). We attributed that reduced enthalpy of desorption in the presence of HFIP to a new intermediate energy state that corresponded to the vapor-phase complex, $[4VP \cdots HFIP]_{vapor}$. The surface adsorption of complex became the rate-limiting step and dominated $E_{a,apparent}$ (Fig. 4 (c)). An alternative explanation for the increased $E_{a,apparent}$ is that the introduction of HFIP led to a shift from the adsorption-limited regime (with a negative $E_{a,apparent}$) to a reaction-limited

one (with a positive $E_{a,apparent}$), which is unlikely given the electron-withdrawing nature of HFIP. In contrast, AcOH reduced the $E_{a,apparent}$ to −87.1±6.0 kJ/mol, 22.1 kJ/mol lower than that obtained using Ar (Fig. 4 (b)), implying that the solvation (at least partially) occurred at the vapor-solid interface (Fig. 4 (c) and (d)).

We further developed a theoretical model to formulate a quantitative understanding of the vapor-phase versus interface solvation (see Theoretical derivation of apparent activation energy section in supplementary materials). Briefly, we estimated the energy of the vapor-phase complexing of HFIP and 4VP from our experimental data to be 28.3 kJ/mol, which closely matches that of their reported hydrogen bonding energy (−33 kJ/mol[39]), thus confirming their vapor-phase solvation. Similarly, we estimated the energy of interface complexing of 4VP and AcOH from our experimental data to be −31.8 kJ/mol, matching the reported hydrogen bonding energy of −32.7 kJ/mol[37]. We attributed the interface solvation by AcOH to the greater polarity of the solvent and the stabilizing effects at the interface that facilitate the molecular complex formation [40,41].

That greater presence of AcOH at the interface compared to HFIP was corroborated by the reduction of film thickness upon removal of the solvents, which was ~3-8% for HFIP (Extended Data Fig. 5, corresponding to ~3.0-8.1% molar fraction of HFIP in the p4VP film) and ~14-25% for AcOH (corresponding to ~23.3-38.3% molar fraction of AcOH) (Fig. 4 (d)).

Finally, the surface solvation by AcOH versus the vapor-phase solvation by HFIP were demonstrated using MD simulations of the adsorption dynamics (Fig. 4 (e) and (f)). In the presence of HFIP, molecular clusters formed quickly in the vapor phase, followed by their rapid adsorption. In the presence of AcOH, multiple small clusters formed, including AcOH dimers and some 4VP-AcOH complexes. Based on the evolution of the interaction energies of 4VP-HFIP/AcOH and of 4VP-silicon oxide substrate, for the 4VP-HFIP system, solvation and adsorption occurred in two sequential steps (Fig. 4 (g)), whereas for the 4VP-AcOH system, they occurred simultaneously (Fig. 4 (h), as indicated by the simultaneous decrease of the 4VP-AcOH energy and the 4VP-substrate energy). In the first step of the 4VP-HFIP solvation, HFIP complexed with 4VP rapidly in the vapor phase (orange curve in Fig. 4 (g)), reducing the system free energy to ~ −77.0 kcal/mol at 2 ns; in the second step, adsorption of the complex occurred (black curve in Fig. 4 (g)), promoting the 4VP-substrate interaction while releasing HFIP. For 4VP-AcOH, the 4VP-substrate interaction energy stabilized at −122.8±9.3 kcal/mol, ~22 kcal/mol higher than that for HFIP, implying attenuated 4VP-substrate interaction due to the interface solvation (Fig. 4 (h)). As a point of comparison (Extended Data Fig. 6), the interaction energy evolution during the adsorption of 10 4VP and 10 EtOH molecules showed strong exothermic adsorption of 4VP alone, with minimal 4VP-EtOH interactions, confirming minimal to no solvation in that system.

Generalization of solvation to other monomers and substrates

The deposition kinetics of iCVD with solvation were independent of the substrate chemistry, as indicated by the similar deposition rates obtained on four types of substrates, i.e., Si wafer (with a water contact angle of 36.9±1.1°), a carbon-coated substrate (with a water contact angle of 40.8±2.9°), a gold-coated substrate (with a water contact angle of 61.5±2.0°), and a poly(*1H*,*1H*,*2H*,*2H*-perfluorodecyl acrylate) (pPFDA)-coated substrate (with a water contact angle of 121.6±0.2°). The DR of 10.4±0.2 nm/min was observed on all four substrate

during the deposition of 4VP with HFIP (Extended Data Fig. 7). Additionally, AFM images of the p4VP thin films on those substrates (Extended Data Fig. 8) corroborated the attribution of the increased surface roughness that was observed under high P_{HFIP} (Extended Data Fig. 2 (c)) to solvent-assisted dewetting, which often occurs under near- or super-saturation conditions for the solvent. Under the deposition conditions used to collect Extended Data Fig. 8, solvent-assisted dewetting is unlikely to occur, which was confirmed by the similarly flat film morphology observed on the substrates with distinct surface energies.

The solvation strategy could also apply to a broad range of polar monomers bearing hydrogen bond acceptors, such as acrylates, methacrylates, and their derivatives. Here we chose MMA, CHMA, HEMA, DMAEMA and AA because their side chains exhibited a range of varying polarity: a nonpolar group for MMA and CHMA, a weak Lewis base in HEMA (a weak Lewis base), and a strong Lewis base/acid in 4VP, DMAEMA and AA. We also used divinyl benzene (DVB) as a control group to confirm the necessity of hydrogen bonding, which indeed showed similar DR using Ar or HFIP (Fig. 5 (a)). Replacing Ar with HFIP led to *AR* values of 1.06 for MMA, 1.3 for CHMA, 1.4 for HEMA, 1.6 for DMAEMA, and 3.35 for AA, respectively, which correlates well with their polarity[9] (the *AR* of CHMA was likely a result of the carbonyl group and MMA has merely no acceleration effect due to extremely high volatility). Notably, deposition using AA via conventional iCVD has been challenging due to its high volatility (leading to low surface concentration). Introduction of HFIP yielded an AR of 3.35, highlighting the potential of leveraging vapor solvation to overcome the challenges associated highly volatile monomers in adsorption-based CVD methods. This generalizability of the all-dry solvation mirrors its solution-phase counterparts. In fact, a large number of reports on solution polymerization have shown that using HFIP as a solvent can significantly accelerate the kinetics of free radical polymerization for polar monomers through strong hydrogen bonding[42-44]. Similar acceleration effects have not been reported for AcOH in the solution phase, which is another supporting evidence for the unique interface solvation uncovered in this report, which requires a vapor-solid interface (that is absent in solution polymerization).

The solvation engineering approach presents many distinct advantages over traditional all-dry polymerization or solution-based polymerization (Fig. 5 (b)). The straightforward one-step synthesis and the greatly accelerated DR could increase the efficiency of functional polymer coating synthesis by several orders of magnitude (e.g., compared with conventional solution synthesis and spin-coating)[7]. The shortened synthesis time and enhanced surface adsorption of monomers in turn improve monomer utilization efficiency compared to conventional CVD approaches. The expanded range of achievable molecular weights and improved tunability could enable thin-film material properties that were previously inaccessible, such as enhanced hardness without introducing chemical crosslinking (Fig. 5 (b)) or tunable thin-film morphologies (Extended Data Fig. 2(c)). Importantly, only a small amount of solvent is used, which does not require separate purification steps. The drastic reduction of solvent usage delivers the benefits of solvent engineering while maintaining the environmental friendliness of vacuum-based synthesis techniques. By careful selection of the solvent species, solvation could be directed towards the vapor phase or the vapor-solid interface, pointing to a new field of solvation engineering to control a much broader range of materials properties (e.g., porosity).

Conclusion

We developed a solvation engineering strategy and demonstrated its generalizability in terms of solvent and monomer selections. It represents a new degree of freedom that can be leveraged to control polymerization kinetics and materials properties. Our study provided the first evidence of interface solvation by AcOH and provided detailed molecular-level understanding of the vapor-phase versus interface solvation. The methodologies developed here are transferrable to tuning the microenvironment during non-equilibrium physicochemical processes. Solvation engineering is a novel, facile, and effective strategy to control polymerization kinetics, temperature-dependence, and material properties (e.g., molecular weight, surface morphology, mechanical properties) in all-dry polymerization, potentially accelerating agile manufacturing of polymer thin films and speed up their deployment in a broad range of industries. The theoretical framework we established in this report could serve as the foundation for future investigations into a greater variety of solvent-monomer pairs, hence considerably broadening the palette of CVD polymers and their properties and applications. While we focus on hydrogen-bonding-enabled solvation in this report, a vast design space remains to be explored, including ionization-mediated solvation, which will be an important topic in our future investigations.

Materials and Methods

Initiated chemical vapor deposition (iCVD). All the polymeric thin films were synthesized using iCVD in a custom-built vacuum reactor (Sharon Vacuum Co Inc., Brockton, MA, USA). Thermal activation of the initiator was provided by resistively heating a 0.5 mm nickel/chromium filament (80% Ni/ 20% Cr, Goodfellow) mounted as a parallel filament array. Filament temperature was measured using a thermocouple attached to it. The deposition stage that was kept at desired substrate temperatures using a chiller. The vertical distance between the filament array and the stage was 2 cm. Depositions were performed on Si wafers (P/Boron<100>, Purewafer). Initiator (tert-butyl peroxide (TBPO, Sigma-Aldrich, 98%)), monomers (4-vinyl pyridine (4VP, Sigma-Aldrich, 95%), divinylbenzene (DVB, Sigma-Aldrich, 80%), cyclohexyl methacrylate (CHMA, Sigma-Aldrich, 99%), 2-hydroxyethyl methacrylate (HEMA, Sigma-Aldrich, 98%), 2-(dimethylamino)ethyl methacrylate (DMAEMA, Sigma-Aldrich, 98%)) and patch flow (Argon (Ar, Airgas), ethanol (EtOH, Sigma-Aldrich, 99.8%), Acetic acid (AcOH, Sigma-Aldrich, 99%), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, Sigma-Aldrich, 99%)) were used without further purification. During iCVD, 0.6 sccm TBPO was introduced to the reactor at room temperature through a mass flow controller for all the depositions. Monomers and patch flow were heated to desired temperatures (room temperature for EtOH, AcOH, HFIP; 60°C for 4VP, DVB, DMAEMA; 70°C for CHMA, HEMA) in their respective glass jars to create sufficient pressure to drive the vapor delivery into the vacuum chamber.

For all depositions, the chamber pressure was kept at 500 mTorr and the filament array temperature was set to 230°C unless otherwise stated. For the molecular weight series, 1.5 sccm of 4VP, 1.5 sccm of Ar or HFIP and 0.6 sccm of TBPO were simultaneously introduced into the reactor. Stage temperature, controlled by a cooling circulator, was set to 30, 20, 10, and 0°C, and monitored using a thermocouple attached to the stage. For the 4VP/Ar and 4VP/HFIP series, the total flow rate was kept at 3.6 sccm, with 0.6 sccm TBPO, (0.5+0.5×x) sccm 4VP, (2.5−0.5×x) sccm Ar, and (2.5−0.5×x) sccm HFIP, where x=0, 1, 2, 3, 4, 5. The step change in

flowrates was 0.5 sccm for all series, corresponding to a 70 mTorr change in the partial pressure of the species of interest. For the AcOH series, all conditions were kept identical as the HFIP series. For the monomer series, the stage was kept at 30℃ to prevent monomer condensation for CHMA, HEMA and DMAEMA and at 15℃ to enhance monomer adsorption of MMA and AA. The following flowrates were used for each monomer: (i) 1.5 sccm DVB, 1.5 sccm HFIP or Ar, 0.6 sccm TBPO; (ii) 1.5 sccm MMA, 1.5 sccm HFIP, 0.6 sccm TBPO P_{total}=1 Torr; 0.5 sccm CHMA, 1.5 sccm Ar, 1 sccm HFIP. HEMA: 0.5 sccm of HEMA, 1.5 sccm of Ar, 1 sccm of HFIP. DMAEMA: 1.5 sccm of DMAEMA, 0.5 sccm of Ar, 1 sccm of HFIP; 1.5 sccm AA, 1.5 sccm HFIP, 0.6 sccm TBPO. For deposition at high P_M/P_{sat} of 0.4, the deposition conditions are as below: 4VP of 3.4 sccm, Ar or HFIP of 1 sccm, TBPO of 0.6 sccm, total pressure of 1000 mTorr.

In situ interferometry with a HeNe laser source (wavelength = 633 nm, JDS Uniphase) was used to monitor the film growth on a Si substrate. A more accurate film thickness on the Si wafer substrates was measured post-deposition using a J. A. Woollam Alpha-SE spectroscopic ellipsometry at three different incidence angles (65°, 70°, 75°).

Non-ideality assessment. The measurement was conducted in the customized vacuum chamber described above. The monomer and patch flow were introduced into the vacuum chamber as flowrates specified above. The total flowrate was maintained at 3 sccm. The chamber pressure was measured using a Baratron (0-2 Torr, MKS) every 2 seconds. Each flow condition was measured at least twice to perform statistical analyses on the results.

Materials characterization. Fourier transform infrared (FTIR) measurements were performed on a Bruker Vertex V80v vacuum FTIR system in transmission mode. A deuterated triglycine sulfate (DTGS) KBr detector over the rage of 400−4000 cm^{-1} was used with a resolution of 4 cm^{-1}. The measurements were averaged over 128 scans to obtain a sufficient signal-to-noise ratio. All the spectra were baseline corrected by subtracting a background spectrum of Si.

During XPS, samples were analyzed using a Surface Science Instruments SSX-100 ESCA Spectrometer with operating pressure ca. $1x10^{-9}$ Torr. Monochromatic Al Kα x rays (1486.6 eV) with photoelectrons collected from an 800-μm-diameter area. Photoelectrons were collected at a 55° emission angle with source to analyzer angle of 70°. A hemispherical analyzer determined electron kinetic energy, using a pass energy of 150 eV for wide/survey scans. All the samples were stored under vacuum at room temperature for a week before XPS analysis.

Surface roughness and topography was measured using an Asylum Research MFP-3D-BIO AFM. Scans were recorded across 5 x 5 μm or 10 x 10 μm regions at 1.0 Hz in AC-air tapping mode.

The SEM images and elemental mapping were obtained using Zeiss Gemini 500 with an acceleration voltage of 1 or 3 kV. Gold was sputter coated onto all samples prior to imaging.

The NMR spectra were obtained using a Bruker AV500. In preparation for NMR, 2% (volume fraction) 4VP and/or HFIP was dissolved in 600 μL chloroform-d (Aldrich, 99.9%) for ^1H analysis.

Molecular weight of the as-deposited polymer films was characterized by gel permeation

chromatography (GPC) (Waters) equipped with a Waters 410 differential refractive index detector. N, N-dimethylformamide (DMF) was used as the eluent at room temperature.

Nanoindentation was performed using a Berkovich indenter tip (TI-900 Triboindenter, Bruker, Eden Prairie, MN) calibrated to a silica glass standard. A constant max depth test of 150 nm was performed in displacement-controlled mode. Hardness (H) and reduced modulus (Er) were determined from the force vs. displacement curves of each indentation using the following relations:

$$H = \frac{P_{max}}{A_c}, E_r = \frac{S\sqrt{\pi}}{2\sqrt{A_c}}$$

for which S is the contact stiffness (the slope of the load-displacement curve upon initial unloading) and Ac is the projected contact area of the indentation.

Fully atomistic molecular simulation setup. All simulations were performed in the open-source NAMD 2.13 molecular dynamics software[45] using the most recent version of the CHARMM36m forcefield[46]. The molecular structures for 4VP and patch flow were constructed with the Avogradro software[47]. The parameters were obtained from the CHARMM General force field (CGenFF)[48]. The amorphous silica substrate structures and parameters were obtained from the INTERFACE forcefield[49]. The full models for each system were generated and visualized using PACKMOL[50] and Visual Molecular Dynamics (VMD)[51]. Each system consisted of 10 4VP molecules and 10 carrier gas molecules. After initial energy minimization using the conjugate gradient algorithm[45], the simulations were ran for 10 ns each at a temperature of 303.15 K using the canonical (NVT) ensemble. The timestep was set to 2 fs. GROMACS analysis tools[52] and in-house Python scripts were used for post-processing and plotting the figures.

Data availability: All data needed to evaluate the conclusions in the paper are presented in the paper and/or the Supplementary Materials.

Code availability: NAMD is free and open-source code available at https://www.ks.uiuc.edu/Research/namd/. Data processing scripts are available upon request from the authors. The code for data processing could be found following the DOI of 10.24435/materialscloud:1k-qd.

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Author contributions: P.C., R.Y., J.Y., Z.Z., Z.R. and S.B. designed the research and experiments. P.C., Z.Z. conducted the depositions and characterizations. J.Y. conducted all-

atom MD simulation. Z.R. and S.B. supported the nanoindentation experiments. P.C., R.Y., and J.Y. performed the data analysis. P.C. and R.Y. drafted the manuscript. All authors provided critical feedback on experimental design and data analysis and reviewed the manuscript.

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Figure legends

Figure 1. The strategy of vapor-phase solvation to control polymer deposition kinetics, molecular weight, and film mechanical properties.

(a) Schematic illustration of the mechanism of solvation-enhanced polymerization in iCVD. (b) Enhanced rate of polymerization of 4VP by replacing Ar (inert gas) with HFIP (vaporized solvent), while keeping the deposition conditions unchanged otherwise. (c) Molecular weight of p4VP deposited using iCVD, which was tunable in a much broader range, by replacing Ar with HFIP. (d) Improved hardness and indentation modulus of the p4VP films by replacing Ar with HFIP, while keeping the deposition conditions unchanged otherwise. Colum in (b) and center in (d) represent average values. Error bars represent standard deviations (N=3 for (b); 100 for (d)).

Figure 2. Rapid equilibrium of the vapor-phase solvation and the linear correlation between deposition kinetics and solvent partial pressure, P_{HFIP}. (a) Chamber pressure deviated from the predictions based on the ideal gas law when vapors of 4VP and HFIP were co-delivered into the reactor, hinting at vapor-phase solvation. (b) The dependence of ΔP, i.e., the difference between the experimentally measured pressure and the predictions based on the ideal gas law, on P_{4VP} P_{HFIP} (i.e., the product of the partial pressures) was nearly identical at different vapor compositions (while keeping the total flow rate constant), implying that a constant equilibrium constant (i.e., $K = \Delta P/P_{4VP}P_{HFIP}$ was held under these conditions and hinting at the rapid equilibrium of vapor-phase solvation. (c) Dependence of the deposition rate on F_{HFIP} under fixed F_{4VP} of 1 sccm, demonstrating an unanticipated linear correlation between the deposition rate and the nonreactive species, HFIP. (d) Deposition rate decreased linearly as the flow rate of Ar increased (grey curve), while keeping the total chamber pressure constant at 500 mTorr and total flow rate at 3.6 sccm (hence decreasing F_{4VP}), whereas the rate demonstrated a non-linear dependence with respect to F_{HFIP} (orange curve) under similar conditions. The x-axis represents the flow rate of the patch flow, F_P, i.e., F_{Ar} or F_{HFIP}. (e) The acceleration rate as a function of P_{HFIP}, plotted using data from panels (c) and (d). The acceleration rate, defined as the ratio of the iCVD deposition with solvation to that without solvation under the same monomer flow rate, initiator flow rate, total flow rate, total pressure and temperature setting, increased linearly with P_P. Error bars represent standard deviations (N=3 for (c) and (d)).

Figure 3. Generalization of the vapor-phase solvation to other Lewis acids (a-d) Snapshots of the MD simulations of the following stable vapor-phase molecular clusters: (a) 20 4VP molecules, showing interactions among the 4VP molecules; (b) 10-10 4VP-EtOH, showing segregated clusters of 4VP (inside the red dotted circle) surrounded by the weak Lewis acid EtOH; (c) 10-10 4VP-AcOH, showing dimerization of AcOH (inside the dotted circle); and (d) 10-10 4VP-HFIP, showing homogeneous solvation. (e) The formation energy

of the molecular clusters, calculated from the MD simulations. (f) Experimentally measured ΔP when 4VP monomer (at the flow rate of 1 sccm) was co-delivered with the aforementioned vapors (at the flow rate of 2 sccm). (g) Experimentally measured rates of iCVD deposition when 4VP was polymerized in the presence of the aforementioned vapors, while keeping the deposition conditions unchanged otherwise. (h) Dependence of the deposition rate on F_{AcOH} under fixed F_{4VP} of 1 sccm, demonstrating a linear correlation between the deposition rate and the vaporized solvent, AcOH. (i) Deposition rate decreased linearly as P_{Ar} increased (grey curve), while keeping the total chamber pressure constant at 500 mTorr and total flow rate at 3.6 sccm (hence decreasing F_{4VP}), whereas the rate demonstrated a non-linear dependence with respect to the F_{AcOH} (orange curve) under similar conditions. The acceleration rate increased linearly with F_P (denotes F_{Ar} or F_{AcOH}). (j) The acceleration rate as a function of P_{AcOH}, plotted using data from panels (h) and (i). Error bars represent standard deviations, which were calculated using the MD simulation results over 10 ns in (e) and obtained experimentally otherwise (N=3 for (g) and (i)).

Figure 4. Vapor-phase solvation by HFIP and interface solvation by AcOH. (a) The Arrhenius plot for the iCVD polymerization of 4VP, using Ar, AcOH, and HFIP as the patch flow respectively, revealed distinct temperature dependence under the three different solvation regimes. (b) The apparent activation energy for the three solvation regimes, derived from data in (a), hinting at the distinct locations for solvation under each regime. Squares represent fitted apparent activation energy and error bars represent the standard deviation of the residuals. (c) Illustration of the relative positions of the energy states during the coupled solvation-adsorption process, where vapor-phase (denoted by "g" for gas) solvation drives the 4VP-HFIP complexing, and interface (denoted by "a" for adsorbed) solvation drives the 4VP-AcOH complexing. (d) Schematic illustration of the deposition process using vapor complexing solvent and interface complexing solvent as the patch flow. (e-f) Snapshots of the MD-simulated adsorption dynamics for 4VP-HFIP and 4VP-AcOH complexes onto amorphous SiO_2 substrates. The time interval between adjacent images is 1 ns. (g-h) The time-evolution of the system's enthalpy for (g) 4VP-HFIP and (h) 4VP-AcOH during the solvation-adsorption process, which captures the dynamics of the simultaneous interactions of 4VP-solvent and 4VP-SiO_2 substrate.

Figure 5. Universality of solvation engineering in iCVD. (a) The deposition rate and acceleration rate of DVB, MMA, CHMA, HEMA, DMAEMA, AA and 4VP with and without vapor-phase solvation, obtained by using HFIP and Ar as the patch flow, respectively. Vapor phase solvation is universal among polar monomers. Acceleration rate was denoted by the square box. (b) Radar plots comparing common methods for polymer thin film synthesis and processing, including the vapor-solvation-enhanced iCVD (s-iCVD reported here), traditional iCVD, and solution-based polymer coating methods, in terms of their compatibility with large libraries of monomers bearing functional moieties (indicated by "Universality"), efficiency (indicated by "1/Process Time"), versatility (indicated by the tunability in "Mw", i.e., molecular weight and "Morphology"), and environmental friendliness (indicated by "Monomer Utility" fraction and "1/Solvent Amount") to highlight the advantages of the reported approach.

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Supplementary Discussion

Supplementary Discussion

Theoretical derivation of acceleration rate (*AR*)

Under typical iCVD conditions, the BET isotherm can be written as:

$$[M]_{M,surf} = \frac{\rho_M}{MW_M} \times c \times P_M/P_{M,sat} \quad (1)$$

where $[M]_{surf}$ (mol/m^3) is the concentration of surface-adsorbed monomers; ρ_M is density of liquid monomer; MW_M is the molecular weight of monomer; c is the BET constant that describes the enthalpy of a monolayer physisorption. Assuming that the enthalpy of desorption for the first layer (ΔH_{des}) is independent of temperature and much greater than that of the second or subsequent layers, the BET constant could be written as:

$$c \sim \exp\left[\frac{\Delta H_{des} - \Delta H_{vap}}{RT_s}\right] \quad (2)$$

where T_s is the stage temperature in iCVD; R is the ideal gas constant (8.314 [J/mol K]); ΔH_{des} and ΔH_{vap} are the enthalpy of desorption and the heat of vaporization, respectively. If we assume disproportionation or recombination as the main termination mechanisms, the rate of iCVD polymerization, Rp is thus proportional to $P_M/P_{M,sat}$ under constant stage temperature, as we demonstrated in Extended Data Fig. 2 (c).

By considering the vapor-phase complex as a species, we could apply the BET isotherm to the complex as follows:

$$[M]_{C,surf} = \frac{\rho_C}{MW_C} \times c_C \times P_C/P_{C,sat} \quad (3)$$

where $[M]_{C,surf}$ (mol/m^3) is the concentration of surface-adsorbed complex; ρ_C is density of complex in liquid phase; MW_C is the molar mass of the complex; c_C is the BET constant for the complex. As a result, the rate of iCVD polymerization became:

$$Rp = k_1[M]_{M,surf} + k_2[M]_{C,surf} = \frac{\rho_M}{MW_M} k_1 c_M P_{M,sat}^{-1} P_M + \frac{\rho_C}{MW_C} k_2 c_C P_{C,sat}^{-1} P_C \quad (4)$$

which became the following by plugging in $\Delta P = P_C = KP_{4VP} \cdot P_{HFIP}$:

$$Rp = \frac{\rho_{4VP}}{MW_{4VP}} k_1 c_{4VP} P_{4VP,sat}^{-1} P_{4VP} + \frac{\rho_C}{MW_C} k_2 c_C P_{C,sat}^{-1} K P_{4VP} P_{HFIP} \quad (5)$$

where k_1 and k_2 represent overall rate constants that contain a series of fundamental kinetic constants involving chain initiation, chain growth and chain termination. Note that the rate constants for bimolecular reactions are pressure-dependent, especially under low pressure, which may be the case for the vapor-phase complexing. Nevertheless, that potentially pressure-dependent rate constant for vapor-phase complexing is unlikely to impact the rate law. As shown in Equation (5), the rate law captures the overall rate of polymer growth at the vapor-solid interface, during which the vapor-phase complexing is under rapid equilibrium and thus not the rate-determining. Furthermore, depositions of 4VP were performed strictly at the total pressure of 500 mTorr, eliminating any possible effect of pressure. The overall rate constants also follow the Arrhenius relation:

$$k_n = A_n \exp\left(-\frac{E_{a,n}}{RT_s}\right), n = 1, 2 \quad (6)$$

where A_n is the pre-exponential factor, depicting the collision frequency between reactive molecules; $E_{a,n}$ is the apparent activation energy.

Deposition rate, *DR,* can be calculated using *Rp*, as follow:

$$DR = \frac{h_{ml} MW_{4VP} Rp}{\rho_{p4VP}} \quad (7)$$

where h_{ml} is monolayer thickness; ρ_{4VP} is the density of p4VP. Thus, AR can thus be calculated as:

$$AR = \frac{DR(P_{HFIP})}{DR(0)} = \frac{\frac{\rho_{4VP}}{MW_{4VP}} k_1 c_{4VP} P_{4VP,sat}^{-1} P_{4VP} + \frac{\rho_C}{MW_C} k_2 c_C P_{C,sat}^{-1} K P_{4VP} P_{HFIP}}{\frac{\rho_{4VP}}{MW_{4VP}} k_1 c_{4VP} P_{4VP,sat}^{-1} P_{4VP}} = 1 + \frac{K^* \xi}{1+\xi} \approx 1 + K' \; {}_{HFIP} \quad (8)$$

because $1+\xi \approx 1$ and $K' = \left(\frac{\frac{\rho_C}{MW_C} k_2 c_C P_{C,sat}^{-1}}{\frac{\rho_{4VP}}{MW_{4VP}} k_1 c_{4VP} P_{4VP,sat}^{-1}} - 1 \right) K$. K' involves multiple parameters that is associated with inherent properties of molecules and temperature-dependent parameters.

The colored terms represent the properties of monomer and complex that determine the acceleration effect and thus should be used to guide the selection of monomer and solvent. Significance of those color-coded properties is discussed individually below.

1) Molecular weight (MW) of monomer and complex. Based on Equation (8), higher $MW_{monomer}$ and lower $MW_{solvent}$ lead to greater acceleration effect, provided that all other properties remain unchanged (which is extremely unlikely).

2) Overall rate constant of the iCVD polymerization for monomer alone (k_1) and complex (k_2), which captures the effect of complexation on reactivity. For monomers like 4VP and solvents like HFIP or AcOH, solvation decreases the electron density on the vinyl bond, hence rendering $k_2 > k_1$. However, reactivity of a monomer-solvent complex is hard to predict using classical theories. In the extreme case where a solvent ionizes the monomer (e.g., for a strong enough pair of acid and base), even the reaction mechanism would be modified.

3) BET constant (c) and saturation pressures ($P_{M,sat}$ and $P_{C,sat}$). Although a correlation (e.g., from group contribution method) to predict the $P_{C,sat}$ would be useful, the accuracy of such an approach might be limited in this case. Using the molecular properties predicted based on the Joback Group Contribution Method, the saturation pressure (at 25°C) for 4VP•••HFIP is estimated to be 3 mTorr. However, a deposition performed at P_{4VP} = 208 mTorr and P_{HFIP} = 208 mTorr (and thus P_c much greater than 3 mTorr, the predicted saturation pressure) led to no visible condensation, as shown in Extended Data Fig. 2 (a) and (b). We thus resorted to the all-atom MD simulation for assessments of the complexing propensity.

4) Equilibrium constant, K, for solvation. Strong interactions between monomer and vapor solvent leads to a high K value, further amplifying the enhanced adsorption and modified reactivity. A quantitative estimate for K can be obtained by simulation.

Definition of apparent activation energy ($E_{a,apparent}$)

$$k = A \cdot \exp\left(-\frac{E_{a,apparent}}{R \cdot T_{stage}} \right) \quad (9)$$

where k is the apparent rate constant of iCVD, which describes the overall effect of the surface-bound kinetic processes, including surface solvation, adsorption, and surface polymerization; and $E_{a,apparent}$ is the apparent activation energy of surface-bound processes.

Theoretical derivation of apparent activation energy (AR)

Below, we describe a physics-based theoretical model to formulate a quantitative understanding of the experimentally obtained apparent activation energies. We start by expressing the saturation pressures (e.g., $P_{4VP,sat}$) in the form of the Clausius-Clapeyron equation:

$$P_{sat} \sim exp\left(-\frac{\Delta H_{vap}}{RT_s}\right) \quad (10)$$

where ΔH_{vap}, R, and T_s have been defined previously. Assuming again that the surface adsorption is the rate-limiting step in iCVD polymerization, we could combine equations (2) and (8) to obtain an expression for K' as a function of T_s (by considering the adsorption of molecular complex term):

For vapor solvation, $-\Delta H_{C,form}^{inter}$ is negligible and K is not affected by T_s. Therefore K' can be expressed as:

$$K' \sim \exp\left(\frac{\Delta H_{C,des} - \Delta H_{4VP,des}}{RT_s}\right) \quad (11a)$$

For interfacial solvation, K is affected by T_s, which is described by $\Delta H_{C,form}^{inter}$, as shown below:

$$K' \sim \exp\left(\frac{\Delta H_{C,des} - \Delta H_{4VP,des} - \Delta H_{C,form}^{inter}}{RT_s}\right) \quad (11b)"$$

$$\Delta H_{C,des} = \Delta H_{4VP,des} + \Delta H_{C,form}^{vapor} - \Delta H_{C,form}^{inter} \quad (12)$$

where $\Delta H_{C,form}^{vapor}$ is the enthalpy of the molecular complex forming in the vapor phase and $\Delta H_{C,form}^{inter}$ is the enthalpy of molecular complex forming at the interface. The heat of desorption for the complex [in equation (12)] was calculated using the Hess's Law and by making the key assumption that desorption of the molecular complex can be broken down into three steps (Extended Data Fig. 9):

1) dissociation of the molecular complex (at the solid surface) into 4VP(ad) and HFIP(g), with the enthalpy of $-\Delta H_{C,form}^{inter}$;

2) desorption of the dissociation product, i.e., 4VP(ad), with the enthalpy of $\Delta H_{4VP,des}$;

3) vapor-phase complexation of 4VP and HFIP, with the enthalpy change of $\Delta H_{C,form}^{vapor}$.

We thus arrive at Equation (12): $\Delta H_{C,des} = \Delta H_{4VP,des} + \Delta H_{C,form}^{vapor} - \Delta H_{C,form}^{inter}(12)$.

Thus, the activation energy of K' can be written as:

$K' \sim \exp\left(-\frac{E_{a,K'}}{RT_s}\right) = \exp\left(\frac{\Delta H_{C,form}^{vapor}}{RT_s}\right)$ for vapor solvation and $K' \sim \exp\left(-\frac{E_{a,K'}}{RT_s}\right) = \exp\left(-\frac{\Delta H_{C,form}^{inter} - \Delta H_{C,form}^{vapor} + \Delta H_{C,form}^{inter}}{RT_s}\right)$ for interface solvation.

Thus, for vapor solvation:

$$E_{a,K'} = -\Delta H_{C,form}^{vapor} \quad (13a)$$

and for interface solvation

$$E_{a,K'} = 2\Delta H_{C,form}^{inter} - \Delta H_{C,form}^{vapor} \approx \Delta H_{C,form}^{inter} \quad (13b)$$

where $E_{a,K'}$ is the apparent activation energy corresponding to the AR. Therefore, for a vapor-phase-solvation-dominated process, $\Delta H_{C,form}^{vapor}$ dominated the activation energy, thus, $E_{a,K'} > 0$. Conversely, for an interface-solvation-dominated process, $\Delta H_{C,form}^{inter}$ dominated the activation energy, thus, $E_{a,K'} < 0$. The value of $E_{a,K'}$ should fall between $-\Delta H_{C,form}$ to $\Delta H_{C,form}$"

The disparate effects of P_P and T_s on AR were highlighted by mapping experimental data points onto a 3D space with the corresponding contour plots shown in Extended Data Fig. 10. The data was fitted using equation (8) and (13). The fidelity of the regression was confirmed by performing a linear correlation between the experimental AR and predicted AR. The high correlation coefficients (R^2=0.94 for HFIP and R^2=0.86 for AcOH) indicate that the established kinetic model accurately predicts the deposition kinetics with respect to T_s and P_P.

The AR of HFIP exhibited a positive $E_{a,K'}$ of 28.3 kJ/mol, indicating that higher stage temperatures lead to greater acceleration effects. Based on equation (13), this $E_{a,K'}$ reflects $-\Delta H_{C,form}^{vapor}$, i.e., the energy of molecular complex formation in the vapor phase. In contrast, the AR of AcOH was associated with a negative $E_{a,K'}$ of −31.8 kJ/mol, indicating more favorable acceleration effects at lower stage temperatures. These observations further validate our theoretical model that deconvolutes solvation, adsorption, and polymerization to understand the acceleration effects of iCVD with solvation.

Benchmarks and Definitions of Indicators used in Figure 5 (b)

One of our benchmarks for comparison, i.e., traditional iCVD, refers to the iCVD of polymer thin films using monomer(s), an inert patch flow (e.g., Ar), and an initiator, thus excluding other iCVD variants (e.g., iCVD into liquid substrates and condensed-phase iCVD polymerization). The other benchmark, i.e., solution-based methods, refers to the entire process of synthesis, purification, coating, and other necessary processing steps to yield a polymer thin film from monomer(s). Those solution-based methods are typified by spin-coating below.

"Monomer Utility" refers to the rate of conversion of a monomer to its polymer film (excluding any monomer recycling steps). During the iCVD with solvation, we estimate the monomer utility rate to be 4.5-11.2% (calculated using the deposition rate divided by flow rate and further calibrated using polymer density, monomer molar mass and chamber size), whereas in traditional iCVD, we estimate the monomer utility rate to be 0.8-4.2%. Solution-based polymerization usually have a high yield ranging from 30% to 95%, with a purification yield of 80%-90%. Based on a generic spin-coating protocol (e.g., 20 µl polymer solution with the concentration of 1-5wt% per 1 cm^2 coating area), the monomer utility in the coating step ranges from 0.5% to 5%, with thick films (hundreds of nanometers) leading to higher monomer utility rates. Therefore, the overall monomer utility can range from 0.1% to 4% for spin coating. Ranking: s-iCVD>iCVD>solution-based methods.

"MW" refers to the attainable MW for a particular monomer (e.g., 4VP). For s-iCVD of p4VP, the attainable MW ranges from several kDa to tens of kDa, whereas traditional iCVD of p4VP typically leads to MW below 10 kDa shown by our data. Solution-based synthesis methods could also yield p4VP with MW up to tens of kDa (hence scoring 3/3 on the spider plot). Ranking: solution-based methods>s-iCVD>iCVD.

"Morphology" refers to the controllability over the polymer thin film morphology. In s-iCVD, the film morphology could be adjusted from ultra-smoothness to undulations, as shown in Extended Data Fig. 4, whereas traditional iCVD usually leads to ultra-smooth and conformal coatings. Solution-based coating methods hardly have any control over the film morphology without leveraging additional control measures (such as patterns of surface energy). Ranking: s-iCVD>iCVD>solution-based method.

"Solvent Amount" refers to the amount of solvent used in the entire process of turning a monomer into its polymer film. For s-iCVD, the solvent-to-monomer ratio is typically 0-2, whereas traditional iCVD does not require any solvent. Solution-based methods typically use a solvent-to-monomer ratio of ~10 during polymer synthesis and purification and of 20-100 for coating formation (e.g., in spin-coating), leading to an overall solvent-to-monomer ratio of 200-1000. Ranking for "1/Solvent

Amount": s-iCVD>iCVD>solution-based method.

"Universality" of a method refers to its applicability to different monomers. For s-iCVD, we demonstrated that solvation is generalizable to other polar monomers, which nearly overlaps with the monomer library for traditional iCVD. Traditional iCVD uses monomers that are compatible with free-radical polymerization and have suitable volatility. Solution-based synthesis methods are compatible with a large variety of functional monomers, but the coating/processing of certain polymers (e.g., fluorinated hydrophobic polymers) may be challenging. Ranking: solution-based method>s-iCVD≈iCVD."

"Process Time" refers to the time required to produce a polymer thin film starting from its monomer. For s-iCVD, a typical deposition takes merely tens of minutes, whereas traditional iCVD may take a few hours. Solution-based method could take several days. Taking spin-coating for example, a typical polymer synthesis takes hours to days to complete; purification takes several hours (e.g., to remove a catalyst, solvent etc.); as-obtained polymer often needs to be further dissolved at an appropriate concentration for spin-coating; the coating step itself takes a few minutes to a few hours. As a result, solution-based methods typically span multiple days. Ranking for "1/Process Time": s-iCVD>iCVD>solution-based methods.