

Preparation of Lipophilic Anionic Polymer Networks Based on Tetraphenylborates

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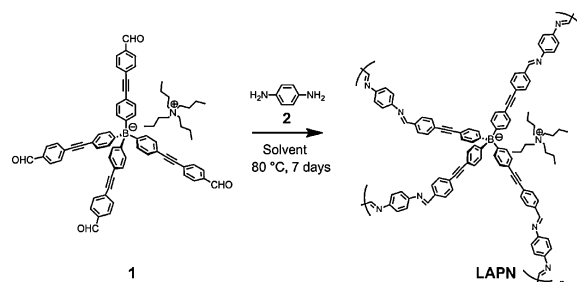
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Novel anionic and lipophilic polymer networks have been successfully synthesized by imine formation between tetraphenylborates and 1,4-phenylenediamine. The obtained polymer networks showed various morphologies depending on the dielectric constant of media used in the synthesis. Moreover, the addition of water led to polymer networks with spherical structure presumably due to suppression of imine formation.

Tetraphenylborates have been paid much attention as promising weakly coordinating anions due to their high solubility and ion-dissociating ability in a wide range of organic media in particular in nonpolar solvents such as chloroform and THF.¹ They have been employed as hydrophobic counter anions for stabilization of electrophilic cationic species for polymerization catalysts and electrolytes for Li batteries.^{2,3} Recently, the applications of ionization in low-dielectric media have been of considerable interest for designing functional materials such as block copolymers,⁴ nanoparticles,⁵ and absorbents.⁶ For one of these examples, we reported poly(alkyl acrylate) gels bearing tetraalkylammonium tetraphenylborate as lipophilic polyelectrolyte gels.^{6a} They showed superior swelling behaviors in less- or nonpolar organic solvents, obviously because of osmotic pressure and electrostatic repulsion derived from dissociation of tetraalkylammonium tetraphenylborate ion pairs attached on the polymer backbone. More recently, we demonstrated construction of layer-by-layer thin films from such lipophilic polyelectrolytes in less-polar media.⁷ These results prompted us to design new porous materials based on tetraphenylborate salts as a divergent core unit. Herein, we report preparation of novel lipophilic anionic rigid polymer networks from tetrasubstituted tetraphenylborate salts as the starting materials by chemical reaction and control of the network structure by electrostatic interaction, i.e., polarity of reaction media. In our knowledge, this is the first example for anionic network constructed from tetraphenylborates among the rapidly growing research fields of covalently crosslinked polymeric materials toward nanoporous materials such as covalent organic frameworks (COFs),⁸ conjugated microporous polymers (CMPs),⁹ and resorcinol-formaldehyde organic networks.¹⁰

A formyl group was introduced in each phenyl group of tetraphenylborate as reaction sites according to Scheme 1, and the resulting tetrafunctionalized core anion **1** was used as a new monomer for the synthesis of lipophilic anionic polymer networks (LAPN). Polymerization and crosslinking reactions through the imine formation were carried out by treatment of **1** with the bifunctional amine **2** with various monomer concentrations and polarity of the media as shown in Scheme 1 and Table 1.

LAPN was prepared by incubation at 80 °C for 7 days in a sealed tube. After the polymerization and crosslinking reaction,



Scheme 1. Preparation of LAPN.

Table 1. Preparation conditions for LAPN

Run	1/mmol ([1]/mM)	2/mmol ([2]/mM)	Solvent (Mixed ratio)	ϵ^a
1	0.0093 (10)	0.019 (20)	Dox ^b :DMSO (5:1)	9.6
2	0.0093 (10)	0.019 (20)	Dox:DMSO (1:1)	16.9
3	0.0093 (10)	0.019 (20)	Dox:DMSO (1:2)	31.7
4	0.011 (200)	0.022 (400)	TCE ^c	8.2
5	0.011 (100)	0.022 (200)	TCE	8.2
6	0.011 (50)	0.022 (100)	TCE	8.2
7	0.011 (10)	0.022 (20)	TCE	8.2
8	0.023 (10)	0.054 (25)	Dox:DMSO:H ₂ O (9:2:2)	29.7
9	0.023 (10)	0.054 (25)	Dox:DMSO:H ₂ O (6:3:1)	36.4

^aDielectric constant estimated from volume fraction. ^b1,4-Dioxane. ^c1,1,2,2-Tetrachloroethane.

the polymer networks were deposited as powder in low-dielectric media ($\epsilon < 10$, see Figure S1),¹¹ while they formed gels in the high-dielectric ones ($\epsilon > 20$). In the presence of water, the reaction mixtures remained in the solution state. The product yield after washing in Run 3 was proved to be 78%. FT-IR spectra show that the peak intensities of aldehyde C=O stretching vibration (1693 cm⁻¹) and aldehyde C-H stretching vibration (2731 cm⁻¹) of monomer **1** decreased and that the peak of C=N stretching vibration (1619 cm⁻¹) appeared, obviously indicating the formation of imine (Figures S2 and S3).¹¹ Indeed, detailed analysis of IR spectra in Run 3 revealed that 92% of aldehyde was consumed, which corresponded to the product

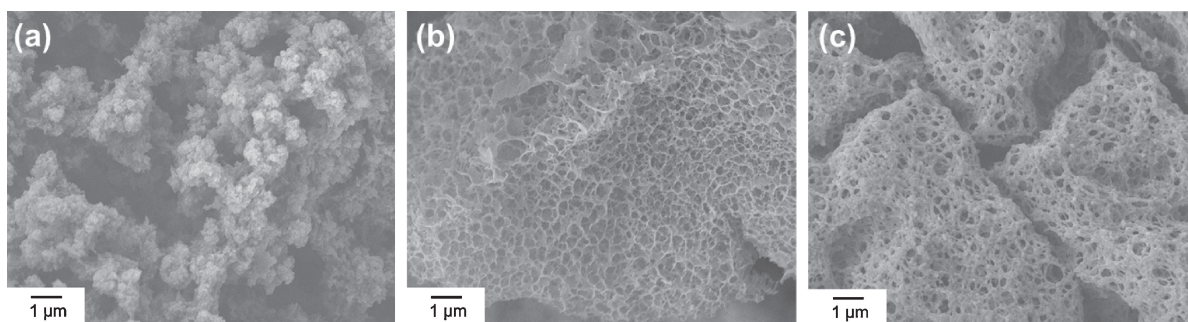


Figure 1. SEM images of LAPN prepared from Runs (a) 1, (b) 2, and (c) 3.

yield mentioned above. In the case of employing 4.0 equiv of aniline as a monofunctional amine with monomer **1** the peak intensity of H on the aldehyde group of monomer **1** was reduced to approximately 20%, as revealed by ^1H NMR spectrum (Figure S4).¹¹ These results suggested that the polymer networks were prepared via sufficient progression of imine formation between monomer **1** and 1,4-phenylenediamine (**2**).

The resulting LAPN was immersed and washed in THF and 1,4-dioxane in sequence for over a day. Then, the SEM samples were freeze-dried. The SEM images showed that high-dielectric media caused LAPN with larger pores in the preparation condition of Runs 1–3. In the low-dielectric media, ionic dissociation was restrained, and the polymer networks adopted aggregated network structure consisting of small spherical particles (Figure 1a). On the other hand in the high-dielectric media, the degree of ionic dissociation was increased, and ionic repulsion induced formation of the expanded porous network structure having submicron-sized diameter (Figures 1b and 1c). The gelation behavior in the high-dielectric media presumably resulted from the suppression of particle aggregation as shown in the expanded structure. Therefore, the morphology differences with polymer networks were affected by electrostatic interaction with dissociation or nondissociation of the monomers during the polymerization.

Next, in the preparation conditions of Runs 4–7, the morphologies of LAPN were investigated with different monomer concentration. As the concentration of the monomer became lower, spherical polymer networks were formed (Figures 2a, 2b, and 2c). Addition of water induced network polymer to form the spherical structure or reverse micelle formation in the preparation conditions of Run 8 (Figure 2d).

In summary, we prepared anionic and lipophilic polymer networks based on tetraphenylborates by imine formation reaction between tetraphenylborate modified with formyl groups and 1,4-phenylenediamine. We succeeded in controlling the morphologies of the polymer networks by utilizing electrostatic interaction in organic solvents.

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References and Notes

- 1 a) I. Krossing, I. Raabe, *Angew. Chem., Int. Ed.* **2004**, *43*, 2066. b) R. J. LeSuer, C. Buttolph, W. E. Geiger, *Anal. Chem.* **2004**,

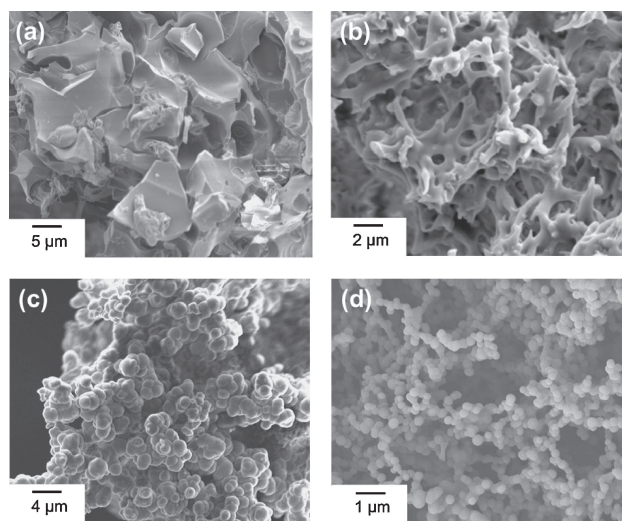


Figure 2. SEM images of LAPN prepared from Runs (a) 4, (b) 5, (c) 7, and (d) 8.

- 76, 6395.
- 2 S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927.
- 3 a) E. A. Rietman, M. L. Kaplan, R. J. Cava, *Solid State Ionics* **1985**, *17*, 67. b) F. Kita, H. Sakata, S. Sinomoto, A. Kawakami, H. Kamizori, T. Sonoda, H. Nagashima, J. Nie, N. V. Pavlenko, Y. L. Yagupolskii, *J. Power Sources* **2000**, *90*, 27.
- 4 C. Cui, E. M. Bonder, F. Jäkle, *J. Am. Chem. Soc.* **2010**, *132*, 1810.
- 5 R. Sánchez, P. Bartlett, *Soft Matter* **2011**, *7*, 887.
- 6 a) T. Ono, T. Sugimoto, S. Shinkai, K. Sada, *Nat. Mater.* **2007**, *6*, 429. b) K. Iseda, M. Ohta, T. Ono, K. Sada, *Soft Matter* **2011**, *7*, 5938. c) T. Ono, T. Sugimoto, S. Shinkai, K. Sada, *Adv. Funct. Mater.* **2008**, *18*, 3936.
- 7 M. Ohta, T. Ono, K. Sada, *Chem. Lett.* **2011**, *40*, 648.
- 8 a) H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O’Keeffe, O. M. Yaghi, *Science* **2007**, *316*, 268. b) F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klöck, M. O’Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, *131*, 4570.
- 9 A. I. Cooper, *Adv. Mater.* **2009**, *21*, 1291.
- 10 a) S. A. Al-Muhtaseb, J. A. Ritter, *Adv. Mater.* **2003**, *15*, 101. b) H. Tamon, H. Ishizaka, M. Mikami, M. Okazaki, *Carbon* **1997**, *35*, 791.
- 11 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.