



Title	Synthesis and properties of - conjugated porous polymers obtained with Mizoroki–Heck reaction of tetra vinyl cyclic siloxane with dibromo fluorene
Author(s)	Naga, Naofumi; Miyanaga, Tomoharu; Wang, Yuting; Nakano, Tamaki
Citation	Journal of Polymer Science, 58(17), 2301-2309 https://doi.org/10.1002/pol.20200268
Issue Date	2020-09-01
Doc URL	http://hdl.handle.net/2115/82647
Rights	This is the peer reviewed version of the following article: Naga, N, Miyanaga, T, Wang, Y, Nakano, T. Synthesis and properties of - conjugated porous polymers obtained with Mizoroki–Heck reaction of tetra vinyl cyclic siloxane with dibromo fluorene. J Polym Sci. 2020; 58: 2301– 2309, which has been published in final form at https://doi.org/10.1002/pol.20200268 . This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.
Type	article (author version)
Additional Information	There are other files related to this item in HUSCAP. Check the above URL.
File Information	manuscript_pol.20200268.pdf



[Instructions for use](#)

1 **Synthesis and properties of π - σ conjugated porous polymers obtained with**
2 **Mizoroki-Heck reaction of tetra vinyl cyclic siloxane with dibromo fluorene**
3
4
5
6

7 Naofumi Naga^{a,b}, Tomoharu Miyanaga^b, Yuting Wang^c Tamaki Nakano^{c,d}
8

9 ^aDepartment of Applied Chemistry, College of Engineering, Shibaura Institute of Technology,
10
11 3-7-5 Toyosu, Koto-ku, Tokyo 135-8548, Japan
12

13 ^bGraduate School of Engineering and Science, Shibaura Institute of Technology, 3-7-5 Toyosu,
14
15 Koto-ku, Tokyo 135-8548, Japan
16
17

18 ^c Institute for Catalysis and Graduate School of Chemical Sciences and Engineering, Hokkaido
19
20 University, N 21, W 10, Kita-ku Sapporo 001-0021, Japan
21
22

23 ^d Integrated Research Consortium on Chemical Sciences, Institute for Catalysis, Hokkaido
24
25 University, N 21, W 10, Kita-ku Sapporo 001-0021, Japan
26
27

28
29
30 Correspondence: Naofumi Naga, Department of Applied Chemistry, Materials Science Course,
31
32 College of Engineering, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo
33
34 135-8548, Japan. E-mail: nnaga@sic.shibaura-it.ac.jp
35
36
37
38
39

40 **(KEYWORDS:** porous polymer; Si-vinylene unit; optical properties)
41
42
43
44
45

46 **ABSTRACT**
47

48 σ - π Conjugated porous polymers were synthesized by the Mizoroki-Heck reaction of cyclic
49
50 siloxane with vinyl groups, 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane (TVMCTS), and
51
52 2,7-dibromo-9,9-dialkylfluorene (RFI) compounds, using a Pd catalyst in
53
54 *N,N*-dimethylformamide (DMF) at 100 °C. The reactions of TVMCTS in combination with
55
56 2,7-dibromo-9,9-dihexylfluorene (HFI), 2,7-dibromo-9,9-dioctylfluorene (OFI), and
57
58 2,7-dibromo-9,9-ethylhexylfluorene (EHFI) yielded porous polymers whose morphologies were
59
60
61
62
63
64
65

1 induced by phase separation during the network formation. The reactions in combination with
2 binary RFl systems, TVMCTS-HFl/OFl, and HFl/EHF1 systems, also yielded porous polymers.
3 Scanning electron microscope images showed porous structures, which were composed by
4 connected globules and/or isolated-deformed holes. The long and branching structure of the
5 alkyl side chains in RFl decreased Young's modulus of porous polymers in compression test.
6 The porous polymers showed emission derived from σ - π conjugated fluorene units on photo
7 excitation. An increase in monomer concentration in the reaction induced red shifts of the
8 emission bands of the porous polymer due to π -stacking of the fluorene units. The porous
9 polymers showed relatively high fluorescence quantum yields of about 0.2-0.3. Quantum yield
10 of the porous polymers with HFl decreased with increasing monomer concentration in the
11 reaction systems.
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28

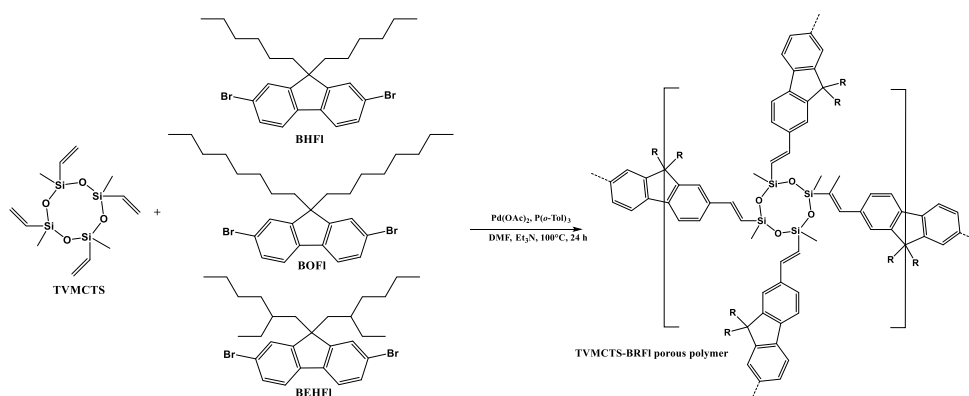
29 INTRODUCTION

30 Porous polymers have been intensively developed and are widely applied for separation filters,
31 columns for chromatograph, support of catalysts and so on.¹⁻⁵ The synthesis of such polymers is
32 generally accompanied by phase separation. We have been developing some porous polymers,
33 which are synthesized by addition reactions between multi-functional monomers as "joint unit"
34 sources, and α,ω -bifunctional comonomers, as "linker unit" sources, in various solvents. For
35 example, addition reaction of multifunctional thiol and diisocyanate in toluene,⁶ Michael
36 addition reaction of multifunctional acrylate and diamine or dithiol in dimethylsulfoxide,⁷ and
37 addition reaction of multifunctional phenol and divinyl ether compounds in acetonitrile⁸
38 successfully yielded porous polymers. The molecular design of network polymer based on the
39 "joint" and "linker" concept has thus been shown to be applicable to a wide variety of porous
40 polymers.
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56

57 Introduction of conjugated units in porous polymers would be important in their applications
58 based on photo-physical features, such as emitting device, sensor, and so on. Various
59
60
61
62
63
64
65

1 π -conjugated polymers with high photoluminescence quantum yield such as
2 poly(*p*-phenylene-vinylene), poly(thiophene), poly(*p*-phenylene), poly(fluorene),
3
4 poly(carbazole), and their copolymers have been developed for emissive polymeric
5
6 materials.⁹⁻¹² These π -conjugated polymers are synthesized by various coupling reactions. Some
7
8 σ - π -conjugated polymers containing Si-vinylene units in the main chain were synthesized by
9
10 the Mizoroki-Heck reaction of divinyl silane compounds and dibromo fluorene or dibromo
11
12 carbazole compounds using a Pd catalyst.¹³ We reported the synthesis of network polymers
13
14 having Si-vinylene units by the same reaction of a multi-functional cyclic siloxane compound
15
16 with vinyl groups, 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane (TVMCTS), and dibromo
17
18 fluorene compounds. The obtained network polymers showed emission derived from σ - π
19
20 conjugation induced by Si-vinylene.¹⁴ Although a possibility of formation of porous polymer
21
22 was suggested in a polymer of TVMCTS and 2,7-dibromo fluorene (without alkyl substituent),
23
24 the obtained polymer was somewhat rigid bulk and did not show clear porous morphology
25
26 through microscopic observation. It was difficult to remove the catalyst residues from the rigid
27
28 bulk polymer, the polymer was black derived from Pd residues. The quantum yield of the
29
30 polymer was too low to determine qualitatively caused by π -stacking of fluorene units without
31
32 alkyl substituent. On the other hand, a porous polymer was synthesized by thiol-ene reaction of
33
34 TVMCTS and multi-functional thiol compounds,¹⁵ which would suggest the possibility of
35
36 formation of porous polymers from TVMCTS as the joint molecule under proper conditions.
37
38 Formation of clear and controlled porous morphology with high porosity in the TVMCTS and
39
40 2,7-dibromo-9,9-dialkyl fluorene (RFl) network polymer should be usable to prepare the σ - π
41
42 conjugated porous polymers with high quantum yield. In this context, we examined
43
44 optimization of the reaction conditions and precise molecular design of the linker molecules to
45
46 obtain the porous polymers with emission property. In this paper, we report the synthesis of
47
48 porous polymers by the Mizoroki-Heck reaction of TVMCTS and RFl compounds using a Pd
49
50 catalyst. The reactions in combination with RFls having di-*n*-hexyl (HFl), di-*n*-octyl (OFl), and
51
52 di-2-ethyl-hexyl (EHFl) groups (Scheme 1) successfully yielded the porous polymers. Effects of
53
54
55
56
57
58
59
60
61
62
63
64
65

1 molecular structure and morphology on mechanical and emissive properties of the porous
2 polymers were investigated through compression test and photoluminescence (PL)
3 spectroscopy.
4
5
6
7
8
9



23 **SCHEME 1** Synthesis of σ - π conjugated porous polymers by the Mizoroki-Heck reaction of
24 TVMCTS with RFI.
25
26

27 **EXPERIMENTAL**

28 **Materials**

29
30
31
32
33
34 1,3,5,7-Tetravinyltetramethylsiloxane (TVMCTS) (Chisso Co., Ltd.) was used without further
35 purification. HFI, OFI, and EHFI were commercially obtained from Tokyo Chemical Industry
36 Co., Ltd., and used as received. Palladium(II) acetate ($\text{Pd}(\text{OAc})_2$) (Aldrich Chemical Co., Ltd.),
37 tri-*o*-tolylphosphine ($\text{P}(\text{o-Tol})_3$) (Kanto Chemical Co., Ltd.), triethylamine (NEt_3) (Kanto
38 Chemical Co., Ltd.), and *N,N*-dimethylformamide (DMF) (dehydrated grade, Kanto Chemical
39 Co., Ltd.) were commercially obtained and used as received.
40
41
42
43
44
45
46
47
48
49

50 **Synthesis of porous polymers**

51
52 Polymerization was carried out in a 10 mL ampoule tube. A reaction of TVMCTS with HFI
53 (monomer concentration: 30 wt%) is described as a reference. HFI (1 mmol), $\text{P}(\text{o-Tol})_3$ (0.12
54 mmol), and $\text{Pd}(\text{OAc})_2$ (0.02 mmol) were added to the ampoule tube under a nitrogen
55 atmosphere. After the addition of TVMCTS (0.5 mmol), DMF (2.0 mL), and NEt_3 (1.5 mmol),
56
57
58
59
60
61
62
63
64
65

1 the ampoule tube was sealed by burning off. The reaction was heated, standing without stirring
2
3 in a heater equipped with an aluminum block, at 100°C for 24 h. The ample tube was carefully
4
5 and safety broken by a pair of pliers to take out the polymer. The resulting polymer was washed
6
7 with a large excess of DMF in a microwave washer, and the solvent was replaced with methanol
8
9 by immersion. The polymer obtained was dried under the atmospheric conditions for 24 h
10
11 following in vacuo at room temperature for 6 h. Other porous polymers were synthesized using
12
13 the same procedures. The molar ratio of vinyl group to Br was fixed 1.0 in all the experiments.
14
15
16
17
18

19 **Analytical procedures**

20
21 FT-IR spectra of porous polymers were recorded on a Jasco FT/IR-410 or Shimadzu FTIR-8400
22
23 spectrometer in pulse Fourier transform mode. The samples were prepared in KBr pressed discs
24
25 or between KBr-Real Crystal IR-Card and Slip (International Crystal Laboratories). Scanning
26
27 electron microscopy (SEM) images of the porous polymers were acquired by a JEOL
28
29 JSM-7610F microscope with a LEI detector at an acceleration voltage of 3.0 kV. Surface area of
30
31 the porous polymers were measured by nitrogen sorption using an Autosorb 6AG
32
33 (Quantachrome), and determined by Brunauer-Emmett-Teller (BET) equation. Mechanical
34
35 properties of the gels were investigated by the compression test with Tensilon RTE-1210
36
37 (ORIENTEC Co. LTD.). The test samples were cut to 0.6-0.7 cm cube, and pressed at a rate of
38
39 0.5 mm/min at room temperature. Absorbance spectra were measured with a JASCO V-550 and
40
41 V-570 spectrophotometers. Photoluminescence (PL) spectroscopy was investigated using a
42
43 JASCO FP-8500 spectrophotomere with excitation at 270 nm (λ_{max} of the absorption
44
45 spectroscopy of 9,9-dialkyl fluorenes). The measurement was conducted at room temperature,
46
47 and the sample was set in a quartz cell for powder sample without pressure. Absolute quantum
48
49 yield of the porous polymers was measured by a C9920-02G (Hamamatsu Photonics K.K.)
50
51 spectrophotometer using an integration sphere with excitation at 270 nm (integration: 440-640
52
53 nm).
54
55
56
57
58
59
60
61
62
63
64
65

RESULTS AND DISCUSSION

The Mizoroki-Heck reaction of TVMCTS in combination with HFl was investigated with Pd(OAc)₂ catalyst in DMF at 100 °C. The reaction systems containing 20, 30, and 40 wt% monomers yielded porous polymers. A soft plated polymer was obtained in the reaction containing 10 wt% monomers. Mixture of gel and solid portions was formed in the reactions containing 50 wt% monomers. Polymerizations of TVMCTS with OFI or EHF1 successfully yielded the porous polymers almost quantitatively. The porous polymers were also obtained from the reactions of TVMCTS in combination with binary HFl/OFI, and HFl/EHF1 (equivalent molar feed ratio) systems. By contrast, the polymerizations of TVMCTS with RFl having small alkyl substituent, methyl, and ethyl, yielded none-porous rigid bulk polymers. The reaction systems with large alkyl substituted RFl, decyl, dodecyl, formed none-porous soft precipitates. The most likely explanation for these results is that bulkiness of the alkyl substituent of RFl would affect state of π -stacking of RFl units in the polymer network. The small alkyl substituent should not hinder the π -stacking of RFl units with high interaction and yielded rigid structure. By contrast, the large alkyl substituent of RFl would prevent from stacking of RFl units, which should decrease the rigidity of the network. The alkyl substituent with C6-C8 would induce moderate π -stacking of RFl units, which should be suitable to form the porous polymers.

FT-IR spectra of the TVMCTS, HFl, and TVMCTS-HFl porous polymer are shown in Figure 1 (a), (b), and (c), respectively. Absorption peaks derived from vinyl group in TVMCTS, at around 960 and 3055 cm⁻¹, were disappeared in TVMCTS-HFl porous polymer. The broad peak derived from Si-O-Si unit of TVMCTS was detected at around 1050 cm⁻¹. The peaks derived from phenyl groups of fluorene unit were detected at around 1450 cm⁻¹ (C=C stretching of phenyl) and at around 790 cm⁻¹ (CH bending of phenyl). The peaks derived from unsaturated C=C unit connected to Si and Si-C unit were detected at around 1600 cm⁻¹ and 1260 cm⁻¹, respectively. These results clarify the formation of the network polymers by the Mizoroki-Heck reaction of TVMCTS in combination with HFl. TVMCTS-OFI and TVMCTS-EHF1 porous polymers showed similar profile in their FT-IR spectra.¹⁶

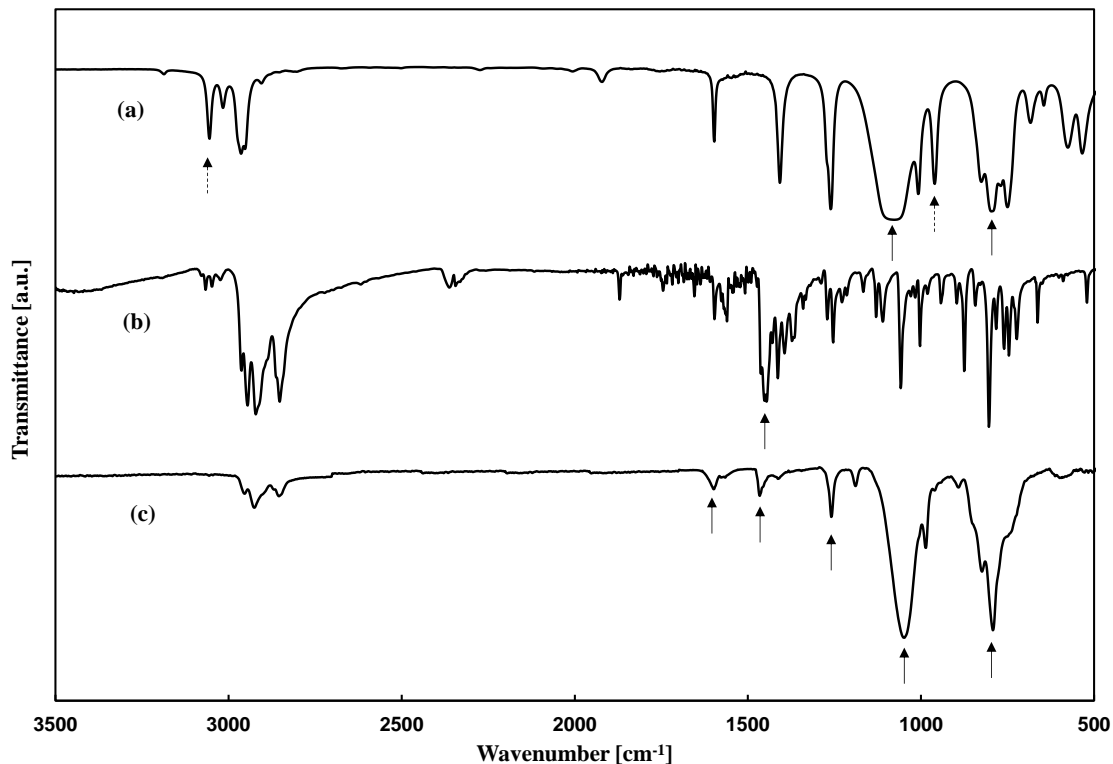
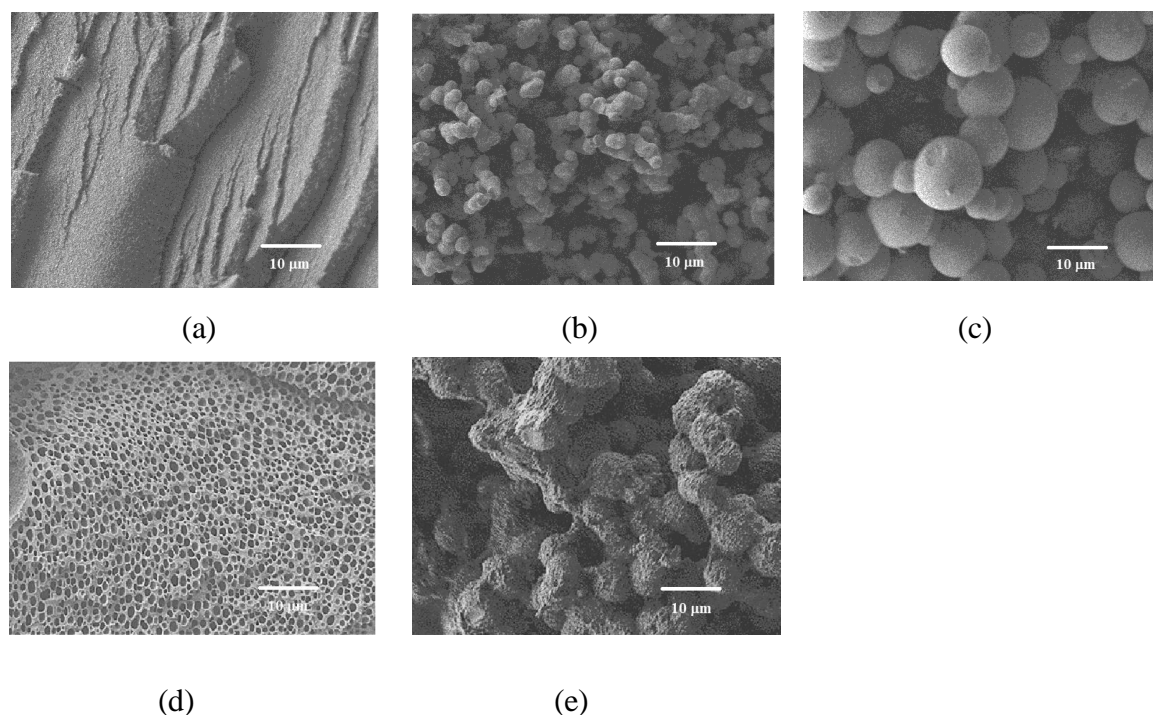


FIGURE 1 FT-IR spectra of (a) TVMCTS-HFl, (b) TVMCTS-OFl, and (c) TVMCTS-EHFl polymers, monomer concentration in the reaction system: 20 wt%.

SEM images of the TVMCTS-HFl polymers are shown in Fig. 2. The morphology of the polymers was strongly affected by the monomer concentration in the reaction system. The porous polymer obtained from the reaction containing 10 wt% of monomer (TVMCTS-HFl 10 wt%) formed layer structure about 3 μm thickness, as shown in Figure 2 (a). The volume of the resulting polymer of the reaction was much lower (plate structure) than that of the other porous polymers obtained from the reactions with higher monomer concentrations. The results indicate that the reaction system containing 10 wt% monomers could not form the porous structure in the resulting polymer. An increase in monomer concentration in the reaction system induced the porous structure formed by connected globules about 2 μm (TVMCTS-HFl 20 wt%) or 3-10 μm (TVMCTS-HFl 30 wt%) diameters, as shown in Figure 2 (b) and (c). Further increase of the monomer concentration in the reaction system, 40 wt%, yielded the porous polymer (TVMCTS-HFl 40 wt%) composed by isolated holes about 1 μm diameter, as shown in Fig. 2

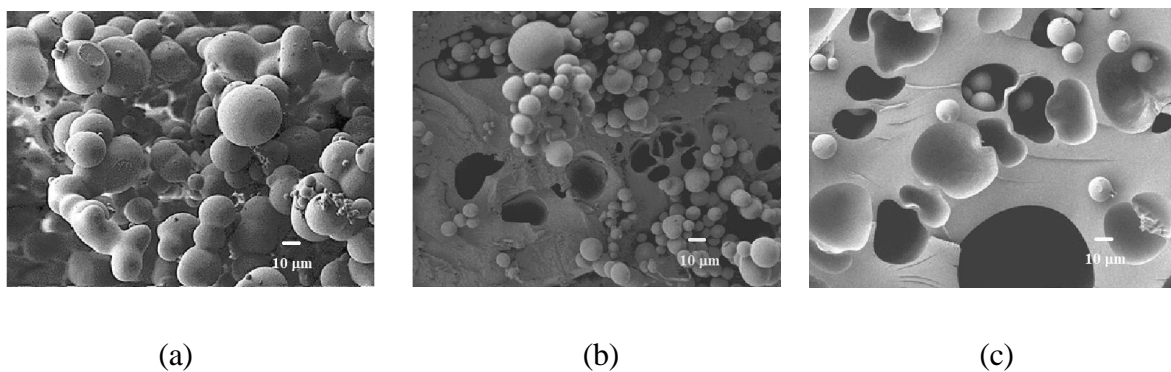
1 (c). The monomer concentration in these reaction systems should transfer the phase separation
2 state. The TVMCTS-HFI 20 and 30 wt% porous polymers would be formed at the late stage of
3 spinodal decomposition, as previously reported.⁷ The morphology of isolated holes observed in
4 the TVMCTS-HFI 40 wt% porous polymer would be derived from highly internal phase
5 emulsion (HIPE). Increase of the monomer concentration would induce formation of the
6 emulsion in the reaction system caused by change of the solubility parameter of the total
7 reaction system. The reaction at 80 °C also yielded the porous polymer in 1-week reaction. The
8 porous polymer showed connected globules with rough surface, as shown in Figure 2 (e). Slow
9 reaction rate should cause inhomogeneity on the surface of the globules.
10
11
12
13
14
15
16
17
18
19
20

21 Related surface area of TVMCTS-HFI 20 wt% porous polymer (run 2) determined by BET
22 method was less than limit of detection, less than 2 m²/g. The small surface was derived from
23 not micro-porous but the macro-porous structure of the porous polymer.
24
25
26
27
28
29
30



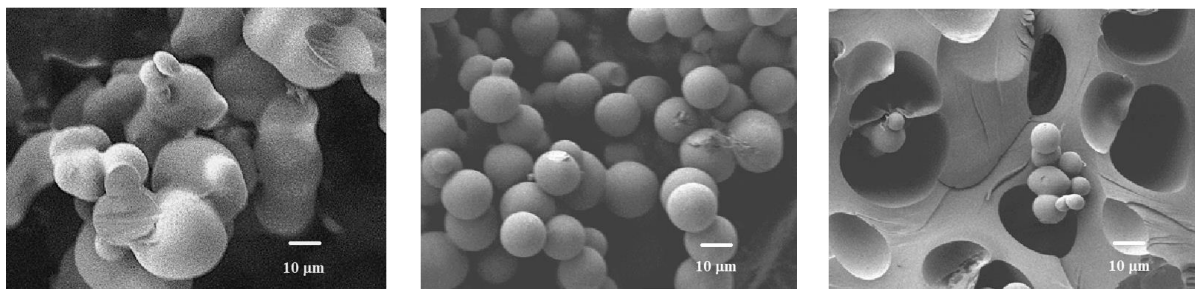
55 **FIGURE 2** SEM images of TVMCTS-HFI polymers obtained from the reaction systems
56 containing (a) 10 wt%, (b) 20 wt%, (c) 30 wt%, and (d) 40 wt% monomer at 100 °C in 24 h,
57 and (e) 20 wt% monomer at 80 °C in 1 week.
58
59
60
61
62
63
64
65

1 Figure 3 shows SEM images of the TVMCTS-OFl polymers. The TVMCTS-OFl polymer
2 obtained from the reaction containing 20 wt% of monomers formed porous polymer composed
3 by the connected globules ranged from 5 to 40 μm diameter. By contrast, the globules and
4 deformed isolated holes were co-existed in the TVMCTS-OFl 30 and 40 wt% porous polymers.
5 The hole structure would be derived from HIPE, as observed in the TVMCTS-HFl 40 wt%
6 porous polymer. The number of globules decreased with increasing in the monomer
7 concentration of the reaction system. These results indicate that the increase of the monomer
8 concentration would transfer the phase separation state from spinodal decomposition to HIPE.
9
10
11
12
13
14
15
16
17
18
19
20



34 **FIGURE 3** SEM images of TVMCTS-OFl porous polymers obtained from the reaction
35 systems containing (a) 20 wt%, (b) 30 wt%, and (c) 40 wt% monomer at 100 °C in 24 h.
36
37
38

39
40 SEM images of the TVMCTS-EHFl polymers are shown in Figure 4. The TVMCTS-EHFl 20
41 and 30 wt% polymers showed porous structure composed by the connected globules ranged
42 from 10 to 50 μm diameter. The TVMCTS-EHFl 40 wt% porous polymer showed isolated
43 holes about 30-50 μm diameter and small number of globules less than 10 μm diameter. The
44 reaction system containing 40 wt% monomers should induce HIPE as observed in the
45 TVMCTS-OFl 40 wt% porous polymer.
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65



(a)

(b)

(c)

FIGURE 4 SEM images of TVMCTS-EHF1 porous polymers obtained from the reaction solutions containing (a) 20 wt%, (b) 30 wt%, and (c) 40 wt% monomer at 100 °C in 24 h.

The reactions of TMCTS in combination with binary HF1/OF1 and HF1/EHF1 (equivalent molar feed ratio) systems also yielded the porous polymers. SEM images of the TVMCTS-HF1/OF1 or TVMCTS-HF1/EHF1 porous polymers are summarized in Figure 5. The TVMCTS-HF1/OF1 or TVMCTS-HF1/EHF1 20 wt% porous polymer showed morphology composed by the connected globules less than 10 μm diameter. The TVMCTS-HF1/OF1 or TVMCTS-HF1/EHF1 30 wt% porous polymer showed co-existence of small and large globules about 5 μm and 50-100 μm diameters, respectively. One explanation for the results may be inhomogeneity of the phase separation in those reactions. The small globules would be formed at the early stage of the polymerization under high monomer concentration. Monomer concentration in the reaction solutions decreased with increasing in polymerization time, and large globules would be yielded at the late stage of the polymerization. Coexistence of different monomer concentrations in the reaction system derived from phase equilibrium might be another account.

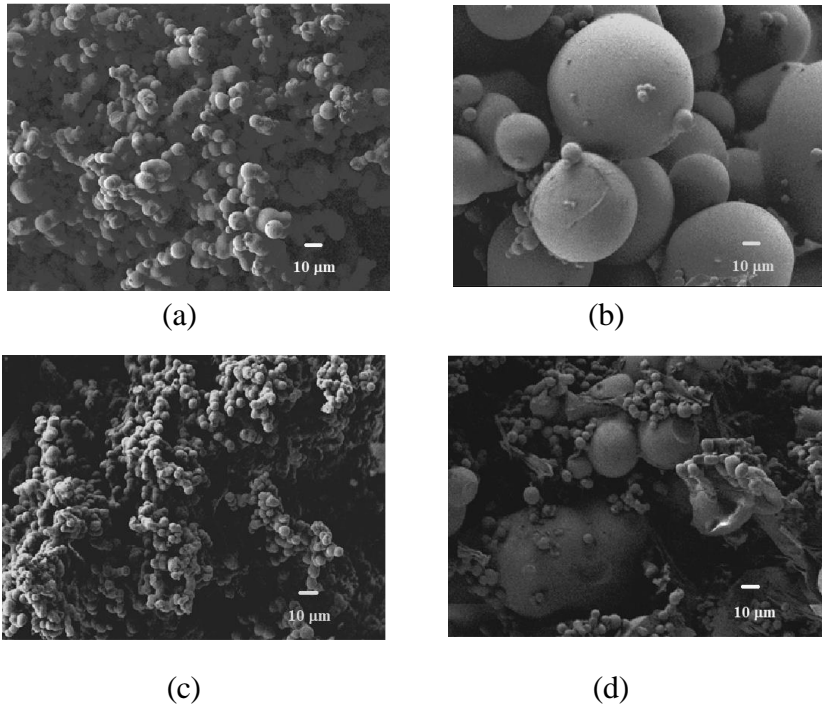


FIGURE 5 SEM images of TVMCTS-HFI/OFl (a, b) and TVMCTS-HFI/EHFl (c, d) porous polymers obtained from the reaction solutions containing (a) 20 wt%, (b) 30 wt%, (c) 20 wt%, and (d) 30 wt% monomer at 100 °C in 24 h.

Mechanical properties of the porous polymers were investigated by compression test. The porous polymers were not breakable under the compression of 50 N. Figure 6 shows stress-strain curves of the TVMCTS-HFI 20, 40 wt%, TVMCTS-OFl 20 wt%, and TVMCTS-EHFl 20 wt% porous polymers. The Young's modulus values of the TVMCTS-RFl 40 wt% porous polymers were much higher than those of the TVMCTS-RFl 20 wt% porous polymers, as summarized in Table 1. The morphology composed by isolated holes in the TVMCTS-RFl 40 wt% porous polymers should induce rigid features of the porous polymers. The Young's modulus value of the porous polymers obtained with OFl or EHFl was lower than that of the polymer with HFl. Bulkiness of alkyl side chains in OFl and EHFl would make the porous polymer soft. The TVMCTS-HFI/OFl and TVMCTS-HFI/EHFl porous polymers showed similar Young's modulus values to those of the TVMCTS- OFl and TVMCTS-EHFl porous polymers.

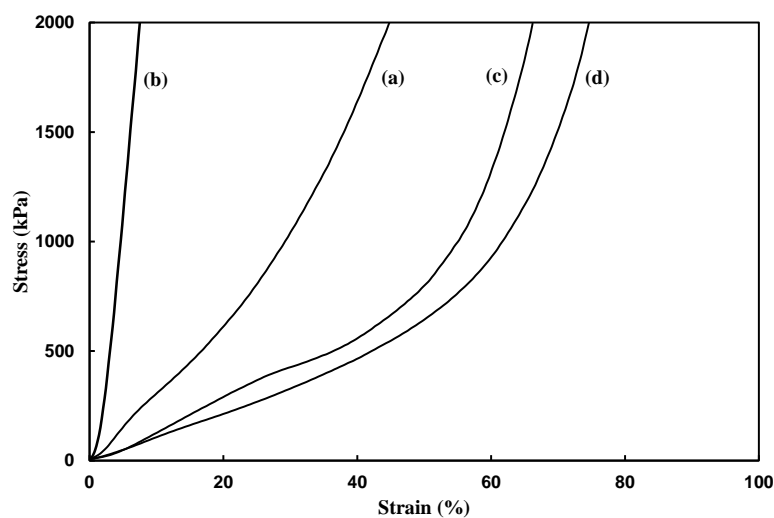


FIGURE 6 Stress-strain curves of (a) TVMCTS-HFI 20 wt%, (b) TVMCTS-HFI 40 wt%, (c) TVMCTS-OFI 20 wt%, and (d) TVMCTS-EHFI 20 wt% porous polymers.

TABLE 1 Structure and properties of TVMCTS-RFI polymers^a

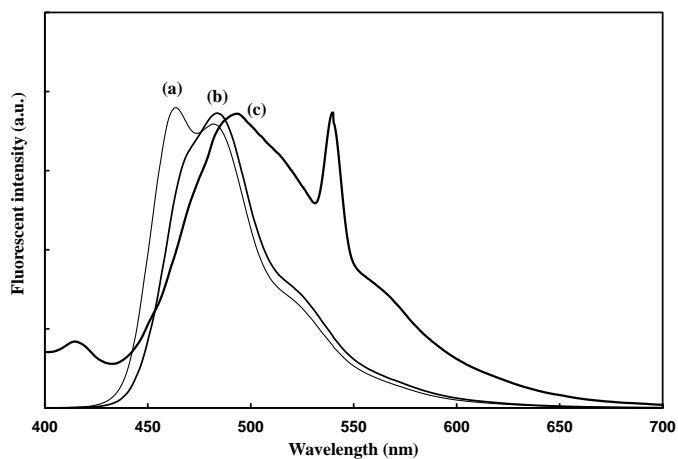
Run	RFI	Monomer concentration n wt%	Surface structure	Young's modulus kPa	Emission ^c nm		Quantum yield
					$\lambda_{\max 0}$	$\lambda_{\max 1}$	
1	HFI	10	layer				
2	HFI	20	globule	31.0	464	482	0.25
3	HFI	30	globule	37.4		484	0.19
4	HFI	40	hole	231.5		493	0.10
5 ^b	HFI	20	globule				
6	OFI	20	globule	9.9		485	0.16
7	OFI	30	hole& globule			491	0.19
8	OFI	40	hole& globule	107.7		494	0.15
9	EHFI	20	globule	9.8	470	491	0.13
10	EHFI	30	globule			492	0.15
11	EHFI	40	hole& globule	104.8		495	0.13
12	HFI/OFI	20	globule	9.5	465	483	0.27
13	HFI/OFI	30	globule			490	0.09
14	HFI/EHFI	20	globule	7.6	469	485	0.33
15	HFI/EHFI	30	globule		470	489	0.09

^a Conditions: RFI (1 mmol), (runs 10, 11: HFI/OFI = 0.5/0.5 mmol/mmol, runs 12, 13: HFI/EHFI = 0.5/0.5 mmol), P(*o*-Tol)₃ (0.12 mmol), Pd(OAc)₂ (0.02 mmol), TVMCTS (0.5 mmol), NEt₃ (1.5 mmol), solvent: DMF, 100 °C in 24 h (^b run 5: 80°C in 1 week). ^c Emission from 0-0 ($\lambda_{\max 0}$) and 0-1 ($\lambda_{\max 1}$) singlet transition excited with 270 nm.

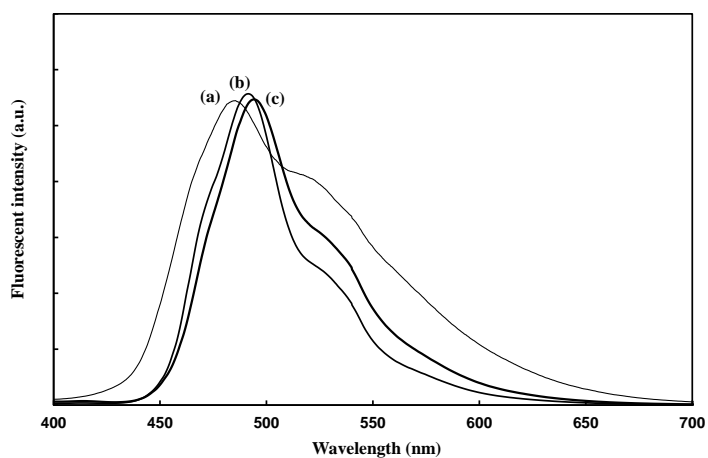
Emissive features of the porous polymers were studied using PL spectroscopy.¹⁷ Normalized PL spectra of the TVMCTS-RFI porous polymers are shown in Figure 7. The results are

1 summarized in Table 1. All the porous polymers showed emission bands at around 490, and 535
2 nm assigned to 0-1, and 0-2 intrachain singlet transitions, respectively. In the case of the
3 TVMCTS-HFI and TVMCTS-EHFI 20 wt% porous polymers, an emission band at around 470
4 nm assigned to 0-0 intrachain singlet transition was detected. By contrast, the TVMCTS-OFI 20
5 wt% porous polymer did not show the corresponding emission. One explanation of the results is
6 that the aggregation of the dioctyl fluorene units would be accelerated even in the
7 TVMCTS-OFI reaction system with low (20 wt%) monomer concentration. The aggregation of
8 dioctyl fluorene units was reported in poly(9,9-di-n-octyl fluorene-2,7-diyl) solutions.¹⁸⁻²⁰
9 Similar aggregation of dioctyl fluorene units may occur in the TVMCTS-OFI 20 wt%. The
10 emission band at around 470 nm was not observed in the TVMCTS-HFI and TVMCTS-EHFI 30
11 and 40 wt% porous polymers. Increasing of the monomer concentration in the reaction
12 systems would induce aggregation of the fluorene units, which would disappear the emission
13 from 0-0 intrachain singlet transition, and the state would be fixed during the polymerization.²¹
14 An increase of monomer concentration in the reaction systems caused slight red shifts of the
15 emission bands at around 490 nm in the resulting porous polymers. The red shifts would be
16 derived from π -stacking of fluorene units in the porous polymers as observed in the
17 corresponding liner polymers.¹³

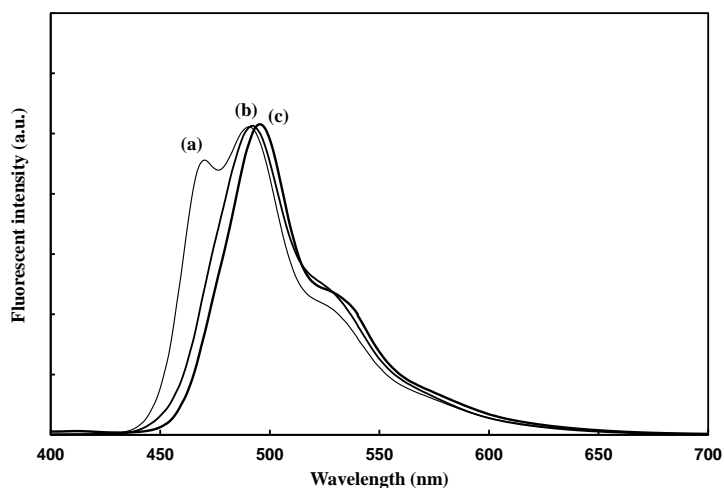
18 The porous polymers obtained from binary HFI/OFI and HFI/EHFI systems, monomer
19 concentration in the reaction solution: 20, 30 wt%, showed emission band assigned 0-1
20 intrachain singlet transition ranged from 483 nm to 490 nm.²² Both the TVMCTS-HFI/EHFI 20
21 and 30 wt% porous polymers showed the emission band at around 470 nm assigned 0-0
22 intrachain singlet transition. By contrast, the TVMCTS-HFI/OFI 30 wt% porous polymer did
23 not show the corresponding emission. Existing of OFI would effectively disappear the emission
24 derived from 0-0 intrachain singlet transition, as observed in the TVMCTS-OFI porous
25 polymer.



(i)



(ii)



(iii)

FIGURE 7 PL spectra of (i) TVMCTS-HFI, (ii) TVMCTS-OFl, and (iii) TVMCTS-EHFl porous polymers, monomer concentration in the reaction solution: (a) 20 wt%, (b) 30 wt%, and (c) 40 wt%.

1
2
3 Absolute quantum yield of the porous polymers was measured using PL method. The quantum
4
5 yields are summarized in Table 1. The porous polymers obtained from the reaction solutions
6
7 containing 20 wt% monomers showed relatively high quantum yield about 0.2. The
8
9 TVMCTS-HfI/OFl and TVMCTS-HfI/EHfI porous polymers showed higher quantum yield
10
11 than the TVMCTS-HfI porous polymer. The binary RfI system would prevent formation
12
13 of the π -stacking of fluorene units, which induces quenching of the emission. In the case of the
14
15 TVMCTS-HfI porous polymer, the quantum yield decreased with increasing in the monomer
16
17 concentration in the reaction systems. The similar tendency was observed in the
18
19 TVMCTS-HfI/OFl and TVMCTS-HfI/EHfI porous polymers. By contrast, the clear relation
20
21 between the quantum yield and the monomer concentration in the reaction system was not
22
23 observed in the TVMCTS-OFl and TVMCTS-EHfI porous polymers. These results indicate
24
25 that the monomer concentration in the reaction systems containing HfI affected the quantum
26
27 yield of the resulting porous polymers. Poly(9,9-di-n-hexyl fluorene-2,7-diyl) solutions with
28
29 high concentration show clear concentration quenching.²³ One explanation of the present results
30
31 is that the concentration quenching, which would be occurred in the solution state before phase
32
33 separation in the resection system, should reflect to the emission of the resulting porous
34
35 polymers.
36
37
38
39
40
41
42
43

44 CONCLUSIONS

45
46 The Mizoroki-Heck reaction of TVMCTS and HfI, OFl, and EHfI at 100 °C in DMF
47
48 successfully yielded the porous polymers. The porous polymers were preferentially formed in
49
50 the reaction solutions containing 20-40 wt% monomers. The binary RfI systems, HfI/OFl or
51
52 HfI/EHfI, also yielded the corresponding porous polymers. The monomer concentration of the
53
54 reaction systems strongly affected the morphologies, mechanical properties, and emission bands of
55
56 the resulting porous polymers. The increase of the monomer concentration tended to transfer the
57
58 morphology from connected globules to isolated holes. The porous polymers showed
59
60
61
62
63
64
65

1 emission bands at around 490, and 535 nm assigned to 0-1, and 0-2 intrachain singlet transition
2 of the σ - π conjugated fluorene units, respectively. The TVMCTS-HFl, EHFl 20 wt% porous
3 polymers showed the emission at 470 nm derived from 0-0 intrachain singlet transition of the
4 fluorene units. The porous polymers, especially obtained from the binary RFl systems, showed
5 relatively high quantum yield.
6
7

8
9
10
11 The present synthetic method, the Mizoroki-Heck reaction of multi-functional siloxane
12 compounds having vinyl groups and RFl, is useful to prepare the σ - π conjugated porous
13 polymers containing Si-vinylene units with high quantum yield. The obtained porous polymers
14 would be widely usable due to their features: porosity, photophysical properties, thermal
15 stability, and chemical resistance. Furthermore, dissociation of the globules in the porous
16 polymers would yield micro emissive micro-particles. Studies on applications of the porous
17 polymers are under way, and the results will be reported elsewhere.
18
19
20
21
22
23
24
25
26
27
28
29

30 REFERENCES AND NOTES

31
32
33 **1** Wu, D.; Xu, F.; Sun, B.; Fu, R.; He, H.; Matyjaszewski, K. *Chem Rev* 2012, 112, 3959–4015.

34
35 **2** Wu, J.; Xu, F.; Li, S.; Ma, P.; Zhang, X.; Liu, Q.; Fu, R.; Wu, D. *Adv Mater* 2019, 31.

36
37 **3** Tan, L.; Tan, B. *Chem Soc Rev* 2017, 46, 3322-3356.

38
39 **4** Ahmed, D. S. ; El-Hiti, G. A.; Yousif, E.; Ali, A. A.; Hameed, A. S. *J Polym Res* 2018, 25, 75.

40
41 **5** Hentze, H. P.; Antonietti, M. *Rev in Molecular Biotechnol* 2002, 90 27-53.

42
43 **6** Naga, N.; Michida, R.; Kudo, S.; Nagami, Y.; Moriyama, K.; Nageh, H.; Furukawa, H.;
44 Nakano, T. *Mater Today Commun* 2019, 18, 153-162.

45
46 **7** Naga, N.; Fujioka, S.; Inose, D.; Ahmed, K.; Nageh, H.; Nakano, *RSC Adv* 2020, 10, 60-69.

47
48 **8** Naga, N.; Hasegawa, K.; Nageh, H.; Nakano, T. *Polym Bull* 2019.

49
50 **9** Morin, P. O.; Bura, T.; Leclerc, M. *Mater Horiz* 2016, 3, 11-20.

51
52 **10** Feast, W. J.; Tsibouklis, J.; Pouwer, K. L.; Groenendaal, L., Meijer, E. W. *Polymer* 1996, 37,
53 5017-5047.

54
55 **11** Skotheim, T.A.; Reynolds, J. Eds., *Conjugated Polymers: Theory, Synthesis, Properties, And*

1 Characterization (Handbook of Conducting Polymers, Fourth Edition), CRC Press 2006.

2
3 **12** Barford, W. Ed., Electronic and Optical Properties of Conjugated Polymers, Oxford U. Press,
4
5 New York, 2005.

6
7 **13** Naga, N.; Tagaya, N.; Noda, H.; Imai, T.; Tomoda, H. J Polym Sci Part A Polym Chem 2008,
8
9 46, 4513-4521.

10
11 **14** Naga, N.; Sugano, Y.; Senda, A. Int J Chem 2017, 9, 1-9.

12
13 **15** Liu, Z.; Ou, J.; Lin, H.; Liu, Z.; Wang, H.; Dong, J.; Zou, H. Chem Commun 2014, 50,
14
15 9288-9290.

16
17 **16** FT-IR spectra of TVMCTS-OFl and TVMCTS-EHF1 porous polymers are available in
18
19 Supporting Information.

20
21 **17** UV-vis spectrum TVMCTS-OFl porous polymer is available in Supporting Information.

22
23 **18** Perevedentsev, A.; Stavinou, P. N.; Bradle, D. D. C.; Smith, P. J Polym Sci Part B Polym
24
25 Phys 2015, 53, 1481-1491.

26
27 **19** Xu, L.; Zhang, J.; Peng, J.; Qiu, F. J Polym Sci Part B Polym Phys 2015, 53, 633-639.

28
29 **20** Perevedentsev, A.; Chander, N.; Kim, J. S.; Bradley D. D. C. J Polym Sci Part B Polym Phys
30
31 2016, 54, 1995-2006.

32
33 **21** Neher, D. Macromol Rapid Commun 2001, 22, 1365-1385.

34
35 **22** PL spectra of TVMCTS-HFl/OFl and TVMCTS-HFl/EHF1 porous polymers are available in
36
37 Supporting Information.

38
39 **21** Naga, N.; Miyanaga, T.; Furukawa, H. J Polym Sci Part A Polym Chem 2014, 52, 973-984.

40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Graphical Abstract

Synthesis and properties of π - σ conjugated porous polymers obtained with Mizoroki-Heck reaction of tetra vinyl cyclic siloxane with dibromo fluorene

Naofumi Naga^{a,b}, Tomoharu Miyanaga^b, Yuting Wang^c Tamaki Nakano^{c,d}

The Mizoroki-Heck reaction of cyclic siloxane with vinyl groups, 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane (TVMCTS), and 2,7-dibromo-9,9-dialkylfluorene (RFI, R: hexyl, octyl, ethylhexyl) compounds, using a Pd catalyst in *N,N*-dimethylformamide successfully yielded π - σ conjugated porous polymers induced by phase separation during the network formation. The polymerization conditions affected the morphology of the porous structure with connected globules and/or isolated-deformed holes. The porous polymers showed emission derived from π - σ conjugated fluorene and relatively high fluorescence quantum yields

