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A facile synthesis of iodine-functionalized hypercrosslinked polymers†

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Hypervalent iodine compounds have gained significant attention for their applications in highly efficient and environmentally benign chemical transformations. Many homogeneous variants of hypervalent iodine compounds have been investigated; however, the development of the heterogeneous variants is still limited despite their potential applications as recyclable catalysts. In this study, we report a synthesis of novel hypercrosslinked polymers bearing iodine functional groups. These polymers were synthesized using an efficient iodination method, allowing iodine incorporation up to 1.96 mmol g⁻¹. Various iodinated hypercrosslinked polymers, featuring electron-rich and electron-poor substituents, were synthesized with good yields and high iodine incorporation. The utility of these iodinated polymers as a heterogeneous catalyst was demonstrated in an alcohol oxidation, giving the corresponding ketone in high yields. This polymeric catalyst could be easily recovered through simple filtration and reused without any deterioration in the yields of the product.

Introduction

Development of green and efficient syntheses is an important challenge in chemistry. Catalysis offers a solution for more efficient and more environmentally friendly syntheses because catalysts can be used in a sub-stoichiometric amount; thereby, reducing the synthesis cost and waste. Heterogeneous catalysis for organic synthesis has recently gained a lot of attention because heterogeneous catalysts can be recovered and reused with a convenient and inexpensive operation such as simple filtration. Development of new heterogeneous catalysts is therefore important. One commonly used approach to develop heterogeneous catalysts is to functionalize the surface of a material to install reactive functionality necessary for catalysis.¹

Hypercrosslinked polymers (HCPs) are an important class of porous materials with extensive crosslinking in the polymer chains.^{2,3} The structural framework of HCPs generally has a highly porous structure and high surface area, making them suitable for various applications such as catalysis,^{4,5} gas storage,^{6–8} separation,^{9,10} adsorption,¹¹ solid supports,¹² and sensors.¹³ One important advantage of HCPs is their high porosity and high surface area, which allows high functional group incorporation on their surface. HCPs with various

functional groups, such as sulfonic acid,¹⁴ carboxylic acid,¹⁵ amide,¹⁶ hydroxyl group,¹⁷ and amine¹⁸ have been developed. In addition to neutral HCPs, ionic HCPs have been constructed for various applications.^{19–21} However, iodine-functionalized HCPs have not been reported possibly because alkyl or aryl iodide functional groups could interfere with common polymerization methods to synthesize HCPs such as Friedel–Crafts reactions or cross-coupling reactions.

Iodine-functionalized aromatic compounds are an important structural motif in organic chemistry. One important application is its use as a precursor for hypervalent iodine chemistry. Due to their high efficiency, low toxicity, and easy handling, hypervalent iodines have been used for a wide range of chemical transformations, such as oxidation,^{22–24} oxidative addition,²⁵ oxidative cleavage,^{23,26–30} oxidative rearrangement,^{31–37} and oxidative cyclization reactions.^{38,39}

Previously, the development of homogeneous catalytic hypervalent iodines has been reported to make the reactions more environmentally friendly and cost-effective. An approach to develop a catalytic variant for hypervalent iodines is to use iodoarenes as a pre-catalyst and a stoichiometric amount of various oxidants to generate an iodine(I)/iodine(III) catalytic cycle. This approach has been used for various reactions such as C–H activation,^{40,41} oxidative decarboxylation,⁴⁰ Hoffmann rearrangement,⁴² and oxidative cyclization.⁴³

Although homogeneous hypervalent iodine chemistry has been developed, the development of a heterogeneous variant has still been limited. Only a few types of materials, such as silica⁴⁴ and polystyrene^{44–51} have been used as a framework for heterogeneous hypervalent iodine chemistry. A direct

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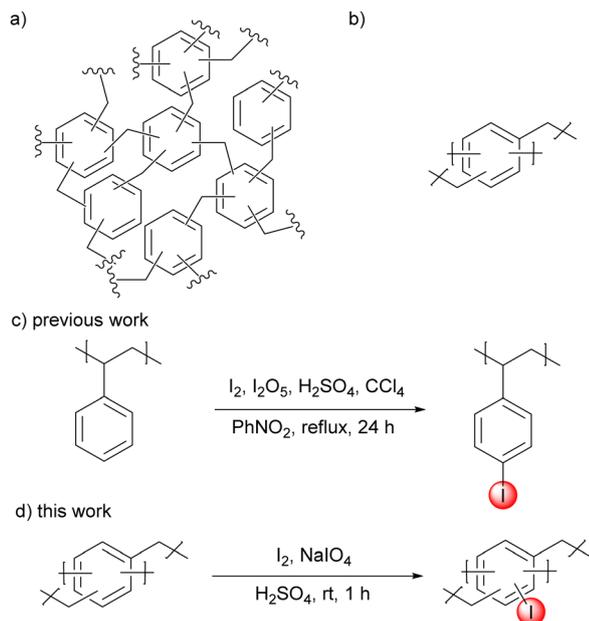


Fig. 1 (a) Hypercrosslinked polymer (HCP), (b) a simplified structure of HCPs, (c) previously reported direct iodination of polystyrene and (d) this work.

iodination of polystyrene offered simple access to iodinated polystyrene, which has been shown to be an effective heterogeneous pre-catalyst for hypervalent iodine chemistry in many chemical reactions. This iodination method (using the I_2/I_2O_5 iodination system and CCl_4 as a solvent under refluxing condition) required harsh reaction conditions with a toxic solvent.⁴⁹ We envisioned that the development of new iodinated polymers for heterogeneous hypervalent iodine chemistry may be accomplished with milder and greener reaction conditions (Fig. 1). Iodinated hypercrosslinked polymers are chosen because their polymeric framework is expected to have high surface area, high porosity, and high thermal and chemical stability. The framework can be conveniently modified with various functional groups (such as electron-rich or electron-poor substituents), which may allow access to hypervalent iodine with different oxidation potentials. Herein, we report a synthesis of novel iodinated hypercrosslinked polymers using mild iodination conditions and use the resulting iodinated polymers as a recyclable heterogeneous catalyst for alcohol oxidation.

Results and discussion

A non-functionalized hypercrosslinked polymer (HCP-H) using a benzene monomer with a methylene linkage was chosen to be the model substrate for the iodination. The polymer was synthesized from the Friedel–Crafts reaction between benzene and dimethoxymethane using the reported procedure in the literature.⁵² A brown solid of HCP-H was obtained in a good yield (quantitative).

To investigate the iodination conditions, three different iodination methods were tested with HCP-H to generate

Table 1 Screening of the iodination conditions

Entry	Condition	Yield (%)	Iodine content (mmol g^{-1})
1 ^a	$I_2/KIO_3/H_2SO_4/AcOH/H_2O$, 80 °C, 10 h	46	0.63
2 ^b	$KI/H_2O_2/H_2SO_4$, MeOH, 60 °C, 24 h	53	0.47
3 ^c	$I_2/NaIO_4/H_2SO_4$, rt, 1 h	58	0.97

^a Reaction conditions: HCP (5 mmol), I_2 (130 mmol, 26 equiv.), KIO_3 (20 mmol, 4 equiv.) in a mixed solvent ($AcOH:H_2O:H_2SO_4/50:4:1$, 550 mL).
^b Reaction conditions: HCP (5 mmol), KI (5 mmol, 1 equiv.), H_2SO_4 (7.5 mmol, 1.5 equiv.), 30% H_2O_2 (10 mmol, 2 equiv.) in MeOH (25 mL).
^c Reaction conditions: HCP (5 mmol), I_2 (4.3 mmol, 0.86 equiv.), $NaIO_4$ (1.4 mmol, 0.28 equiv.) in 98% H_2SO_4 (15 mL).

HCP-I (Table 1). The iodine content in the iodinated hypercrosslinked polymer was determined by a method based on a modified combustion⁵³ and an indirect atomic absorption spectroscopy measurement.

A combination of $I_2/KIO_3/H_2SO_4$ gave the desired iodinated product in 46% yield with the iodine content of 0.63 mmol g^{-1} (entry 1). A system of $KI/H_2O_2/H_2SO_4$ gave the iodinated polymer in 53% yield with the iodine content of 0.47 mmol g^{-1} (entry 2). An $I_2/NaIO_4/H_2SO_4$ oxidative condition gave the iodinated polymer in the highest yield (58%) and the highest iodine content (0.97 mmol g^{-1}) (entry 3). It should be noted that the iodination using $I_2/NaIO_4/H_2SO_4$ did not require heating, and the reaction time was significantly shorter. This condition was chosen for further optimization.

The equivalent of the iodinating agents was subsequently studied (Table 2). Increasing the amount of the reagent led to a higher iodine content in the polymer; however, increasing the amount beyond 2 equivalents did not significantly change the iodine content. The iodination condition with 2 equivalents of the iodinating agent gave the product in 65% yield and the iodine content of 1.96 mmol g^{-1} . This condition was chosen as the optimal condition for further investigation.

With the optimal iodination conditions in hand, HCPs with different substituents were investigated to explore the

Table 2 Screening of the equivalents of iodinating agent

Entry	I_2 (equiv.)	$NaIO_4$ (equiv.)	Yield ^a (%)	Iodine content (mmol g^{-1})
1	0.43	0.14	58	0.97
2	0.54	0.17	44	1.33
3	0.64	0.21	64	1.53
4	0.75	0.24	67	1.57
5	0.86	0.28	65	1.96
6	1.29	0.42	71	2.07

^a The yields were calculated from the stoichiometry based on the molecular weight of the expected structure of the product with an assumption that each aromatic ring was iodinated one time (see ESI).



possibility of using the method for a wider range of materials (Table 3). Alkyl substituents (methyl, ethyl, or isopropyl) did not affect the yields of the iodinated polymers, but the iodine content decreased to 0.90, 1.14, and 1.18 mmol g⁻¹, respectively (entries 2–4). When the substituent was changed to an electron donating methoxy group, the iodine content was 1.05 mmol g⁻¹ (entry 5). These results suggested that substrates with various substituents were well tolerated in this iodination method. The lower iodine content of the substituted polymers may result from the increasing steric demand of the substituents and/or the lower number of iodinating sites on the aromatic rings in the polymers. HCP with an electron withdrawing nitro group gave the iodinated product in 50% yield and the iodine content of 1.11 mmol g⁻¹ (entry 6).⁵⁴

The chemical properties of the iodinated hypercrosslinked polymers were studied using IR spectroscopy (Fig. 2). The IR spectrum of HCP-I (**2a**) exhibited a new absorption at 624 cm⁻¹, corresponding to the C–I stretching. This result suggested that the iodination condition successfully installed iodine functional groups onto the surface of the hypercrosslinked polymers. In addition, a comparison between the IR spectra of HCP-H (**1a**) and HCP-I (**2a**) showed no significant change in the peaks of the polymer framework: C–H stretching of the methylene bridge (2920 cm⁻¹), overlapping of the peaks from C=C stretching of the aromatic ring and O–H bending of water (1676 cm⁻¹), and the C–O stretching of ether or alcohol possibly from the unreacted site of the crosslinker on the polymer (1297 cm⁻¹). For HCPs with different substituents (**2b–2f**), C–I stretching is also observed (see ESI†).

HCP-I (**2a**) was chosen for further characterization and utilization because it had the highest iodine content. The morphology of the HCPs was further studied using scanning electron microscopy (SEM). The SEM images showed that the morphology of HCP-H (Fig. 3(a)–(c)) and that of HCP-I (Fig. 3(d)–(f)) were similar. This result suggested that the polymer backbones of HCP-H and HCP-I were similar, which agreed well with the data from IR spectroscopy. In addition, SEM–EDX elemental mapping was performed to confirm the presence of iodine atoms on the surface of the iodinated polymers (Fig. 4(f)). The elemental mapping data indicated that

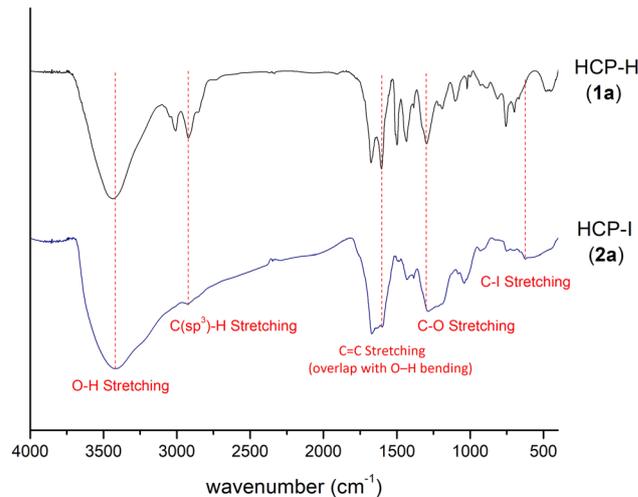


Fig. 2 IR spectra of HCP-H **1a** and HCP-I **2a**.

carbon, oxygen, and iodine atoms were found on the surface of the polymer and that iodine atoms were distributed over the surface of the polymer.

To study the chemical composition on the surface of HCP-I (**2a**), XPS spectra were measured (Fig. 4). The spectrum showed two major peaks located at binding energies of 619.8 and 631.4 eV, which were characteristic peaks of the I-3d spin-orbit doublet (I-3d_{5/2} and I-3d_{3/2}, respectively) in an organic molecule.⁵⁵ These peaks suggested the presence of a C(aromatic)–I bond on the HCP surface.⁵⁶ The detection of C 1s peaks at 283.8, 284.8, 286.0, 287.3, and 289.3 eV described the chemical states of carbon atoms on the surface, which were corresponding to C=C, C–C, C–O, C=O, and O–C=O bonds, respectively.^{57,58} The remaining oxygen atoms from the crosslinking reagent were confirmed by the presence of O 1s signals at 531.2 and 532.8 eV, which were corresponding to the organic O=C and O–C bonds, respectively.⁵⁹ The presence of the carbonyl group might arise from the polymerization of HCP.⁶⁰

The thermal stability of the HCP-I was investigated using TGA analysis (see ESI†). The TGA data showed 2 main ranges of weight loss. The range lower than 100 °C could be associated with the release of physically adsorbed water on the surface of the resin. The moisture adsorbed on the polymer was determined to be around 19%. The mass loss in the range of 300–500 °C was possibly due to the decomposition of the iodine functional group on the surface of the polymers and the breakdown of the polymeric backbone. The TGA result suggested that the novel iodinated polymer was thermally stable up to 300 °C.

To study the porosity property of HCP-I, N₂ adsorption-desorption analysis at 77 K was performed. The data showed a type-IV isotherm with a significant hysteresis loop, similar to that of HCP-H, indicating that the iodination process did not significantly change or destroy the core structure of the polymers. The pattern of the isotherms revealed the presence of micropores and mesopores in the material.⁶¹ The adsorption isotherm (Fig. 5(a)) showed a steep nitrogen gas uptake at low

Table 3 Substrate scope of the iodination^a

Entry	R	Yield (%)	Iodine content (mmol g ⁻¹)
1	H (2a)	65	1.96
2	Me (2b)	70	0.90
3	Et (2c)	67	1.14
4	ⁱ Pr (2d)	70	1.18
5	OMe (2e)	58	1.05
6	NO ₂ (2f)	50	1.11

^a Reaction conditions: HCP (5 mmol), I₂ (4.3 mmol, 0.86 equiv.), NaIO₄ (1.4 mmol, 0.28 equiv.) in 98% H₂SO₄ (15 mL).



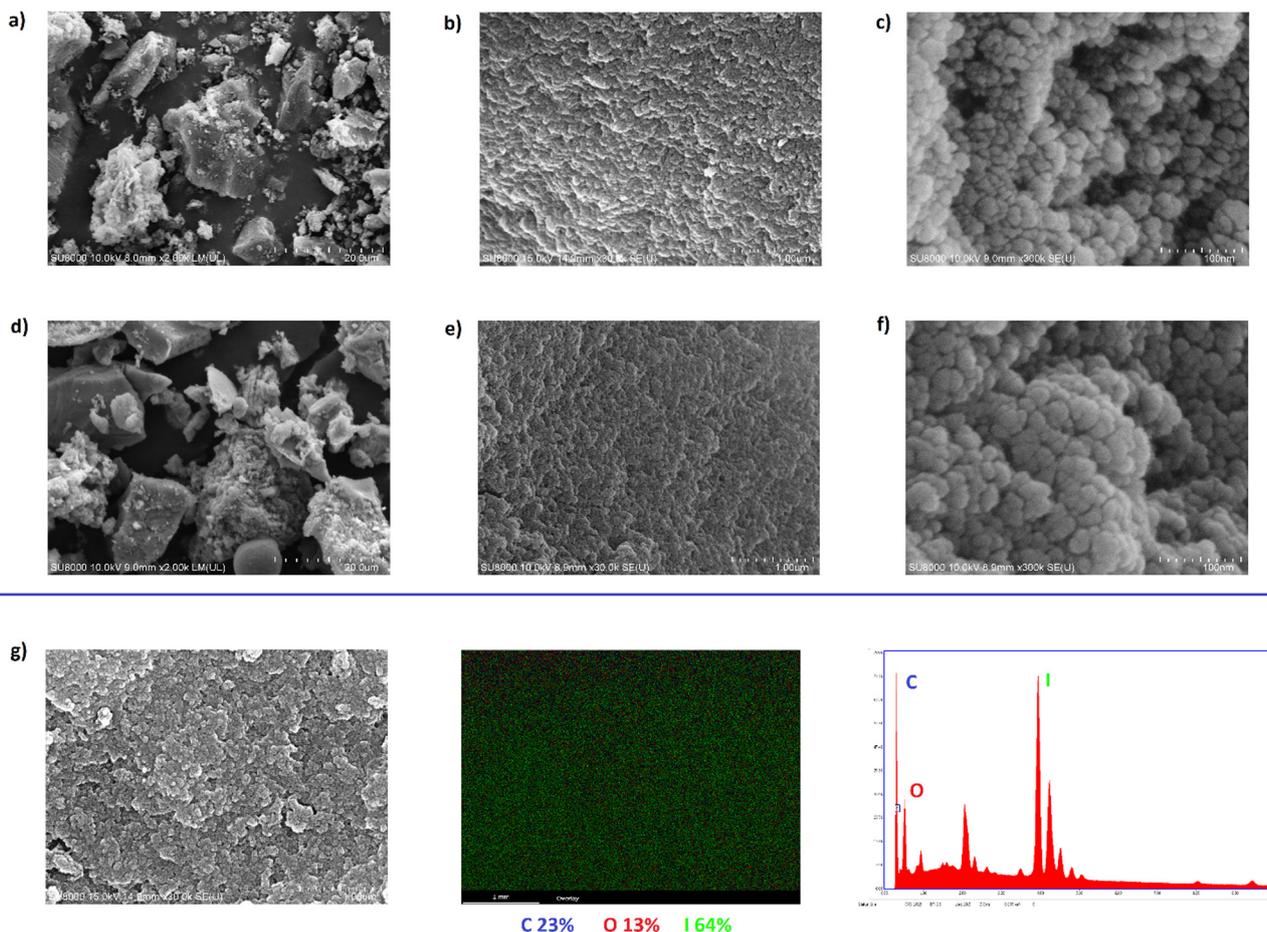


Fig. 3 (a) SEM image of HCP-H (x2.00k), (b) SEM image of HCP-H (x30.0k), (c) SEM image of HCP-H (x300k), (d) SEM image of HCP-I (x2.00k), (e) SEM image of HCP-I (x30.0k), (f) SEM image of HCP-I (x300k) and (g) SEM-EDX elemental mapping of HCP-I.

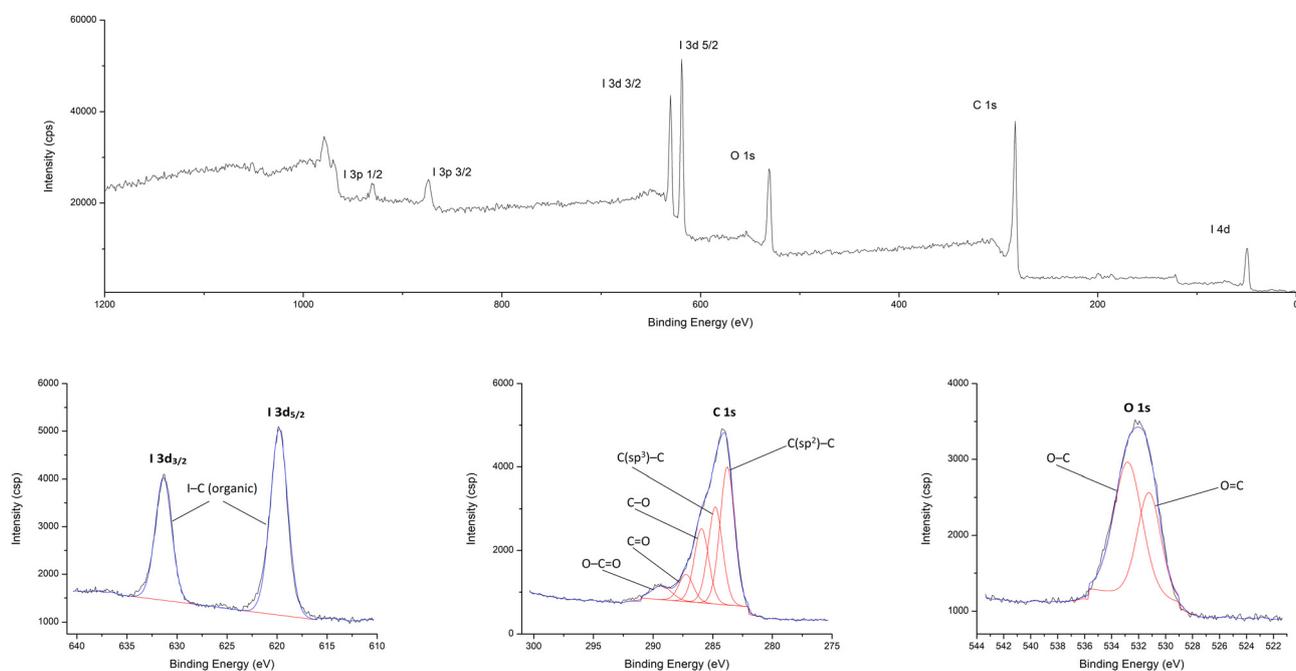


Fig. 4 XPS spectra of HCP-I 2a.



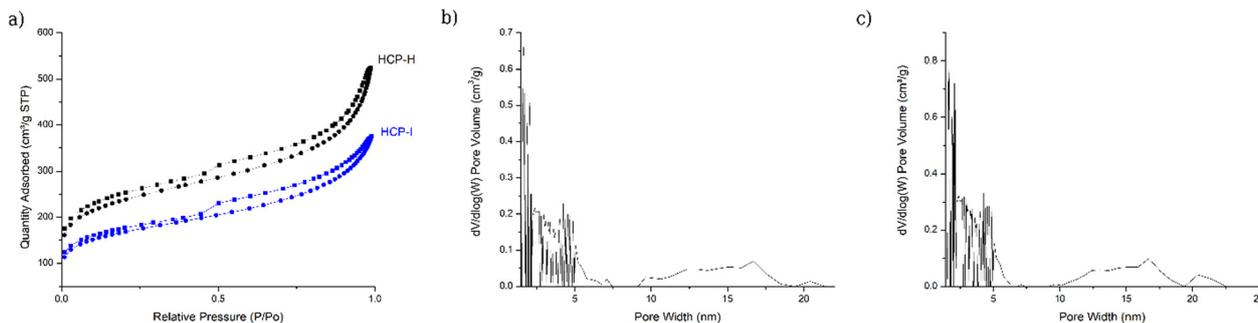


Fig. 5 (a) Adsorption isotherm of HCP-I and HCP-H, (b) pore size distribution of HCP-I and (c) pore size distribution of HCP-H.

relative pressure ($P/P_0 < 0.1$), indicating the abundance of micropores. The adsorption isotherm also displayed a large rise in adsorption at higher relative pressure, which resulted from the presence of mesopores in the polymer. The HCP-I exhibited a high Brunauer–Emmett–Teller (BET) surface area of about $606 \text{ m}^2 \text{ g}^{-1}$ with a total pore volume of approximately $0.20 \text{ cm}^3 \text{ g}^{-1}$, slightly lower than the surface area of HCP-H of $858 \text{ m}^2 \text{ g}^{-1}$ with a total pore volume of approximately $0.60 \text{ cm}^3 \text{ g}^{-1}$. The lower surface area could be due to the installation of heavy iodine atoms. The pore size distribution, using nonlocal density functional theory (NLDFT) for the pillared clay model, showed the distribution of the pore width from 1.7 to 21 nm, with the most abundant pore width around 1.67 nm (Fig. 5(b)), suggesting the presence of both micropores and mesopores in the material. Therefore, HCP-I was classified as a hierarchically structured porous material, which normally has a high surface area, excellent accessibility to active sites, and enhanced mass transport and diffusion.

To illustrate the utility of the iodinated HCPs, HCP-I (**2a**) was used as a heterogeneous catalyst for an oxidation reaction of diphenylmethanol (Table 4). In the presence of the catalyst, the alcohol was effectively converted to the corresponding ketone in 80% yield (entry 3). In the absence of the catalyst, no reaction occurred (entry 1). When HCP-H (**1a**) was used as a catalyst, no product was obtained (entry 2). These results suggested that the iodine functional group was essential for the oxidation. The iodinated material could act as a precursor for the heterogeneous hypervalent iodine catalyst. A comparison between

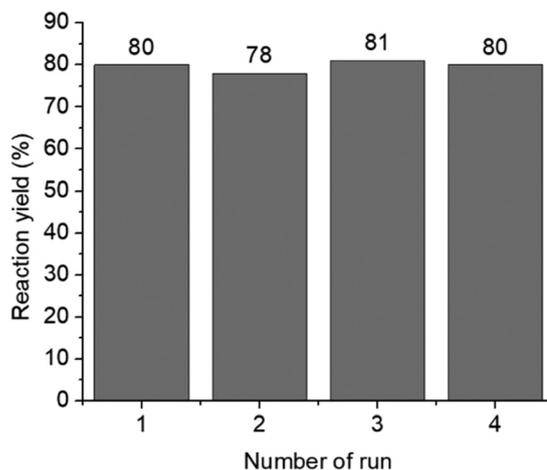


Fig. 6 Recycling experiments of HCP-I **2a**.

HCP-I and commercially available iodinated polystyrene (PS-I, entry 4) showed that under these reaction conditions, HCP-I had significantly better catalytic activity than PS-I.

In addition, the reusability of the HCP-I catalyst in an oxidation of diphenylmethanol was investigated. After the HCP-I catalyst was used in the first run of the reaction, the catalyst was recovered by simple filtration, and the recovered catalyst was used in subsequent runs. The result showed that the catalyst can catalyze subsequent runs of the recycling experiment effectively with no erosion in the yields of the product (Fig. 6). This result showed high robustness and high efficiency of the iodinated hypercrosslinked polymers.

Table 4 Oxidation of diphenylmethanol^a

Entry	Catalyst	Conversion (%)	Yield (%)
1	None	2	0
2	HCP-H (1a)	3	0
3	HCP-I (2a)	100	80
4	PS-I ^b	11	7

^a Reaction conditions: diphenylmethanol (0.25 mmol), catalyst (0.05 mmol, 20 mol%), Oxone[®] (0.5 mmol, 2 equiv.) in MeCN (0.5 mL).

^b Iodinated polystyrene.

Conclusions

In summary, we have reported a synthesis of a novel material with iodine functional groups by functionalization of the surface of hypercrosslinked polymers. The method used mild reaction conditions without destroying the hypercrosslinkage in the polymers. Hypercrosslinked polymers with various substituents were iodinated under this method to give the iodinated polymers in high yields and high iodine incorporation. HCP-I was used as a heterogeneous catalyst for the oxidation of alcohols to give the corresponding ketone in high yields. The



catalyst can be recovered by simple filtration and reused with no deterioration in the yield of the product. Further application of the iodinated hypercrosslinked polymers is under investigation and will be reported in due course.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- P. B. Jagadhane, N. C. Jadhav, O. P. Herlekar and V. N. Telvekar, *Synth. Commun.*, 2015, **45**, 2130–2134.
- J.-X. Jiang and A. I. Cooper, in *Functional Metal-Organic Frameworks: Gas Storage, Separation and Catalysis*, ed. M. Schröder, Springer Berlin Heidelberg, Berlin, Heidelberg, 2010, pp.1–33, DOI: [10.1007/128_2009_5](https://doi.org/10.1007/128_2009_5).
- H. J. Mackintosh, P. M. Budd and N. B. McKeown, *J. Mater. Chem.*, 2008, **18**, 573–578.
- P. Pandey, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, M. G. Kanatzidis, J. T. Hupp and S. T. Nguyen, *J. Mater. Chem.*, 2011, **21**, 1700–1703.
- T. Ratvijitvech, *Polymers*, 2022, **14**, 2749.
- S. Ren, M. J. Bojdys, R. Dawson, A. Laybourn, Y. Z. Khimiyak, D. J. Adams and A. I. Cooper, *Adv. Mater.*, 2012, **24**, 2357–2361.
- A. Thomas, P. Kuhn, J. Weber, M.-M. Titirici and M. Antonietti, *Macromol. Rapid Commun.*, 2009, **30**, 221–236.
- T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9457–9460.
- J. Weber and A. Thomas, *J. Am. Chem. Soc.*, 2008, **130**, 6334–6335.
- N. A. Rakow, M. S. Wendland, J. E. Trend, R. J. Poirier, D. M. Paolucci, S. P. Maki, C. S. Lyons and M. J. Swierczek, *Langmuir*, 2010, **26**, 3767–3770.
- T. Ratvijitvech, *J. Polym. Environ.*, 2020, **28**, 2211–2218.
- T. Ratvijitvech and S. Na Pombejra, *Mater. Today Commun.*, 2021, **28**, 102617.
- O. K. Farha, A. M. Spokoyny, B. G. Hauser, Y.-S. Bae, S. E. Brown, R. Q. Snurr, C. A. Mirkin and J. T. Hupp, *Chem. Mater.*, 2009, **21**, 3033–3035.
- S. K. Kundu and A. Bhaumik, *ACS Sustainable Chem. Eng.*, 2015, **3**, 1715–1723.
- K.-Y. Yan, J.-Y. Chen, X.-Y. Li, Q. Wang and G.-C. Kuang, *Macromol. Chem. Phys.*, 2020, **221**, 1900553.
- V. M. Suresh, S. Bonakala, H. S. Atreya, S. Balasubramanian and T. K. Maji, *ACS Appl. Mater. Interfaces*, 2014, **6**, 4630–4637.
- N. B. McKeown and P. M. Budd, *Chem. Soc. Rev.*, 2006, **35**, 675–683.
- A. Li, Q. Zhang, G. Zhang, J. Chen, Z. Fei and F. Liu, *Chemosphere*, 2002, **47**, 981–989.
- K. Wang, W. Cui, Z. Bian, Y. Liu, S. Jiang, Y. Zhou and J. Wang, *Appl. Catal., B*, 2021, **281**, 119425.
- D. Jia, L. Ma, Y. Wang, W. Zhang, J. Li, Y. Zhou and J. Wang, *Chem. Eng. J.*, 2020, **390**, 124652.
- W. Zhang, F. Ma, L. Ma, Y. Zhou and J. Wang, *ChemSusChem*, 2020, **13**, 341–350.
- T. Dohi, N. Takenaga, A. Goto, A. Maruyama and Y. Kita, *Org. Lett.*, 2007, **9**, 3129–3132.
- W. Zhong, J. Yang, X. Meng and Z. Li, *J. Org. Chem.*, 2011, **76**, 9997–10004.
- T. Wirth, *Angew. Chem., Int. Ed.*, 2005, **44**, 3656–3665.
- S. Schäfer and T. Wirth, *Angew. Chem., Int. Ed.*, 2010, **49**, 2786–2789.
- M. Çelik, C. Alp, B. Coşkun, M. S. Gültekin and M. Balci, *Tetrahedron Lett.*, 2006, **47**, 3659–3663.
- Y.-B. Kang and L. H. Gade, *J. Am. Chem. Soc.*, 2011, **133**, 3658–3667.
- M. Fujita, M. Wakita and T. Sugimura, *Chem. Commun.*, 2011, **47**, 3983–3985.
- M. Fujita, H. Suzawa, T. Sugimura and T. Okuyama, *Tetrahedron Lett.*, 2008, **49**, 3326–3329.
- M. Fujita, Y. Ookubo and T. Sugimura, *Tetrahedron Lett.*, 2009, **50**, 1298–1300.
- M. Kirihara, S. Yokoyama, H. Kakuda and T. Momose, *Tetrahedron*, 1998, **54**, 13943–13954.
- M. Kirihara, T. Nishio, S. Yokoyama, H. Kakuda and T. Momose, *Tetrahedron*, 1999, **55**, 2911–2926.
- X. Li, Z. Xu, E. F. DiMauro and M. C. Kozłowski, *Tetrahedron Lett.*, 2002, **43**, 3747–3750.
- L.-H. Zhang, J. C. Chung, T. D. Costello, I. Valvis, P. Ma, S. Kauffman and R. Ward, *J. Org. Chem.*, 1997, **62**, 2466–2470.
- N. Okamoto, Y. Miwa, H. Minami, K. Takeda and R. Yanada, *Angew. Chem., Int. Ed.*, 2009, **48**, 9693–9696.
- H. R. Khatri and J. Zhu, *Chem. – Eur. J.*, 2012, **18**, 12232–12236.
- Z. Jia, E. Gálvez, R. M. Sebastián, R. Pleixats, Á. Álvarez-Larena, E. Martín, A. Vallribera and A. Shafir, *Angew. Chem., Int. Ed.*, 2014, **53**, 11298–11301.
- J. Y. Cha, Y. Huang and T. R. R. Pettus, *Angew. Chem., Int. Ed.*, 2009, **48**, 9519–9521.
- N. A. Braun, M. A. Ciufolini, K. Peters and E.-M. Peter, *Tetrahedron Lett.*, 1998, **39**, 4667–4670.



- 40 S. K. Alla, R. K. Kumar, P. Sadhu and T. Punniyamurthy, *Org. Lett.*, 2013, **15**, 1334–1337.
- 41 D. Liang, W. Yu, N. Nguyen, J. R. Deschamps, G. H. Imler, Y. Li, A. D. MacKerell, C. Jiang and F. Xue, *J. Org. Chem.*, 2017, **82**, 3589–3596.
- 42 M. Ngatimin, R. Frey, A. Levens, Y. Nakano, M. Kowalczyk, K. Konstas, O. E. Hutt and D. W. Lupton, *Org. Lett.*, 2013, **15**, 5858–5861.
- 43 K. Miyamoto, Y. Sakai, S. Goda and M. Ochiai, *Chem. Commun.*, 2012, **48**, 982–984.
- 44 J.-M. Chen, X.-M. Zeng and V. V. Zhdankin, *Synlett*, 2010, 2771–2774.
- 45 H. Togo and K. Sakuratani, *Synlett*, 2002, 1966–1975.
- 46 J.-M. Chen, X.-M. Zeng, K. Middleton, M. S. Yusubov and V. V. Zhdankin, *Synlett*, 2011, 1613–1617.
- 47 S. V. Ley, A. W. Thomas and H. Finch, *J. Chem. Soc., Perkin Trans. 1*, 1999, 669–672, DOI: [10.1039/A809799B](https://doi.org/10.1039/A809799B).
- 48 S. Abe, K. Sakuratani and H. Togo, *J. Org. Chem.*, 2001, **66**, 6174–6177.
- 49 T. Dohi, M. Ito, K. Morimoto, Y. Minamitsuji, N. Takenaga and Y. Kita, *Chem. Commun.*, 2007, 4152–4154, DOI: [10.1039/B708802G](https://doi.org/10.1039/B708802G).
- 50 J.-M. Chen, X.-M. Zeng, K. Middleton and V. V. Zhdankin, *Tetrahedron Lett.*, 2011, **52**, 1952–1955.
- 51 H. Tohma, H. Morioka, Y. Harayama, M. Hashizume and Y. Kita, *Tetrahedron Lett.*, 2001, **42**, 6899–6902.
- 52 R. Dawson, T. Ratvijitvech, M. Corker, A. Laybourn, Y. Z. Khimyak, A. I. Cooper and D. J. Adams, *Polym. Chem.*, 2012, **3**, 2034–2038.
- 53 D. R. Burfield and S.-C. Ng, *J. Chem. Educ.*, 1984, **61**, 917.
- 54 HCP-NO₂ (**1f**) was synthesized from HCP-H (**1a**) using nitration reaction (see ESI†).
- 55 J. Raymakers, H. Krysova, A. Artemenko, J. Čermák, S. S. Nicley, P. Verstappen, S. Gielen, A. Kromka, K. Haenen, L. Kavan, W. Maes and B. Rezek, *RSC Adv.*, 2018, **8**, 33276–33290.
- 56 H. F. Wang, X. Y. Deng, J. Wang, X. F. Gao, G. M. Xing, Z. J. Shi, Z. N. Gu, Y. F. Liu and Y. Zhao, *Acta Phys. Chim. Sin.*, 2004, **20**, 673.
- 57 N. Dwivedi, R. J. Yeo, N. Satyanarayana, S. Kundu, S. Tripathy and C. S. Bhatia, *Sci. Rep.*, 2015, **5**, 7772.
- 58 R. E. Priestley, A. Mansfield, J. Bye, K. Deplanche, A. B. Jorge, D. Brett, L. E. Macaskie and S. Sharma, *RSC Adv.*, 2015, **5**, 84093–84103.
- 59 A. V. Shchukarev and D. V. Korolkov, *Cent. Eur. J. Chem.*, 2004, **2**, 347–362.
- 60 C. Wilson, M. J. Main, N. J. Cooper, M. E. Briggs, A. I. Cooper and D. J. Adams, *Polym. Chem.*, 2017, **8**, 1914–1922.
- 61 R. Gomes and A. Bhaumik, *J. Solid State Chem.*, 2015, **222**, 7–11.

