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Solid-Phase Radical Polymerization of Halogen Bonding-Based Crystals and Applications to Pre-Shaped Polymer Materials

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Abstract: Liquid vinyl monomers were converted to solid crystals via halogen bonding and underwent solid-phase radical polymerizations through heating at 40 °C or ultraviolet photo-irradiation (250–385 nm). The X-ray crystallography analysis showed the high degree of monomer alignment in the crystals. The polymerizations of the solid monomer crystals yielded polymers with high molecular weights and relatively low dispersities because of the high degree of the monomer alignment in the crystal. As a unique application of this system, the crystalized monomers were assembled to pre-determined structures, followed by solid-phase polymerization, to obtain a two-layer polymer sheet and a three-dimensional house-shaped polymer material. The two-layer sheet contained a unique asymmetric pore structure and exhibited a solvent-responsive shape memory property and may find applications to asymmetric membranes and polymer actuators.

Solid-phase polymerization (SPP) is a technique to polymerize solid monomers or monomer (co)crystals. SPP has attracted interest in step-growth polymerization for synthesizing, e.g., polyamides and polyesters, since the 1960s and generally yields polymers with high molecular weights.^[1,2]

The emergence of crystal engineering broadens the horizon in creating crystal lattices of monomers.^[3–7] Several noncovalent interactions such as hydrogen bonding, π - π stacking, and host-guest interaction have been used to build monomer crystals, which was combined with topochemical reactions such as [2+2] cycloaddition^[8–11] and 1,4-addition of diacetylenes,^[12–17] enabling topochemical SPP.^[18–20] However, the special design and synthesis of the monomers required for topochemical SPP poses a limitation of the narrow monomer scope.

Free radical polymerization is robust and widely used to synthesize polymers from a variety of vinyl monomers. In this polymerization, the generated propagating radicals (polymer*) are highly reactive for propagation and termination. In solution, termination occurs randomly, leading to poor control in the molecular weight and broad molecular weight distribution (Figure 1A). Free radical polymerization was also used in SPP to polymerize acrylamides, acrylates, and methacrylates.^[21–26] So far, hydrogen bonding has been mainly used to create the monomer crystals. Also, high-energy ultraviolet or γ -ray irradiation has been used to initiate the polymerization in many cases.^[21–23] An SPP system that is amenable to other vinyl monomers (without hydrogen bonding functionalities) and uses a mild polymerization condition is desirable to expand the applications but is still challenging.

Herein, we report free-radical SPP of vinyl monomers using halogen bonding (Figure 1B). Halogen bonding was used for topochemical SPP but has not been used for free-radical SPP.^[27,28] (In the present paper, we refer to topochemical SPP, when the new bond formation occurs at the topochemical distance and hence the crystal lattice is unchanged (the tacticity

is regulated) via the polymerization. Generally, free-radical SPP would not meet this condition in a strict sense.) Halogen bonding ($R-X\cdots Y$) is a noncovalent bonding between an electron-accepting halogen (X) and an electron-donating group (Y).^[29–33] Halogen bonding is a directional 180° interaction and the strength increases in the order of $R-F \ll R-Cl < R-Br < R-I$. We use vinyl monomers (**1–7** (Figure 2)) containing Y and 1,4-diiodotetrafluorobenzene (**1**-C₆F₄-I, **8** (Figure 2)) containing iodine atoms for X to generate co-crystals. I-C₆F₄-I was chosen because iodine forms the strongest halogen bonds compared to the other halogens and the diiodide structure can bridge two monomers (Figure 1b). The halogen bonding can align the monomers and I-C₆F₄-I (linker) in a repeated manner. The monomers in the crystals can be polymerized with a radical source, which may give high molecular weight and narrow molecular weight distribution because of the restricted termination in the rigid crystals. This technique can expand the monomer scope to various vinyl monomers containing nitrogen or other electron-donating atoms (as Y) and also requires only a mild condition (heating at 40 °C or UV irradiation). Another interesting feature is that we are able to convert the liquid (Y-containing) monomers to solid monomers before the polymerization via crystallization. This feature inspired us to assemble the crystals to pre-construct desired complex material structures such as a multi-layer sheet and a three-dimensional (3D) structure and utilize SPP to fix those structures. Liquid monomers are converted to desired pre-determined shapes before polymerization, which is a novel venue of polymer engineering.

Figure 1. Radical polymerizations of (A) monomer in solution and (B) co-crystal monomer in solid-state.

Monomers (halogen bonding acceptors)

Linker (halogen bonding donor)

Photo-initiator

Crosslinkable monomer

Figure 2. Structures of monomers (1–7), a halogen bonding linker **8**, a photo-initiator, and a crosslinkable monomer used in this work.

The studied monomers (Figure 2) include 4-vinylpyridine (4VP, **1**), 2-vinylpyridine (2VP, **2**), 2-vinylpyrazine (2VPz, **3**), 1-vinylimidazole (1VI, **4**), *N*-vinylpyrrolidone (NVP, **5**), and *N,N*-dimethylacrylamide (DMA, **6**), which are liquids at room temperature (rt, 22 °C). The crystals were prepared via vapor diffusion and evaporation methods (Supporting Information). Because the evaporation method is robust and suitable to scale-up, all crystals shown below were prepared via the evaporation method. The monomer and I-C₆F₄-I were mixed at a 2/1 molar ratio in dichloromethane (solvent) for two monomer molecules to be bridged by one I-C₆F₄-I molecule. The crystals were generated in gram scales by gradually evaporating dichloromethane with a rotary evaporator at rt in a few hours. Single-crystal X-ray analysis (Table 1 and Figures S13–S18) showed that the crystals of **1–6** were co-crystals containing the monomer and I-C₆F₄-I. I-C₆F₄-I was regularly aligned via the π - π stacking.^[34] The monomers were thereby aligned linearly, and the monomer lines are separated in parallel manners (Figure 1B). The distances between the adjacent vinyl groups in the crystals ranged from 3.42 Å to 8.88 Å (Table 1). The distances are sufficiently short for the propagation to occur. The NMR and FTIR analyses also confirmed the co-presence of the monomer and I-C₆F₄-I in the crystals (Supporting Information). Acrylamide (AA, **7**) was also studied but did not form a co-crystal with I-C₆F₄-I (formed a self-crystal of AA via hydrogen bonding, Figure S19).

Table 1. X-ray Crystallography Data of Crystal Monomers.

Crystal	$d_{\text{vinyl-vinyl}}$ (Å)	$d_{\pi-\pi}$ (Å)	C–I...N(O) angles (°)	R factor (%)
1 • 8	6.55	6.33	178.0	5.22
2 • 8	8.88	9.21	175.3	4.54
3 • 8	3.42	5.00	175.6	4.20
4 • 8	4.01	4.13	176.4	2.57
5 • 8	4.42	7.29	173.5	4.56
6 • 8	4.33	7.02	174.6	2.74
7	3.92	3.92	–	6.09

The obtained crystals were thermally stable in paraffin oil (inert solvent) at least up to 50 °C for 24 h, showing no damage in the crystal packing structures (Supporting Information). Thus, we chose 40 °C as the polymerization temperature. The differential scanning calorimetry (DSC) analysis also showed that the melting points (breaking of halogen bonding) of the

crystals were above the polymerization temperature (40 °C) (Supporting Information). The SPPs derived from monomers **1**, **2**, and **4** were conducted by placing the crystals in paraffin oil containing tert-butyl peroxyneodecanoate (ND70) as a thermal initiator at 40 °C for 1 day (entries 1, 3 and 5, Table 2). After the SPP, no polymers were detected in paraffin oil, meaning that the crystal did not dissolve and the polymerization occurred in the crystals. The SPP of **1** (entry 1, Table 2) yielded a polymer with a high molecular weight ($M_n = 740000$) and a moderate dispersity ($\bar{D} = M_w/M_n = 2.03$), where M_w and M_n are the weight- and number-average molecular weights, respectively. The monomer conversion reached 88%. For comparison, we carried out solution-state polymerizations of **1** in paraffin oil without I-C₆F₄-I (entry 2, Table 2). While the monomer conversion were similar in SPP (88%) and in solution (92%), M_n was larger in SPP (740000) than in solution (330000) and $\bar{D}$ was significantly smaller in SPP (2.03) than in solution (5.23). The SPPs of **2** and **4** also gave larger M_n and smaller $\bar{D}$ values than the solution polymerizations of **2** and **4** (entries 3–6, Table 2). As mentioned, in solution, polymer[•] can diffuse and terminate randomly among chains. In contrast, in the crystal, the monomers were restricted in the crystal lattice. The polymer[•] in the crystal could only react with the closest monomer for propagation and hardly react with a monomer in another monomer line in a long distance. Thus, polymer[•] would scarcely diffuse to another monomer line, and chain termination would significantly be suppressed, leading to the higher M_n values in SPP. No change in the tacticity (stereoregularity) was observed in the SPP and the solution polymerization (Figure S21, Supporting Information), probably because the free rotation of vinyl groups was not restricted in the crystal during the propagation at 40 °C. No significant change in the tacticity was also observed even at a lower temperature of –35 °C for the photo-initiated SPP (shown below) and the solution polymerization (Figure S24, Supporting Information). No change in the tacticity was also found in free-radical SPP using hydrogen bonding crystals because of non-topochemical distance between the two vinyl groups.^[35,36] The topochemical distance of the two vinyl monomers to form a new C–C bond is approximately 2.5 Å. In free-radical SPP, the polymerization could occur in the monomer crystal even if the vinyl–vinyl distance is larger than 2.5 Å. The free rotation of the vinyl group in the crystal seems to occur in the propagation step.

Table 2. Polymerizations of Crystallized and Non-crystallized Monomers at 40 °C for 24 h.

Entry	Mode	$M^{[a]}$	$[M]_0/[I-C_6F_4-I]_0$ /[ND70] ₀ ^[b]	Conv (%) ^[c]	M_n ($\times 10^3$) ^[d]	$\bar{D}^{[d]}$
1	SPP	1	2/1/0.055	88	740	2.03
2	Solution ^[e]	1	2/0/0.055	92	330	5.23
3	SPP	2	2/1/0.65	100	120	1.71
4	Solution ^[e]	2	2/0/0.65	100	34	2.29
5	SPP	4	2/1/0.65	88	48	1.07
6	Solution ^[e]	4	2/0/0.65	94	26	1.57

[a] Monomer. [b] Polymerization in paraffin oil (monomer/paraffin oil = 30/70 wt% for entries 1 and 2 and 10/90 wt% for entries 3–6). [c] Monomer conversion. [d] Polystyrene-calibrated DMF-GPC values. [e] Solution-phase polymerization.

Scheme 1. Solvent-free SPP.

Table 3. Solvent-free SPP Under Heating and UV-irradiation.

entry	Monomer	Initiator	[Monomer] ₀ /[I-C ₆ F ₄ -I] ₀ /[initiator] ₀ ^[a]	t (h)	Conv (%) ^[b]	M _n ^[c]	Đ ^[c]
1	4VP (1)	ND70	2/1/0.16	24	98	100000	1.58
2	4VP (1)	DMPA	2/1/0.06	10	93	60000	5.50
3	2VP (2)	DMPA	2/1/0.02	20	73	10000	2.27
4	2VPz (3)	DMPA	2/2/0.02	23	76	27000	1.50
5	1VI (4)	DMPA	2/1/0.06	24	53	8500	1.22
6	NVP (5)	DMPA	2/1/0.02	24	84	47000	1.91
7	DMA (6)	DMPA	2/1/0.02	3	86	31000	7.79

[a] Thermal polymerization at 40 °C for entry 1 and UV-induced polymerization at rt for entries 2–7. [b] Monomer conversion. [c] DMF-GPC values calibrated with polystyrene for entries 1–6 and poly(methyl methacrylate) for entry 7.

In the mentioned systems, the radical source (ND70) was dissolved in paraffin oil, and the radical was supplied from the paraffin oil to the crystal. Here, we prepared three-component crystals of a monomer, I-C₆F₄-I, and a radical source and studied SPP without a solvent (no paraffin oil). The radical source (0.02–0.12 equiv to monomer) was a thermal initiator ND70 or a photo-initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA). The radical is expected to be generated inside the crystal under heating (40 °C) or UV-irradiation ($\lambda = 365$ nm), initiating SPP. This technique enables us to convert the liquid monomers to the solid monomer crystals and assemble the crystals to construct desired architectures before the polymerization. We pressed the crystals with a hydraulic press to form monomer sheets, and the sheets were polymerized in the dry state (without paraffin oil) (Scheme 1). The sheets kept the original shapes after the polymerization. The color changed from white to yellow after the polymerization, resulting from the decomposition of the photo-initiator DMPA. No decomposition of I-C₆F₄-I was observed (Supporting Information). In both thermal and UV-irradiation conditions (Table 3), the SPPs of **1–6** resulted in relatively high monomer conversions (53–98% for 3–24 h) with M_n values of 8500–100000 and $\bar{D}$ values of 1.22–7.79, showing the successful solvent-free SPP of several vinyl monomers. Comparing with the SPP in paraffin oil (external radical supply), the solvent-free SPP (internal radical supply) resulted in lower M_n values, which would be because the radical concentrations in the crystal can be higher with the internal radical supply. This result demonstrates the fabrication of pre-shaped polymer architectures through the conversion of the liquid monomers to the solid monomers followed by the post solvent-free SPP.

Exploiting this technique, we further fabricated more complicated structures, i.e., a two-layer polymer sheet and a 3D-house-shaped structure (Figure 3). To fix the polymer structures, we used a small amount of a cross-linkable monomer, i.e., ethylene glycol dimethacrylate (EGDMA), as a co-monomer. We prepared four-component mixtures of a monomer (**5** or **6**), EGDMA, I-C₆F₄-I, and DMPA (photo initiator). The X-ray crystallography showed that the monomer and I-C₆F₄-I formed co-crystals (93wt%) which were dispersed in EGDMA and DMPA (7wt%) to form slightly tacky solids (Supporting

Information). We prepared the monomer sheets of **5** and **6** and subsequently pasted the two sheets together to obtain a two-layer monomer sheet. After the UV-irradiation for 24 h, the crosslinked polymer sheet containing poly(*N*-vinylpyrrolidone) (PNVP) and poly(*N,N*-dimethylacrylamide) (PDMA) was obtained. The sheet was purified (washed) with ethanol to remove I-C₆F₄-I and unreacted monomers. The shape of the sheet remained unchanged after purification, meaning the successful crosslinking and fabrication of the two-layer polymer sheet (Figure 3A). For a demonstration purpose, a 3D-house-shaped crosslinked PNVP was also fabricated using the co-crystal of **5** (Figure 3B).

The scanning electron microscopy (SEM) images (Figure 4) of the purified two-layered PNVP/PDMA sheet shows a fused (crosslinked) interface between the two layers. Also, a network structure with micrometer-sized pores was observed. The pore sizes were much larger than the molecular size of the removed I-C₆F₄-I. The macro-pores would be generated via the non-isotropic swelling of polymers during the removal of I-C₆F₄-I. The pores in the two layers differed in size, suggesting that the pore size is tunable using different monomers.

Figure 3. Synthesis of crosslinked (A) two-layer polymer sheet and (B) 3D-house-shaped polymer structure from pre-shaped co-crystals.

Figure 4. SEM images of the two-layer PNVP/PDMA sheet. (A) side view and (B) cross-section of the PNVP (left) and PDMA (right) layers.

The two-layer sheet also exhibited a solvent-responsive actuator property because of the different swelling behaviors of PNVP and PDMA (Figure 5). In the dry state, the sheet was flat. In ethanol, the PNVP layer tended to swell more than the PDMA layer, leading to a flat-to-bowl shape change. The shape change was reversible. By immersing the sheet in diethyl ether, the original flat shape was recovered, because both layers were deswollen in their common poor solvent (diethyl ether). The two-layer polymer sheet with the different pore sizes and the actuating property may find applications to asymmetric membranes,^[37] catalyst supports,^[38] and hydrogel actuators.^[39]

Figure 5. Solvent-responsive behavior of the two-layer PNVP/PDMA sheet.

In conclusion, we developed a robust and versatile method to convert liquid monomers to solid co-crystals via halogen bonding and obtain polymers with high M_n values and relatively low $\bar{D}$ values via radical SPP. The co-crystals were assembled to the tailored structures, enabling the fabrication of a two-layer polymer sheet with a pore structure and an actuation property and a 3D-shaped polymer structure. This method enables the use of liquid monomers to pre-shape the desired polymeric structures and may serve as a novel polymer engineering tool.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Solid-Phase Synthesis • Polymerization • Crystal • Halogen Bonding • Pre-Shaped Polymer Material Structure

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Entry for the Table of Contents

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