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

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(KEYWORDS: porous polymer; Si-vinylene unit; optical properties)

ABSTRACT

σ - π Conjugated porous polymers were synthesized by the Mizoroki-Heck reaction of cyclic siloxane with vinyl groups, 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane (TVMCTS), and 2,7-dibromo-9,9-dialkylfluorene (RFl) compounds, using a Pd catalyst in *N,N*-dimethylformamide (DMF) at 100 °C. The reactions of TVMCTS in combination with 2,7-dibromo-9,9-dihexylfluorene (HFl), 2,7-dibromo-9,9-dioctylfluorene (OFl), and 2,7-dibromo-9,9-ethylhexylfluorene (EHFl) yielded porous polymers whose morphologies were

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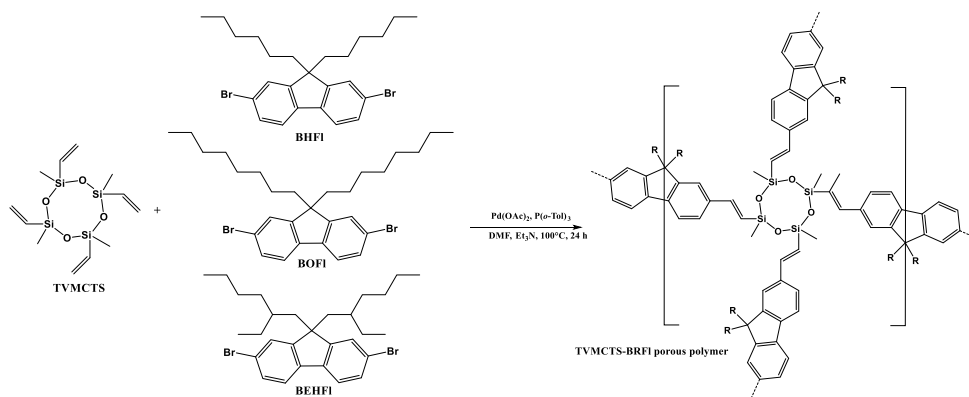
29 INTRODUCTION

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31 Porous polymers have been intensively developed and are widely applied for separation filters,
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33 columns for chromatograph, support of catalysts and so on.¹⁻⁵ The synthesis of such polymers is
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35 generally accompanied by phase separation. We have been developing some porous polymers,
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37 which are synthesized by addition reactions between multi-functional monomers as "joint unit"
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39 sources, and α,ω -bifunctional comonomers, as "linker unit" sources, in various solvents. For
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41 example, addition reaction of multifunctional thiol and diisocyanate in toluene,⁶ Michael
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43 addition reaction of multifunctional acrylate and diamine or dithiol in dimethylsulfoxide,⁷ and
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45 addition reaction of multifunctional phenol and divinyl ether compounds in acetonitrile⁸
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47 successfully yielded porous polymers. The molecular design of network polymer based on the
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49 "joint" and "linker" concept has thus been shown to be applicable to a wide variety of porous
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51 polymers.
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57 Introduction of conjugated units in porous polymers would be important in their applications
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59 based on photo-physical features, such as emitting device, sensor, and so on. Various
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π -conjugated polymers with high photoluminescence quantum yield such as poly(*p*-phenylene-vinylene), poly(thiophene), poly(*p*-phenylene), poly(fluorene), poly(carbazole), and their copolymers have been developed for emissive polymeric materials.⁹⁻¹² These π -conjugated polymers are synthesized by various coupling reactions. Some σ - π -conjugated polymers containing Si-vinylene units in the main chain were synthesized by the Mizoroki-Heck reaction of divinyl silane compounds and dibromo fluorene or dibromo carbazole compounds using a Pd catalyst.¹³ We reported the synthesis of network polymers having Si-vinylene units by the same reaction of a multi-functional cyclic siloxane compound with vinyl groups, 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane (TVMCTS), and dibromo fluorene compounds. The obtained network polymers showed emission derived from σ - π conjugation induced by Si-vinylene.¹⁴ Although a possibility of formation of porous polymer was suggested in a polymer of TVMCTS and 2,7-dibromo fluorene (without alkyl substituent), the obtained polymer was somewhat rigid bulk and did not show clear porous morphology through microscopic observation. It was difficult to remove the catalyst residues from the rigid bulk polymer, the polymer was black derived from Pd residues. The quantum yield of the polymer was too low to determine qualitatively caused by π -stacking of fluorene units without alkyl substituent. On the other hand, a porous polymer was synthesized by thiol-ene reaction of TVMCTS and multi-functional thiol compounds,¹⁵ which would suggest the possibility of formation of porous polymers from TVMCTS as the joint molecule under proper conditions. Formation of clear and controlled porous morphology with high porosity in the TVMCTS and 2,7-dibromo-9,9-dialkyl fluorene (RFl) network polymer should be usable to prepare the σ - π conjugated porous polymers with high quantum yield. In this context, we examined optimization of the reaction conditions and precise molecular design of the linker molecules to obtain the porous polymers with emission property. In this paper, we report the synthesis of porous polymers by the Mizoroki-Heck reaction of TVMCTS and RFl compounds using a Pd catalyst. The reactions in combination with RFls having di-*n*-hexyl (HFl), di-*n*-octyl (OFl), and di-2-ethyl-hexyl (EHFl) groups (Scheme 1) successfully yielded the porous polymers. Effects of

molecular structure and morphology on mechanical and emissive properties of the porous polymers were investigated through compression test and photoluminescence (PL) spectroscopy.



SCHEME 1 Synthesis of σ - π conjugated porous polymers by the Mizoroki-Heck reaction of TVMCTS with RFl.

EXPERIMENTAL

Materials

1,3,5,7-Tetravinyltetramethylsiloxane (TVMCTS) (Chisso Co., Ltd.) was used without further purification. HFl, OFl, and EHFl were commercially obtained from Tokyo Chemical Industry Co., Ltd., and used as received. Palladium(II) acetate ($\text{Pd}(\text{OAc})_2$) (Aldrich Chemical Co., Ltd.), tri-*o*-tolylphosphine ($\text{P}(\text{o-Tol})_3$) (Kanto Chemical Co., Ltd.), triethylamine (NEt_3) (Kanto Chemical Co., Ltd.), and *N,N*-dimethylformamide (DMF) (dehydrated grade, Kanto Chemical Co., Ltd.) were commercially obtained and used as received.

Synthesis of porous polymers

Polymerization was carried out in a 10 mL ampoule tube. A reaction of TVMCTS with HFl (monomer concentration: 30 wt%) is described as a reference. HFl (1 mmol), $\text{P}(\text{o-Tol})_3$ (0.12 mmol), and $\text{Pd}(\text{OAc})_2$ (0.02 mmol) were added to the ampoule tube under a nitrogen atmosphere. After the addition of TVMCTS (0.5 mmol), DMF (2.0 mL), and NEt_3 (1.5 mmol),

1 the ampoule tube was sealed by burning off. The reaction was heated, standing without stirring
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3 in a heater equipped with an aluminum block, at 100°C for 24 h. The ample tube was carefully
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5 and safety broken by a pair of pliers to take out the polymer. The resulting polymer was washed
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7 with a large excess of DMF in a microwave washer, and the solvent was replaced with methanol
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9 by immersion. The polymer obtained was dried under the atmospheric conditions for 24 h
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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.
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19 **Analytical procedures**

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

The Mizoroki-Heck reaction of TVMCTS in combination with HfI 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 EHfI successfully yielded the porous polymers almost quantitatively. The porous polymers were also obtained from the reactions of TVMCTS in combination with binary HfI/OFI, and HfI/EHfI (equivalent molar feed ratio) systems. By contrast, the polymerizations of TVMCTS with RfI having small alkyl substituent, methyl, and ethyl, yielded none-porous rigid bulk polymers. The reaction systems with large alkyl substituted RfI, decyl, dodecyl, formed none-porous soft precipitates. The most likely explanation for these results is that bulkiness of the alkyl substituent of RfI would affect state of π -stacking of RfI units in the polymer network. The small alkyl substituent should not hinder the π -stacking of RfI units with high interaction and yielded rigid structure. By contrast, the large alkyl substituent of RfI would prevent from stacking of RfI units, which should decrease the rigidity of the network. The alkyl substituent with C6-C8 would induce moderate π -stacking of RfI units, which should be suitable to form the porous polymers.

FT-IR spectra of the TVMCTS, HfI, and TVMCTS-HfI 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-HfI 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 HfI. TVMCTS-OFI and TVMCTS-EHfI porous polymers showed similar profile in their FT-IR spectra.¹⁶

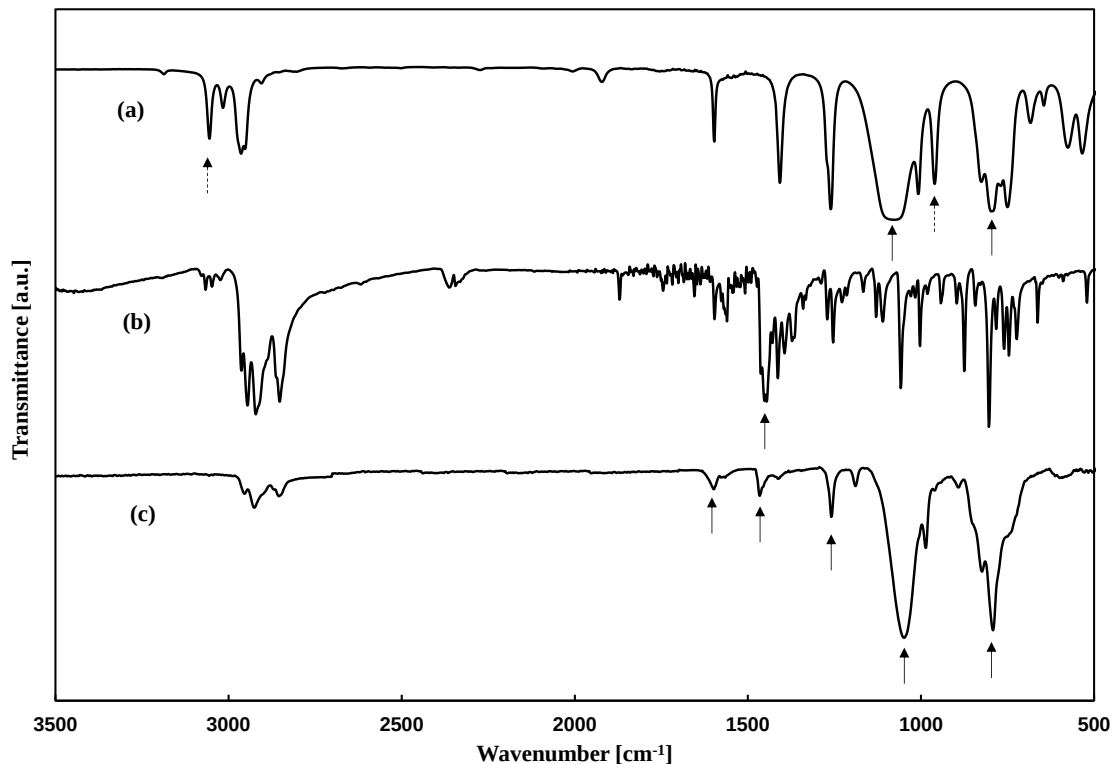


FIGURE 1 FT-IR spectra of (a) TVMCTS-HFl, (b) TVMCTS-OFl, and (c) TVMCTS-EHFl polymers, monomer concentration in the reaction system: 20 wt%.

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

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

Related surface area of TVMCTS-HFl 20 wt% porous polymer (run 2) determined by BET method was less than limit of detection, less than 2 m²/g. The small surface was derived from not micro-porous but the macro-porous structure of the porous polymer.

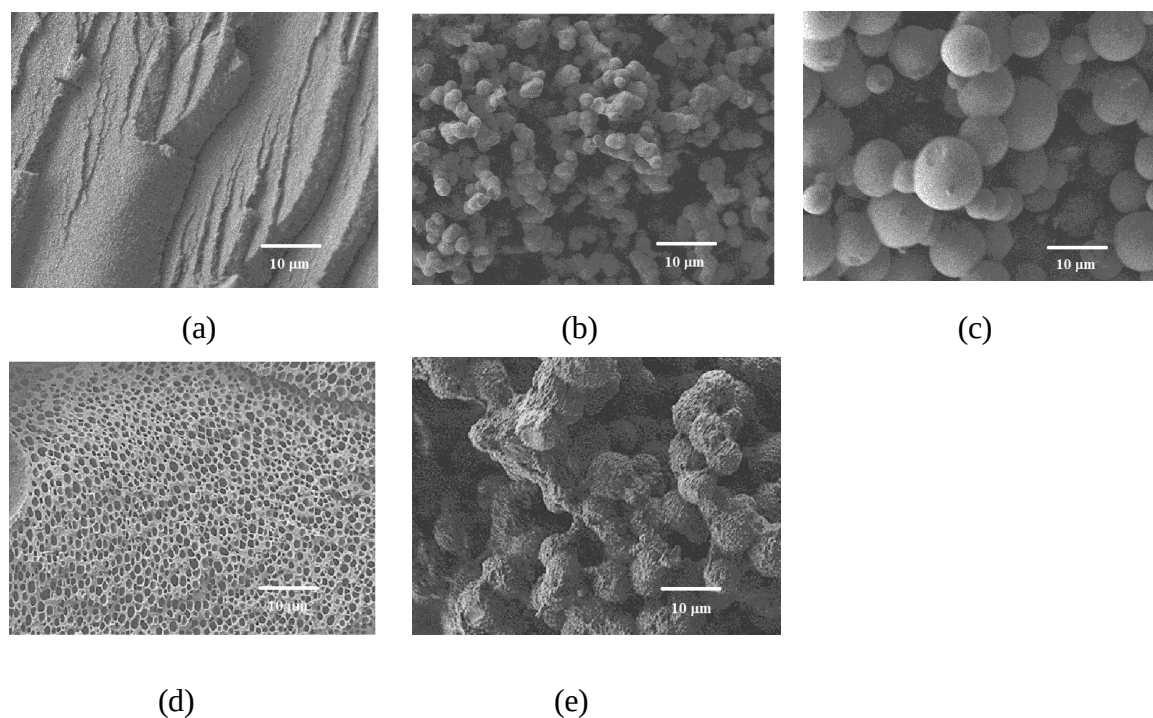


FIGURE 2 SEM images of TVMCTS-HFl polymers obtained from the reaction systems containing (a) 10 wt%, (b) 20 wt%, (c) 30 wt%, and (d) 40 wt% monomer at 100 °C in 24 h, and (e) 20 wt% monomer at 80 °C in 1 week.

Figure 3 shows SEM images of the TVMCTS-OFI polymers. The TVMCTS-OFI polymer obtained from the reaction containing 20 wt% of monomers formed porous polymer composed by the connected globules ranged from 5 to 40 μm diameter. By contrast, the globules and deformed isolated holes were co-existed in the TVMCTS-OFI 30 and 40 wt% porous polymers. The hole structure would be derived from HIPE, as observed in the TVMCTS-HFI 40 wt% porous polymer. The number of globules decreased with increasing in the monomer concentration of the reaction system. These results indicate that the increase of the monomer concentration would transfer the phase separation state from spinodal decomposition to HIPE.

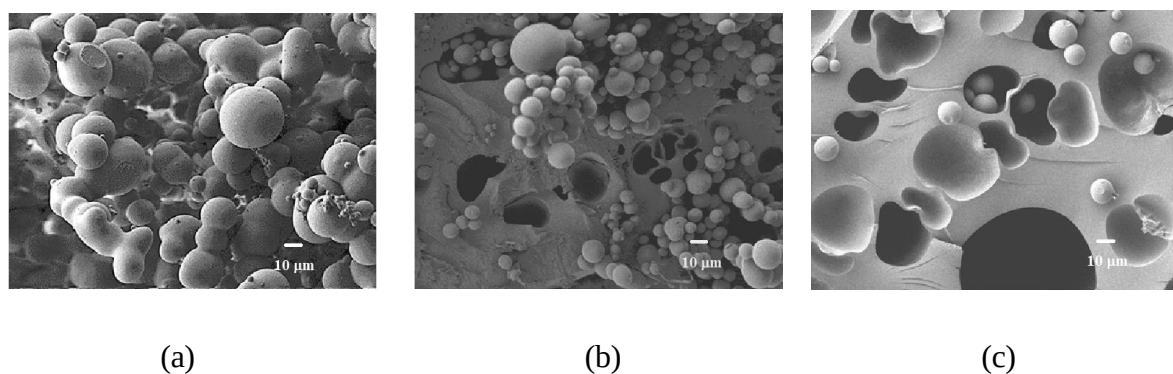


FIGURE 3 SEM images of TVMCTS-OFI porous polymers obtained from the reaction systems containing (a) 20 wt%, (b) 30 wt%, and (c) 40 wt% monomer at 100 °C in 24 h.

SEM images of the TVMCTS-EHFI polymers are shown in Figure 4. The TVMCTS-EHFI 20 and 30 wt% polymers showed porous structure composed by the connected globules ranged from 10 to 50 μm diameter. The TVMCTS-EHFI 40 wt% porous polymer showed isolated holes about 30-50 μm diameter and small number of globules less than 10 μm diameter. The reaction system containing 40 wt% monomers should induce HIPE as observed in the TVMCTS-OFI 40 wt% porous polymer.

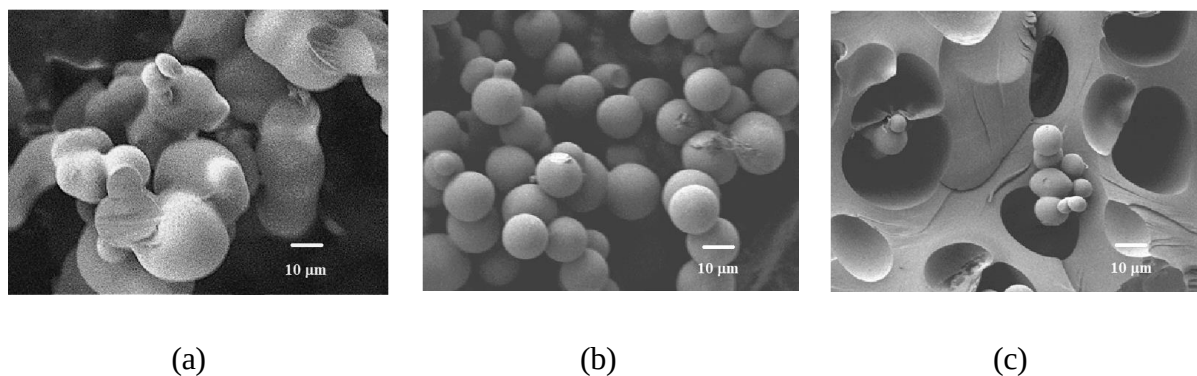


FIGURE 4 SEM images of TVMCTS-EHFl porous polymers obtained from the reaction solutions containing (a) 20 wt%, (b) 30 wt%, and (c) 40 wt% monomer at 100 °C in 24 h.

The reactions of TMCTS in combination with binary HF1/OF1 and HF1/EHFl (equivalent molar feed ratio) systems also yielded the porous polymers. SEM images of the TVMCTS-HF1/OF1 or TVMCTS-HF1/EHFl porous polymers are summarized in Figure 5. The TVMCTS-HF1/OF1 or TVMCTS-HF1/EHFl 20 wt% porous polymer showed morphology composed by the connected globules less than 10 µm diameter. The TVMCTS-HF1/OF1 or TVMCTS-HF1/EHFl 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.

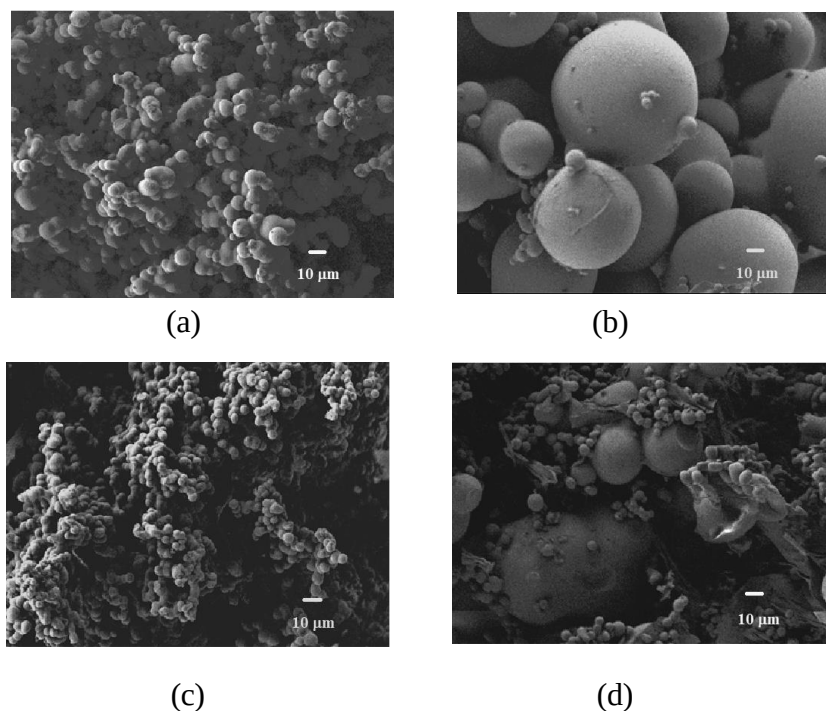


FIGURE 5 SEM images of TVMCTS-HFl/OFI (a, b) and TVMCTS-HFl/EHFl (c, d) porous polymers obtained from the reaction solutions containing (a) 20 wt%, (b) 30 wt%, (c) 20 wt%, and (d) 30 wt% monomer at 100 °C in 24 h.

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-HFl 20, 40 wt%, TVMCTS-OFI 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 OFI or EHFl was lower than that of the polymer with HFl. Bulkiness of alkyl side chains in OFI and EHFl would make the porous polymer soft. The TVMCTS-HFl/OFI and TVMCTS-HFl/EHFl porous polymers showed similar Young's modulus values to those of the TVMCTS- OFI and TVMCTS-EHFl porous polymers.

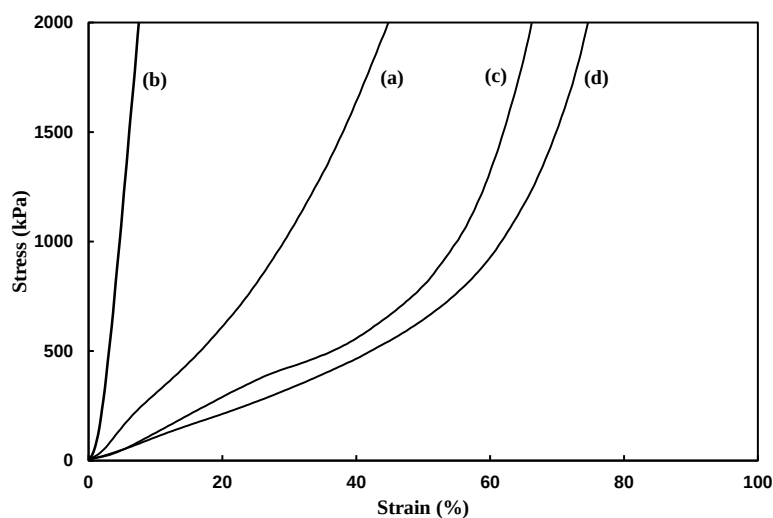


FIGURE 6 Stress-strain curves of (a) TVMCTS-HFl 20 wt%, (b) TVMCTS-HFl 40 wt%, (c) TVMCTS-OFl 20 wt%, and (d) TVMCTS-EHFl 20 wt% porous polymers.

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

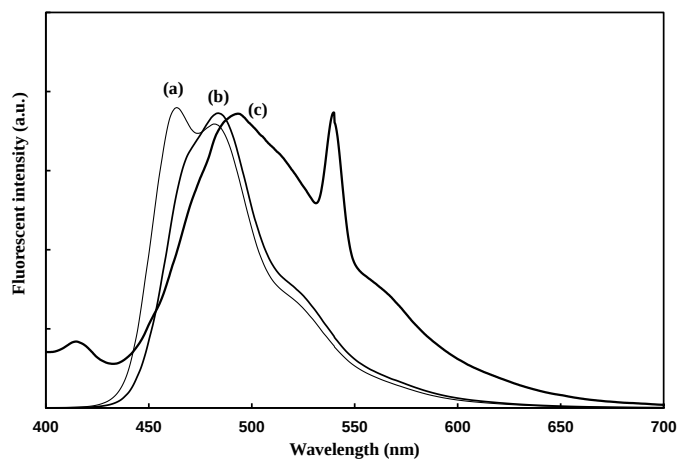
Run	RFl	Monomer concentration n wt%	Surface structure	Young's modulus kPa	Emission ^c nm		Quantum yield
					$\lambda_{\max 0}$	$\lambda_{\max 1}$	
1	HFl	10	layer				
2	HFl	20	globule	31.0	464	482	0.25
3	HFl	30	globule	37.4		484	0.19
4	HFl	40	hole	231.5		493	0.10
5 ^b	HFl	20	globule				
6	OFl	20	globule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

^a Conditions: RFl (1 mmol), (runs 10, 11: HFl/OFl = 0.5/0.5 mmol/mmol, runs 12, 13: HFl/EHFl = 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.

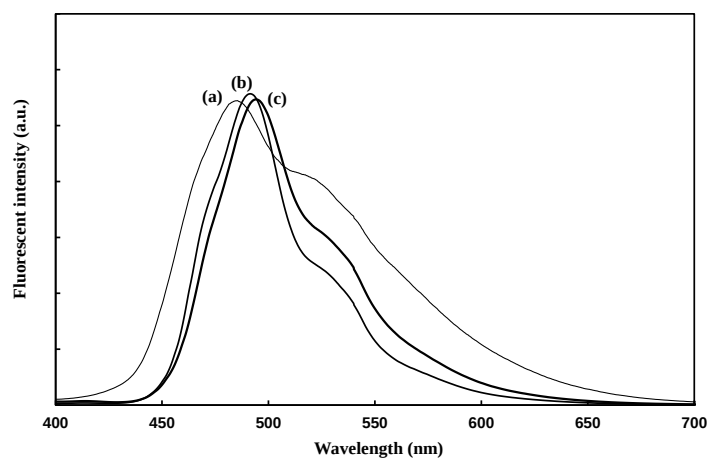
Emissive features of the porous polymers were studied using PL spectroscopy.¹⁷ Normalized PL spectra of the TVMCTS-RFl porous polymers are shown in Figure 7. The results are

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

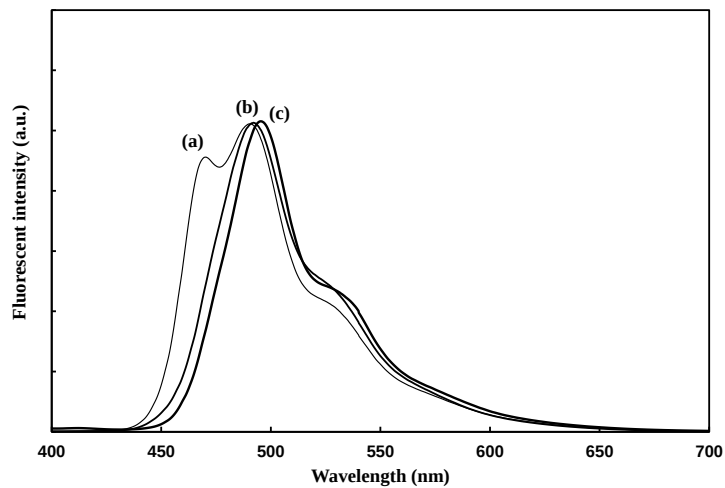
The porous polymers obtained from binary HfI/OfI and HfI/EHfI systems, monomer concentration in the reaction solution: 20, 30 wt%, showed emission band assigned 0-1 intrachain singlet transition ranged from 483 nm to 490 nm.²² Both the TVMCTS-HfI/EHfI 20 and 30 wt% porous polymers showed the emission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



(i)



(ii)



(iii)

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

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

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46 The Mizoroki-Heck reaction of TVMCTS and HfI, OfI, and EHfI at 100 °C in DMF
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48 successfully yielded the porous polymers. The porous polymers were preferentially formed in
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50 the reaction solutions containing 20-40 wt% monomers. The binary RfI systems, HfI/OfI or
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52 HfI/EHfI, also yielded the corresponding porous polymers. The monomer concentration of the
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54 reaction systems strongly affected the morphologies, mechanical properties, and emission bands of
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56 the resulting porous polymers. The increase of the monomer concentration tended to transfer the
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58 morphology from connected globules to isolated holes. The porous polymers showed
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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.
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8 The present synthetic method, the Mizoroki-Heck reaction of multi-functional siloxane
9 compounds having vinyl groups and RFl, is useful to prepare the σ - π conjugated porous
10 polymers containing Si-vinylene units with high quantum yield. The obtained porous polymers
11 would be widely usable due to their features: porosity, photophysical properties, thermal
12 stability, and chemical resistance. Furthermore, dissociation of the globules in the porous
13 polymers would yield micro emissive micro-particles. Studies on applications of the porous
14 polymers are under way, and the results will be reported elsewhere.
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31 REFERENCES AND NOTES

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Graphical Abstract

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

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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

