Nanoporous Hypercrosslinked Polymers Containing T_g Enhancing Comonomers

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ABSTRACT: Hypercrosslinked polymers containing functionalized alternating copolymer sequences of substituted stilbene or styrene and N-aryl substituted maleimides have been synthesized. Alternating copolymers containing these comonomers possess semi-rigid structures and incorporation of these units into the precursor polymer particles for hypercrosslinking leads to a systematic increase in T_g and chain stiffness of these materials as the concentration of the comonomers is increased. Surface area and porosity of the subsequent hypercrosslinked polymers were investigated using nitrogen adsorption/desorption isotherms at 77 K. These hypercrosslinked polymers exhibit BET surface areas ranging from 1058 m²/g at 25 mol% alternating copolymer incorporation down to loss of measurable surface area at ca. 60% incorporation. The experimental surface area results correlate with predictions from simulations

and serve as model systems for future studies on specifically functionalized hypercrosslinked polymer particles.

KEYWORDS: hypercrosslinked polymer, nanoporous, semi-rigid alternating copolymers

INTRODUCTION

Nanoporous organic polymers, which are defined as materials with pore sizes of 1-100 nm [1,2], include hypercrosslinked polymers (HCPs) [3–5], covalent organic frameworks (COFs) [6–9], and polymers of intrinsic microporosity (PIMs) [10–13] etc. In the late 1960s [14], Davankov et al. proposed an approach to synthesize hypercrosslinked polymers termed “Davankov-type resin” [14,15]. Since then, hypercrosslinked polymers have been intensively studied and have been suggested for applications in areas such as chromatography, adsorption, gas storage, and/or separations [5,16–19]. The preparation of hypercrosslinked polymers typically involves the suspension polymerization of vinylbenzyl chloride and divinylbenzene, followed by intramolecular post-crosslinking reaction via Lewis acid catalyzed Friedel-Crafts alkylation [17,19]. These hypercrosslinked polymers exhibit BET surface areas up to 2000 m²/g [17].

Fréchet, Svec, and coworkers systematically studied a series hypercrosslinked polyanilines as another type of network system [20]. They found that the rigidity of the polymer backbone is crucial to maintain high surface area, because longer and more flexible crosslinkers used in the synthesis resulted in lower surface area of polymers [20]. These results suggested that decreasing the flexibility in a hypercrosslinked polymer resin could hinder the collapse of pore structures and therefore lead to higher surface area materials [18,20].

Sterically congested alternating copolymers containing stilbene and maleic anhydride or maleimide have been investigated in our group [21–29]. Functionalities of these alternating copolymers can be precisely controlled by incorporating various substituted stilbene and maleimide monomers. The steric congestion of extra phenyl groups from the stilbene units yields unique properties. Persistence length measurements by small-angle X-ray scattering (SAXS) and size exclusion chromatography (SEC) on a series of *tert*-butyl carboxylate functionalized stilbene and styrenic alternating copolymers showed that these copolymers are semi-rigid and adding extra phenyl groups enhanced the chain stiffness of the backbones [25,26]. Solution studies on the polyanions from the above series of copolymers also reveal semi-rigid structures [27]. Porous properties of these copolymers showed that the addition of phenyl rings to the polymer backbone increased surface areas [28].

The incorporation of semi-rigid alternating copolymer dyads into hypercrosslinked polymer particles offers potentially attractive possibilities of reducing collapse of pores during the hypercrosslinking chemistry, while at the same time delivering specific functionalities into the particles from carefully chosen substituents on the alternating comonomer pairs. In this paper, we enchain T_g enhancing comonomers, 4-methyl substituted stilbene or styrene and *N*-substituted maleimide, into Davankov-type hypercrosslinked systems in order to increase the rigidity of the polymer backbones. We report here the synthesis of hypercrosslinked polymers containing various levels of semi-rigid *N*-substituted maleimide–substituted stilbene or styrene alternating sequences. We investigated the effect of these semi-rigid alternating sequences on the polymer backbones using thermal analysis of precursor particles before the hypercrosslinking reactions. Surface area and porosity of the hypercrosslinked polymers were explored and correlated to the rigidity of polymer backbones. The results will provide guidance for the

synthesis of hypercrosslinked polymers containing high levels of functional groups in the hypercrosslinked polymers from the enchainment of specifically functionalized alternating comonomer pairs.

EXPERIMENTAL SECTION

Materials. 4-Methylbenzyl chloride (Aldrich, 98%), triethyl phosphite (Aldrich, 98%), benzaldehyde (Aldrich, $\geq 99\%$), t BuOK (Aldrich, 1.0 M solution in THF), maleic anhydride (Aldrich, 99%), toluene (Fisher, certified ACS), *m*-toluidine (Aldrich, 99%), acetic anhydride (Aldrich, 98%), sodium acetate (Aldrich, anhydrous), methanol (Fisher, HPLC grade), sodium 1,2-dichloroethane (Aldrich, $\geq 99\%$), FeCl_3 (Aldrich, 97%), poly(vinyl alcohol) (Aldrich, 87-89% hydrolyzed), sodium chloride (Fisher, certified ACS crystalline) were used as purchased. AIBN was recrystallized from methanol.

Instrumental Characterization. Proton nuclear magnetic resonance (^1H NMR) was utilized to confirm the chemical composition of the monomers and non-crosslinked polymers. CDCl_3 -d and DMSO-d_6 were used as the solvents. ^1H NMR was obtained on Varian Utility 400 MHz or JOEL EclipsePlus 500 MHz spectrometers at 25 °C. Infrared analysis, using a Midac FTIR spectrometer, was used to confirm the incorporation of *N*-substituted maleimide. Thermogravimetric Analysis (TGA) was employed to study the thermal stability of polymer precursors and hypercrosslinked polymers using TA instrument model Q5000. Samples were heated from 30 to 600 °C at a heating rate of 10 °C/min under nitrogen. Thermal transitions such as glass transition temperatures (T_g s) were obtained by Differential Scanning Calorimetry (DSC) using a TA instrument model Q1000. Samples were measured using heat/cool/heat method at heating and cooling rate of 20 °C under nitrogen. SEM micrographs were obtained using the LEO (Zeiss) 1550 field emission scanning electron microscope. The surface areas were

calculated using the Brunauer-Emmett-Teller (BET) equation and data from nitrogen adsorption/desorption isotherms at 77 K obtained with a TriStar II 3020 surface area analyzer (Micromeritics, Norcross, GA). Prior to analysis, the sample were degassed at 140 °C overnight.

(*E*)-4-Methyl Stilbene (4MSTB). (*E*)-4-Methyl stilbene was synthesized via the Wittig-Horner reaction using 4-methyltoluene(diethylphosphonate) and benzaldehyde (Scheme 1) [24]. To synthesize 4-methyltoluene(diethylphosphonate), 4-methylbenzylchloride (15.0 g, 107 mmol) and triethyl phosphite (70.9 g, 427 mmol) were stirred in a 250 ml flask and heated to 160 °C for 24 h. The remaining triethyl phosphite was removed by vacuum distillation at 80 °C under 0.2 mmHg to afford a colorless liquid (27.1 g, 100%). 4-Methyltoluene(diethylphosphonate) (27.1 g, 112 mmol) and benzaldehyde (11.9 g, 112 mmol) in dry THF (60 ml) were stirred in a 250 ml round bottom flask cooled in an ice bath. ^tBuOK (1.0 M in THF, 120 mL) was then added dropwise. The solution formed was stirred at room temperature for an additional 24 hours after which it was poured into water (500 ml). The product was precipitated from the solution, filtered and washed with water and vacuum dried overnight to yield (*E*)-4-methyl stilbene (white crystalline solid, 18.7 g, 86%). ¹H NMR (CDCl₃, 500 MHz) δ ppm: 7.52 – 7.08 (m, 11H), 2.37 (s, 3H) (Figure S1). Melting point: 117 – 118 °C (lit. [30]: 118 – 120 °C).

Scheme 1. Synthesis of (*E*)-4-methyl stilbene

***N*-(3-Methylphenyl)maleimide (3MPMI).** *N*-(3-Methylphenyl)maleimide was synthesized from a two-step reaction (Scheme 2). The second step of the reaction used a modified literature

method [31]. To synthesize *N*-(3-methylphenyl)maleamic acid, maleic anhydride (10.0 g, 102 mmol) and toluene (8 ml) were stirring in a 100 ml flask. *m*-Toluidine (11.1 g, 102 mmol) was added drop wise. During the addition, 15 ml toluene was added to maintain a good slurry consistency, after which the mixture was refluxed for 15 minutes. The product precipitated from solution was filtered warm and vacuum dried for 24 h to afford light yellow solid (19.63 g, 94%). ^1H NMR (DMSO, 400 MHz) δ ppm: 10.27 (s, 1H), 7.43 – 6.87 (m, 4H), 6.42 (d, 1H), 6.26 (d, 1H), 2.23 (s, 3H). A mixture of *N*-(3-methylphenyl)maleamic acid (17.6 g, 85.9 mmol), acetic anhydride (43.8 g, 429 mmol) and anhydrous sodium acetate (3.52 g, 42.9 mmol) was heated at 100 °C for 6 h. The reaction mixture was cooled and poured in ice water. The crude product was then washed with ice water and vacuum distilled (62 °C, 0.2 mmHg) to afford *N*-(3-methylphenyl)maleimide (yellow liquid, 15.1 g, 94%). The crude product was purified by column chromatography (silica gel, hexane-ethyl acetate = 5:1). The first band afforded pure product as a yellow liquid (6.19, 41%) (lit. [32] 78%) ^1H NMR (CDCl_3 , 500 MHz) δ ppm: 7.36 (m, 1H), 7.22 - 7.10 (m, 5H), 2.34 (t, 3H) (Figure S2).

Scheme 2. Synthesis of *N*-(3-methylphenyl)maleimide

Hypercrosslinked Copolymers. For clarity, we named the polymers in a number order. (Scheme 3) The lightly crosslinked polymer precursors with only styrene as comonomer were named as **P1-P6**, and the corresponding hypercrosslinked copolymers were named **HCP1-HCP6**; the precursors with styrene and 3MPMI were named as **P7-P11**, while the corresponding hypercrosslinked copolymers were **HCP7-HCP11**; the precursors with 4MSTB and 3MPMI were named as **P12-P16**, while the corresponding hypercrosslinked copolymers were **HCP12-**

HCP16. For example, hypercrosslinked copolymers **HCP1-16** were prepared following a modified literature procedure (Scheme 3) [17,19]. For example, to prepare **HCP12**, (*E*)-4-methyl stilbene (4MSTB) (0.519 g, 2.67 mmol), *N*-(3-methylphenyl)maleimide (3MPMI) (0.500 g, 2.67 mmol), vinylbenzyl chloride (VBC) (2.446 g, 16.04 mmol) and divinylbenzene (DVB) (0.071 g, 0.44 mmol) were added to a three-neck, 250 ml round bottom flask equipped with a mechanical stirrer, gas inlet, and condenser. Additionally, to the mixture, poly (vinyl alcohol) (0.332 g, 9.4 wt%), sodium chloride (1.462 g, 41.4 wt%), and DI water (45 ml) were added. The polymerization was initiated with 2,2'-azobis(isobutyronitrile) (0.018 g, 0.5 wt%). The mixture was stirred under N₂ at 80 °C for 6 h. The polymer beads were filtered, extracted with methanol and diethyl ether via Soxhlet extraction, and dried under vacuum at 50 °C for 24 h to yield a white solid (2.063 g, 58%). The precursor **P12** (1.913 g) was swollen in 1,2-dichloroethane (30 ml) for 2 h. Then FeCl₃ (1.997 g) was added and the mixture was heated at 80 °C for 18 h. The hypercrosslinked polymer was extracted with THF to remove any uncrosslinked polymer and vacuum dried at 50 °C for 24 h to afford a brown powder (1.319 g, 82%).

Scheme 3. Synthesis of hypercrosslinked copolymers (**HCP1-16**).

FT-IR was used to confirm incorporation of 3MPMI into the precursor particles (Figure S3). Stretching adsorption bands of the carbonyl group were observed around 1700 cm^{-1} for precursor particles containing 3MPMI monomer. Elemental analysis data of **HCP7-16** are shown in Table 1. **HCP7-16** contain 1.7-3.9 wt% N indicating that maleimide monomers were successfully incorporated into these hypercrosslinked networks. The slight offset from the theory may be due to the small amount residual FeCl_3 in the hypercrosslinked polymers.

Table 1. Elemental analysis results for **HCP7-16**.

Sample	Theory			Found		
	C	H	N	C	H	N
HCP7	86.1	6.9	2.2	79.5	5.9	1.7

HCP8	83.6	6.5	3.0	76.1	5.7	2.7
HCP9	82.5	6.4	3.4	78.3	5.9	2.7
HCP10	81.3	6.6	3.8	77.3	5.9	3.7
HCP11	80.1	6.1	4.2	77.0	6.0	3.9
HCP12	88.1	6.9	1.9	80.1	6.0	1.7
HCP13	85.2	6.6	2.5	78.9	6.7	2.3
HCP14	84.4	6.4	2.8	75.3	5.9	2.5
HCP15	83.7	6.3	3.0	77.0	5.7	3.5
HCP16	82.9	6.2	3.3	75.9	5.5	3.9

Molecular Simulation. Simulations were performed on the HCPs incorporating 3MPMI (**HCP7**, **HCP9**, and **HCP11**), which were compared to the control systems incorporating styrene presented in previous work (**HCP1**, **HCP2**, **HCP4**, and **HCP6**) [33]. Note that, unlike the experimental samples, DVB was not included in order to simplify the structures for the simulations. The HCPs were generated using the Polymatic simulated polymerization algorithm [34,35] with a two-stage implementation to mimic the experimental synthesis to some extent, as was done previously [33,36]. As such, linear polymers were first polymerized, which were then post-crosslinked in the swollen state. The swollen state was mimicked by fixing the simulation box at a low density (0.6 g cm^{-3}) and using a shifted Lennard-Jones potential ($5 \text{ \AA}$) during the crosslinking procedure. Equilibration to the dried state at 330 K and 1 bar was performed by application of a 21-step molecular dynamics (MD) scheme incorporating simulations at high temperatures and pressures [34,37]. Note that the Lennard-Jones cutoff was set back to $15 \text{ \AA}$ during the equilibration in order to achieve appropriate interactions of the final polymers in the

dried state. This methodology has been effective for generating accurate structures of network polymers [33,36], among others.

A united atom model was used with bonded interactions taken from the polymer consistent force field (PCFF [38]) and Lennard-Jones parameters from the transferable potentials for phase equilibria (TraPPE [39,40]). Periodic boundary conditions on cubic boxes (final box sizes of $L \approx 32\text{-}38 \text{ \AA}$) were used. Energy minimization and molecular dynamics simulations were performed in LAMMPS [41]. The Nosé-Hoover thermostat and barostat were used to control temperature and pressure in the NPT and NVT ensembles, and a 1 fs time step was used with the velocity-Verlet time integrator. Geometric surface areas were calculated from the simulations using the Poreblazer code using a nitrogen-size spherical probe [42]. For each system studied, five independent boxes were generated using the methodology as described above.

RESULTS AND DISCUSSION

Thermal Properties. Thermal properties of the lightly crosslinked precursors (**P1-16**) before the hypercrosslinking reactions and the hypercrosslinked polymers (**HCP1-16**) were investigated by differential scanning calorimetry (DSC). Glass transition temperatures (T_g s) of **P1-16** are in the range of 90-230 °C, and are shown in Table 2. After hypercrosslinking no T_g was observed (**HCP1-16**), which is due to the inhibition of the chain mobility. Precursors **P1-P6** exhibit T_g s of 90-105 °C. The T_g of polyvinyl benzyl chloride (PVBC) is reported as 73 °C [43] while the T_g of polystyrene (PSTR) is 100 °C [44]. Although **P1** contained 98 mol% of VBC, it showed a higher T_g than PVBC. The low degree of crosslinking introduced by 2 mol% of DVB, likely decreases the chain mobility, and thus raises the T_g of **P1**. T_g s modestly increase from **P1** to **P6** as the amount of STR increases. Poly(styrene-*alt*-*N*-phenyl maleimide) exhibits T_g of 223 °C [45],

which is much higher than the T_g of the styrenic polymers. The incorporation of 3MPMI raised the T_g s of precursors (**P7-11**) to 121-189 °C, compared to the precursors only with styrene as comonomer (**P1-6**), which have T_g s of 89-105 °C. From **P7** to **P11**, T_g s increase as the STR-3MPMI mol% increases, the trend is shown in Figure 1.

Functionalized stilbene and *N*-substituted phenyl maleimide alternating copolymers have excellent thermal stability and our previous research showed no observable T_g s in DSC experiments below the decomposition temperature (> 350 °C) [21]. **P12-16**, which contain both 4MSTB and 3MPMI units, exhibit higher T_g s (up to 225 °C) compared to the T_g s of **P1-6** and **P7-11** at comparative compositions (Figure 1). Therefore, the incorporation of T_g enhancing comonomer pairs into the backbone accomplished the goal of raising the T_g and decreasing the mobility of the polymer backbone in the lightly crosslinked polymer precursors.

Figure 1. Glass transition temperatures of **P1-16** as a function of monomer concentration.

Table 2. Glass transition temperatures of precursors and porous properties of hypercrosslinked polymers.

	STR (mol%)	STR- 3MPMI (mol%)	4MSTB- 3MPMI (mol%)	VBC (mol%)	DVB (mol%)	Precursors	Hypercrosslinked Polymers			
						T_g (°C)	SA_{BET} (m ² /g)	$V_{p, micro}$ (cm ³ /g) ^a	V_p^{total} (cm ³ /g) ^b	Pore Size (nm) ^c
1	0	0	0	98.0	2.0	96	1577	0.628	1.039	1.1
2	24.5	0	0	73.5	2.0	93	1342	0.540	0.900	1.0
3	40.0	0	0	58.0	2.0	89	1263	0.583	1.022	1.1
4	49.0	0	0	49.0	2.0	103	908	0.368	0.613	0.8
5	60.0	0	0	38.0	2.0	102	878	0.359	0.591	0.5
6	73.5	0	0	24.5	2.0	105	508	0.209	0.350	1.2
7	0	24.5	0	73.5	2.0	121	1058	0.436	0.660	0.9
8	0	40.0	0	58.0	2.0	148	318	0.130	0.173	1.1
9	0	49.0	0	49.0	2.0	166	256	0.106	0.148	0.9
10	0	60.0	0	38.0	2.0	187	0	0	0	0
11	0	73.5	0	24.5	2.0	189	0	0	0	0
12	0	0	24.5	73.5	2.0	130	940	0.385	0.560	0.5
13	0	0	40.0	58.0	2.0	162	774	0.318	0.455	1.1
14	0	0	49.0	49.0	2.0	177	552	0.226	0.343	0.9
15	0	0	60.0	38.0	2.0	199	0	0	0	0
16	0	0	73.5	24.5	2.0	225	0	0	0	0

^aMicropore volumes determined from nitrogen adsorption isotherm at $P/P_0 = 0.14$; ^bTotal pore volumes determined from nitrogen adsorption isotherm at $P/P_0 = 0.98$; ^cPore sizes determined from nitrogen adsorption isotherm by the non-local density functional theory method (NLDFT).

Porosity and BET Surface Area. Using SEM, spherical structures were observed for precursor particles, which are typical for the products of suspension polymerization (Figure 2a scale 20 μ m), a higher magnification SEM micrograph of the precursor showed a smooth surface and no porous structure (Figure 2b, scale 2 μ m). Porous structures were observed for hypercrosslinked polymers (Figure 2c, scale 10 μ m, and Figure 2d, scale 2 μ m), although micropores (with pore widths < 2 nm) are too small to be observed under such magnification. Previously reported SEM micrographs of hypercrosslinked polystyrenes exhibited a similar visible porous structure change.[46]

Figure 2. SEM micrographs of **P12** (a, scale 20 μm) (b, scale 2 μm) and **HCP12** (c, scale 10 μm) (d, scale 2 μm).

Nitrogen adsorption/desorption isotherms of these hypercrosslinked polymers were obtained at 77 K. Figure 3 shows adsorption/desorption isotherms of **HCP7-9** and **HCP12-14** (Adsorption/desorption isotherms of HCP1-6 can be found in Figure S5). Type I isotherms were observed for these copolymers according to the classification given by International Union of Pure and Applied Chemistry (IUPAC) [47]. High nitrogen uptakes at low relative pressure ($P/P_0 < 0.2$) indicate that these copolymers possess micropores (with pore widths < 2 nm). The pore size distributions were assessed by the non-local density functional theory method (NLDFT) on nitrogen adsorption isotherms by using the SAIEUS program (Figure S4). [48] The pore sizes of HCP7-9 and HCP12-14 were within the range of 0.5 nm to 1.2 nm, which is in the same range as the control HCP1-6 and other literature reported hypercrosslinked polystyrenes. [5] Surface areas

were calculated using the Brunauer-Emmett-Teller (BET) equation [49]. The relative pressure (P/P_0) for the linear region of BET plot was chosen in the range of 0.05-0.16 based on the recommendations for microporous samples [50]. BET surface areas, micropore volumes, total pore volumes and pore sizes of **HCP1-16** are summarized in Table 2.

Figure 3. Nitrogen adsorption (closed symbol)/desorption (open symbol) isotherms at 77 K for **HCP7-9** (a) and **HCP12-14** (b).

Styrenic hypercrosslinked copolymers **HCP1-6** are used as controls. A systematic decrease in surface areas from 1577 to 508 m²/g was observed when the mole percentage of STR increases from 0 to 75% (Figure 4). This observation is consistent with previous research reported by Sherrington and coworkers [16]. The decrease in surface areas is likely due to the dilution of VBC units, which served as the crosslinker in the post-crosslinking reaction. Therefore, maintaining a high level of chloromethyl groups is crucial in preparing high surface area polymers.

Figure 4. Surface areas of HCP1-16 (see **Table 2**) as a function of monomer concentration.

The T_g enhancing comonomer containing hypercrosslinked copolymers **HCP7-11** and **HCP12-16** exhibit surface areas of 1058 m²/g at ca. 25 mol% incorporation of the alternating comonomer pairs. A faster decrease in surface areas as the comonomer (STR-3MPMI or 4MSTB-3MPMI) concentration increases, as compared to the styrene copolymers, was observed. No porosity was observed in hypercrosslinked copolymers containing more than 60% STR-3MPMI or 4MSTB-3MPMI. The origin of this total loss of porosity is not fully understood at this time. An inspection of Figure 4 shows that the surface areas of these copolymers showed a similar but steeper systematic decrease compared to the styrene copolymer containing samples **HCP2-6** at comparable substitution levels.

Molecular Simulations. Simulations were performed on the HCPs containing 3MPMI (**HCP7**, **HCP9**, and **HCP11**) and compared to simulations of the control styrenic systems (**HCP1**, **HCP2**, **HCP4**, and **HCP6**) [33] and the experimental results. Geometric SAs from the simulations are given in Figure 5 with the experimental BET surface areas. For both systems, the

trends in the simulated and experimental surface areas were in agreement, where the surface area decreased with increasing monomer concentrations of STR or 3MPMI-STR (0, 25, 50, and 75%). In particular, the simulations of the HCPs containing 3MPMI are in excellent agreement with the corresponding experimental data at all compositions. Although proper trends were observed in the simulations of the styrenic HCPs, the surface areas deviated from the experiments at concentrations of 50 and 75%. It is expected that these deviations result from the differences in the amount of DVB in the simulations (0%) and experiments (2%), which is believed to affect uniformity of the distribution of crosslinks throughout the material [33,46]. Nevertheless, the agreement between simulation and experiment is quite strong given that the simulations were generated based only on the composition of the polymers.

Figure 5. Surface areas of the styrenic and 3MPMI containing HCPs compared for the simulations and experiments, as well as a hypothetical fully crosslinked system (VBC-3MPMIc).

It is expected that a large reason for the decrease in the surface areas of the HCPs with increasing monomer concentration is due to the decrease in the degree of crosslinking. In order to test this hypothesis, hypothetical systems were considered in the simulations that modified the

3MPMI containing HCPs to be fully crosslinked, like the control system with 0% styrene. To this end, structures were generated in the simulations that replaced the $-\text{CH}_3$ group in 3MPMI with a $-\text{CH}_2\text{Cl}$ group (denoted 3MPMIc) and the STR units with VBC, such that every monomer could form a crosslink. In these hypothetical systems, the surface areas remained relatively constant as the monomer concentration was increased (Figure 5). These results support the hypothesis that the loss in crosslinking is largely responsible for the loss in surface area in the HCPs introduced in this work, and suggest that the surface area can be restored by reintroducing crosslinks to each monomer.

Effect of T_g Enhancing Comonomers on Porosity. As discussed in the previous section, both experimental and simulation results suggested that a high concentration of crosslinker (VBC in our case) in the post-crosslinking reaction is important for the formation of high porosity. The results also showed that the incorporation of chain stiffening moiety into the HCPs decreased the surface areas.

Previous simulation study on HCPs STR-DVB showed that the lower the densities of the polymer particles during the crosslinking in the swollen state, the higher the surface areas [33]. The densities in the swollen state are affected by the swelling properties of the polymer precursors. The incorporation of stiffening units into polymer backbone can decrease the chain mobility, resulting in a decrease in swelling properties and thus increase the densities of the precursors. Furthermore, the lower chain mobility may affect the crosslinking efficiency. Both of the reasons mentioned above may lead to the systematic lower surface area of T_g enhancing comonomer containing hypercrosslinked polymers compared to the controls.

CONCLUSIONS

Incorporation of chain stiffening, T_g enhancing comonomers into hypercrosslinked polymers is reported in this paper. The thermal analysis of polymer precursors indicates that the incorporation of these comonomers, which have semi-rigid characteristics, systematically enhanced the T_g s of the lightly crosslinked precursor polymers. Nitrogen sorption measurements showed the subsequent hypercrosslinked polymers contain micropores and have BET SAs of approximately 1000 m²g at 25% comonomer incorporation. As the concentration of T_g enhancing comonomer increases, the loss of mobility of the polymer backbones and loss of crosslinks leads to a loss of surface area. These experimental results are consistent with simulation results and the sharp decreases in surface area are likely a result of both dilution of crosslinking functionality and loss of crosslinking efficiency due to loss of chain mobility as the T_g s are increased. The results of the surface area versus comonomer content of the polymer particles serve as model systems for the design and preparation of specifically functionalized hypercrosslinked polymer particles where the comonomers are used to deliver specific functional groups into the particles. Our current research involves incorporation of various functional groups into these hypercrosslinked systems with the objective of preparation specific gas sorbants and will be the subject of a future publication.

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