

A Novel Family of Low Molecular-Weight Organic Gels. 1,3,5-Tris(*N*-phenyl-*N*-4-stearoylaminophenylamino)benzene and 4,4',4''-Tris(*N*-phenyl-*N*-4-stearoylaminophenyl-amino)triphenylamine / Organic Solvent Systems

Takuya KAMIYAMA, Yoshiaki YASUDA, and Yasuhiko SHIROTA[†]

Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Yamadaoka, Suita, Osaka 565-0871, Japan

(Received February 28, 1999)

ABSTRACT: For the purpose of developing a novel family of low molecular-weight organic gels and examining the relationship between molecular structures of gel-forming compounds and morphologies of resulting gels, novel low molecular-weight organic compounds, 1,3,5-tris(*N*-phenyl-*N*-4-stearoylaminophenylamino)benzene (TSA-TDAB) and 4,4',4''-tris(*N*-phenyl-*N*-4-stearoylaminophenylamino)triphenylamine (TSA-TDATA), were designed and synthesized. Both TSA-TDAB and TSA-TDATA were found to form thermoreversible gels with a variety of organic solvents at low concentrations below 10 wt%. Comparison of the infrared absorption spectra between the gels and the corresponding solutions of TSA-TDAB and TSA-TDATA showed that the intermolecular hydrogen bonding plays an important role for gel formation. The morphologies of the xerogels of TSA-TDAB and TSA-TDATA were dependent upon the solvent. Fibrous three-dimensional networks were observed for the xerogels of both compounds except for the xerogels obtained from TSA-TDAB/nonpolar solvent gels. A TSA-TDATA/benzonitrile gel containing tetra-*n*-butylammonium perchlorate was found to function as a new type of electrochromic material, exhibiting a reversible color change on electrochemical oxidation and reduction.

KEY WORDS Low Molecular-Weight Gel / Hydrogen Bonding / Thermoreversible Sol-Gel Transition / Three-Dimensional Network / Ionic Conductivity / Electrochromism /

Polymer gels have received a great deal of attention not only from scientific interest but also for their practical applications.¹⁻⁵ Recently, gels composed of low molecular-weight organic compounds have also been receiving growing attention. However, there have been few studies of low molecular-weight organic gels in contrast to extensive studies of polymer gels. Hitherto reported low molecular-weight organic compounds that form gels with organic solvents comprise derivatives of cholesterol, amino acids and sorbitol as well as cyclic depsipeptide and others.⁶⁻²⁷

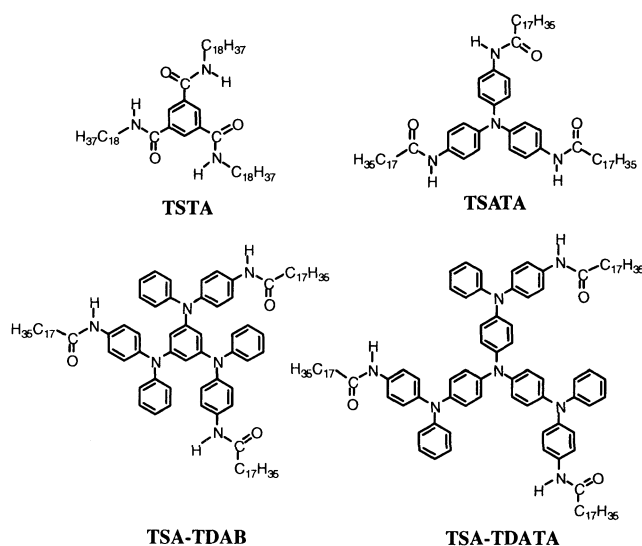
It is generally understood that the formation of both polymer and low molecular-weight organic gels is based on three-dimensional networks of a gel-forming material in which a large amount of liquid is incorporated. These networks in low molecular-weight organic gels are thought to arise from weak intermolecular interactions instead of the covalent bonding, which is responsible for polymer gels that are classified as chemical gels.

It is of great interest and importance to elucidate how three-dimensional networks in low molecular-weight organic gels are formed and to establish guidelines for the molecular design of gel-forming organic compounds. Network structure clarification and determination of the properties of low molecular-weight organic gels are further aspects meriting attention. In addition, it is expected that low molecular-weight organic gels with functional groups may constitute a new class of organic functional materials that take the form of a solid with no apparent fluidity but nevertheless contain solvent within.

We have been studying the creation of novel low molecular-weight organic gels and their structures, properties, and applications. We have designed and synthesized several novel families of gel-forming organic compounds with π -electron systems as a core moiety, intermolecular hydrogen bonding sites, and long alkyl chains, *e.g.*, *N,N',N''*-tristearyltrimesamide (TSTA)¹⁹ and

4,4',4''-tris(stearoylamino)triphenylamine (TSATA),²⁰ finding that these compounds readily form gels with a variety of organic solvents at low concentrations. We have studied the relationship between molecular structures and gel-forming properties and have shown that both the intermolecular hydrogen bonding between the N-H and C=O groups in the amide moiety and the presence of alkyl groups with an appropriate length play an important role for gel formation. The scanning electron microscopy (SEM) images of the xerogels of TSTA and TSATA showed fibrous bundle structures that lead to three-dimensional networks. It has also been shown that both TSTA and TSATA gels containing a supporting electrolyte exhibit high ionic conductivities comparable to those of the corresponding solutions^{19,20} and that a TSATA/benzonitrile gel functions as a new type of electrochromic material.²⁰

In the present study, we have designed and synthesized novel organic compounds containing larger π -electron



[†] To whom correspondence should be addressed.

systems as a core moiety, 1,3,5-tris(*N*-phenyl-*N*-4-stearoylamino)phenylamino)benzene (TSA-TDAB) and 4,4',4''-tris(*N*-phenyl-*N*-4-stearoylamino)phenylamino)triphenylamine (TSA-TDATA), in order to develop a further new family of low molecular-weight organic gels, and investigated their gel-forming properties and the morphologies of resulting gels.^{26,27} An application of the resulting gel as an electrochromic material has also been examined.

EXPERIMENTAL

Materials

Solvents were purified and dried by ordinary methods. Iodobenzene, potassium iodide, potassium iodate, potassium carbonate, 18-crown-6, copper powder, and triethylamine were commercially available and used as received. 1,3,5-Tribromobenzene, *p*-nitroaniline, and triphenylamine are also commercially available and were purified by recrystallization. Stearoyl chloride was prepared from high-purity stearic acid (Nippon Oil and Fats Co., Ltd.) by the reaction with phosphorus pentachloride and purified by vacuum distillation (183°C / 3 mmHg). Raney nickel catalyst was prepared according to the following procedure: 7.6 g of Raney nickel alloy powder (Wako Pure Chemical Industries, Ltd.; Ni content, ca. 50%) was added to 80 cm³ of an aqueous sodium hydroxide solution (18 %). Then, the suspension was heated at 100°C for 1 h, during which hydrogen evolved vigorously. The resulting alkaline solution was decanted, and the nickel was washed 15 times with 50 cm³ portions of distilled water, followed by washing with portions of THF. Tetra-*n*-butylammonium perchlorate (Tokyo Chemical Industries, Ltd.) was recrystallized from ethanol three times, dried at 70°C for 24 h, stored in a desiccator, and redried *in vacuo* at room temperature immediately before use.

Synthesis

1,3,5-Tris(N-phenyl-N-4-stearoylamino)phenylamino)benzene (TSA-TDAB). TSA-TDAB was synthesized according to the following procedure. *N*-4-Nitrophenyl-*N*-phenylamine was prepared by the Ullmann coupling reaction of *p*-nitroaniline with iodobenzene at 188°C for 12 h in the presence of copper powder, potassium carbonate and 18-crown-6 (crude yield: 53%). 1,3,5-Tris(*N*-4-nitrophenyl-*N*-phenylamino)benzene (TN-TDAB) was prepared by the Ullmann coupling reaction of *N*-4-nitrophenyl-*N*-phenylamine (1.7g) with 1,3,5-tribromobenzene (0.63g) in mesitylene at 160°C for 12 h (0.40g, crude yield: 28%). TN-TDAB (0.82g) was hydrogenated in the presence of a Raney nickel catalyst (0.80g) to give 1,3,5-tris(*N*-4-aminophenyl-*N*-phenylamino)benzene (TA-TDAB). After removal of the catalyst by filtration, stearoyl chloride (1.6g) was added dropwise into a THF solution containing TA-TDAB and triethylamine (0.52g) to form TSA-TDAB (0.77g, crude yield: 47%). The product was purified by several reprecipitations from THF into acetone. *m p*: 161–162°C; mass spectrum (FD) *m/z*: 1423 (*M*⁺); ¹H-NMR (400 MHz, THF-*d*₈, ppm): 8.83 (s, 3H, N-H), 7.43 (d, 6H, *J* = 8.8 Hz, ArH), 7.09 (t, 6H, *J* = 7.8 Hz, ArH), 6.96 (d, 6H, *J* = 8.3 Hz, ArH), 6.92 (d, 6H, *J* = 8.8 Hz, ArH), 6.80 (t, 3H, *J* = 7.3 Hz, ArH), 6.31 (s, 3H, ArH), 2.25 (t, 6H, *J* = 7.3 Hz, stearoyl 2-H), 1.67 (t-t, 6H, *J* = 6.8 Hz, stearoyl 3-H), 1.34–1.29 (m,

84H, stearoyl 4-H—17-H), 0.88 (t, 9H, *J* = 6.8 Hz, stearoyl 18-H); IR (KBr, cm⁻¹): 3315 (ν_{N-H}), 2918, 2849 (ν_{C-H}), 1656 (ν_{C=O}). *Anal. Calcd.* for C₉₆H₁₃₈N₆O₃: C, 80.96%; H, 9.77%; N, 5.90%. *Found*: C, 80.46%; H, 9.76%; N, 5.80%.

4,4',4''-Tris(N-phenyl-N-4-stearoylamino)phenylamino)triphenylamine (TSA-TDATA). TSA-TDATA was synthesized in a similar manner. 4,4',4''-Tris(*N*-4-nitrophenyl-*N*-phenylamino)triphenylamine (TN-TDATA) was prepared by the Ullmann coupling reaction of tris(4-iodophenyl)amine (3.8g) with *N*-4-nitrophenyl-*N*-phenylamine (5.2g) in mesitylene at 160°C for 12 h in the presence of copper powder (3.1g), potassium carbonate (6.9g) and 18-crown-6 (0.69g) (3.5g, crude yield: 66%). TN-TDATA (0.26g) was hydrogenated in the presence of a Raney nickel catalyst (5.7g) to yield 4,4',4''-tris(*N*-4-aminophenyl-*N*-phenylamino)triphenylamine (TA-TDATA), which was reacted with stearoyl chloride (1.2g) to give TSA-TDATA (0.26g, crude yield: 54%) and purified in the same way as TSA-TDAB. *m p*: 239–240°C; MS (FD) *m/z*: 1590 (*M*⁺); ¹H-NMR (600 MHz, THF-*d*₈, ppm): 8.85 (s, 3H, N-H), 7.53 (d, 6H, *J* = 5.9 Hz, ArH), 7.16–6.87 (m, 33H, ArH), 2.25 (t, 6H, *J* = 7.3 Hz, stearoyl 2-H), 1.66 (t-t, 6H, *J* = 7.0 Hz, stearoyl 3-H), 1.37–1.23 (m, 84H, stearoyl 4-H—17-H), 0.89 (t, 9H, *J* = 7.0 Hz, stearoyl 18-H); IR (KBr, cm⁻¹): 3308 (ν_{N-H}), 2921, 2851 (ν_{C-H}), 1658 (ν_{C=O}). *Anal. Calcd.* for C₁₀₈H₁₄₇N₇O₃: C, 81.51%; H, 9.31%; N, 6.16%. *Found*: C, 81.27%; H, 9.24%; N, 6.02%.

Gelation Test

The gelation test was carried out as follows. A weighed amount of each compound was dissolved in an organic solvent (1 cm³) under heat in a capped test tube (diameter: 10 mm). The resulting solution was then cooled to 20°C on standing in a water bath and allowed to stand for 30 min. at 20°C. Gel formation was confirmed by observing that the sample did not flow when the test tube was inverted.

Measurements

Differential scanning calorimetry (DSC) was carried out with a DSC-220C (Seiko Denshi). A sample of gel was placed in a silver pan and sealed. Measurements of IR absorption spectra were carried out using a JEOL JIR-AQS20M FT-IR spectrometer with a Linkam TH-600PM and a L-600 temperature controller. The IR absorption spectra of TSA-TDAB or TSA-TDATA/tetrachloroethylene gel (1 × 10⁻² mol dm⁻³) in an aluminum pan with a NaCl window were measured by a reflection method. SEM images were obtained using a Model S-800 scanning electron microscope (Hitachi, Ltd.). The gel was dried by vacuum evaporation and the resulting xerogel sample was shadowed with gold. The accelerating voltage of SEM was 20 kV. The ionic conductivity of the TSA-TDATA gel (2.0 × 10⁻² mol dm⁻³) containing tetra-*n*-butylammonium perchlorate (1.0 × 10⁻¹ mol dm⁻³) was measured by an alternating current impedance method at 25°C. Impedance measurements were carried out in an electrochemical cell with two Pt electrodes (0.5 cm × 1 cm) at 1.0 V amplitude in a frequency range from 20 Hz to 1 MHz, using a Hewlett Packard Model HP4284A precision LCR meter. Cyclic voltammetry was performed with a Model BAS100B/W (Bioanalytical Systems, Inc.) for a benzonitrile solution (5.0 × 10⁻³ mol dm⁻³) of TSA-TDAB or TSA-TDATA containing tetra-*n*-

butylammonium perchlorate ($1.0 \times 10^{-1} \text{ mol dm}^{-3}$) using a Ag/Ag^+ ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$) reference electrode and a platinum wire as the counter and working electrodes. Electrochromic properties were examined in the following way. A TSA-TDATA/benzonitrile gel ($1.3 \times 10^{-2} \text{ mol dm}^{-3}$) containing tetra-*n*-butylammonium perchlorate ($1.0 \times 10^{-1} \text{ mol dm}^{-3}$) was sandwiched between an indium-tin-oxide (ITO)-coated glass as a working electrode and a glass substrate with a platinum wire (diameter: 0.5 mm) as a counter electrode to make a cell (sample thickness: 1.0 mm). Electrochemical oxidation and reduction were carried out by applying repetitive pulsed voltages of +3.0 V and -3.0 V to the ITO and platinum wire electrodes using a voltage current source/monitor TR 6143 (ADVANTEST). The electronic absorption spectra of the anodically oxidized species were measured *in situ* with a Model U-3500 spectrophotometer (Hitachi, Ltd.).

RESULTS AND DISCUSSION

Synthesis of TSA-TDAB and TSA-TDATA

The new compounds, TSA-TDAB and TSA-TDATA, were synthesized as described in Scheme 1.

Formation of Gels

Both TSA-TDAB and TSA-TDATA were found to form gels with a variety of solvents except for several solvents such as THF, in which both compounds were too soluble to form gels, and *n*-hexane, cyclohexane, methanol, and acetone, in which both compounds were insoluble. TSA-TDAB was soluble in DMF and acetonitrile under heat, but precipitated on cooling to 20°C instead of forming gels. TSA-TDATA was insoluble in these solvents.

The resulting gels of TSA-TDAB and TSA-TDATA were either transparent or opaque, depending on the solvent, concentration, and temperature. Gel-forming ability was evaluated from the minimum concentration required for gel formation. Table I summarizes the minimum concentrations of TSA-TDAB and TSA-TDATA for gel formation. The results show that both compounds immobilize the solvent at low concentrations.

Comparison of the IR absorption spectra between gels at 20°C and the corresponding solutions obtained from gels on heating to 80°C showed that the intermolecular hydrogen bonding between the N-H and C=O groups contribute to gel formation. The absorption bands at 3330 cm^{-1} and 1660 cm^{-1} observed for a TSA-TDAB/tetrachloroethylene gel ($1 \times 10^{-2} \text{ mol dm}^{-3}$) at 20°C, which are attributed to the hydrogen-

bonded N-H and C=O stretching vibrations, shifted to 3450 cm^{-1} and 1700 cm^{-1} , respectively, in the solution at 80°C, which are due to the free N-H and C=O stretching vibrations (Figure 1). Similar results were obtained with regard to the TSA-TDATA gels. It is understood that the intermolecular hydrogen bonding is a driving force for molecular aggregation, leading to the formation of three-dimensional networks.

Table I. Minimum concentrations of TSA-TDAB and TSA-TDATA for gel formation at 20°C

Solvent	Minimum concentration / g dm^{-3}	
	TSA-TDAB	TSA-TDATA
decalin	12	2
benzene	16	7
toluene	18	12
benzonitrile	10	18
nitrobenzene	7	14
1,2-dichloroethane	4	12
tetrachloroethylene	14	1
ethanol	5	insol.
1-propanol	5	insol.
2-propanol	4	insol.
DMSO	10	ppt.

insol.: insoluble; ppt.: precipitation.

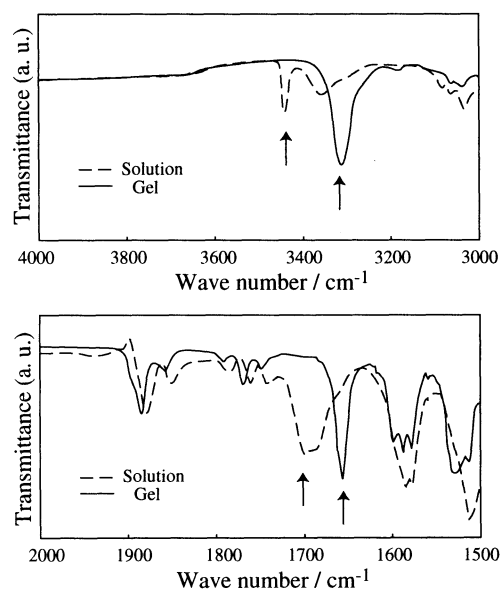
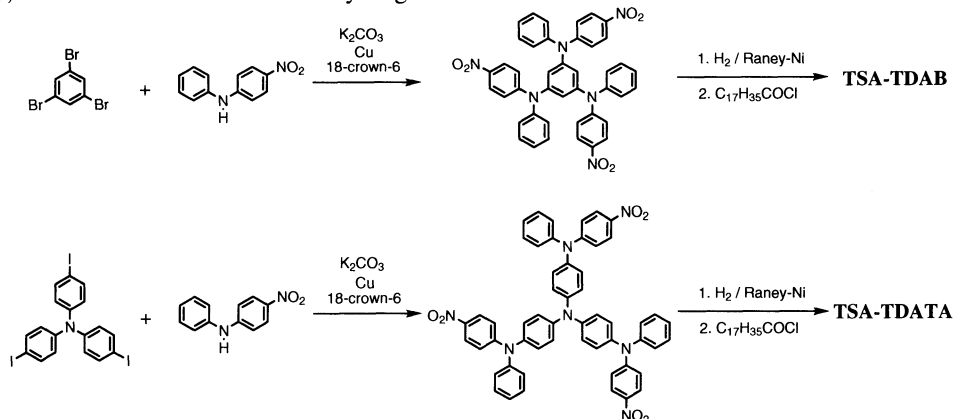


Figure 1. IR absorption spectra of a TSA-TDAB/tetrachloroethylene gel at 20°C and the corresponding solution at 80°C.



Scheme 1. Synthesis of TSA-TDAB and TSA-TDATA.

Sol-gel Transitions

The resulting gels were found to exhibit well-defined thermoreversible sol-gel transitions, as measured by differential scanning calorimetry (DSC). Figure 2 shows DSC curves of a TSA-TDAB/benzonitrile (1.0×10^{-2} mol dm⁻³) system. When a gel was heated, an endothermic peak ($\Delta H = 1.6$ mJ mg⁻¹) due to the transition from the gel into a solution was observed. When the solution was cooled, an exothermic peak ($\Delta H = -1.7$ mJ mg⁻¹) due to the transition from the solution into the gel appeared. This behavior was observed repeatedly in the processes of heating and cooling. The transition temperatures from gel to solution and from solution to gel measured from DSC curves are listed in Table II. The transition temperatures varied depending upon the solvent contained in the gel and the concentration of a gel-forming compound. Usually the transition temperature from gel to solution was higher than that from solution to gel. It is suggested that gel formation takes place via supersaturation of the gel-forming compound. As Figure 3 shows, the transition temperatures from gel to solution and from solution to gel increased with increasing concentration of the gel-forming compound.

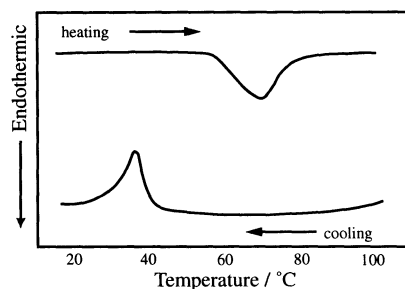


Figure 2. DSC curves of a TSA-TDAB/benzonitrile (1.0×10^{-2} mol dm⁻³) system. Heating rate: 5°C min⁻¹.

Table II. Sol-gel transition temperatures for TSA-TDAB and TSA-TDATA gels at 1.0×10^{-2} mol dm⁻³

Compound	Solvent	$T_{\text{gel to sol}} / ^\circ\text{C}$	$T_{\text{sol to gel}} / ^\circ\text{C}$
TSA-TDAB	decalin	65	41
	1,2-dichloroethane	58	41
	nitrobenzene	70	36
	benzonitrile	69	36
TSA-TDATA	decalin	70	42
	nitrobenzene	78	43
	benzonitrile	74	35

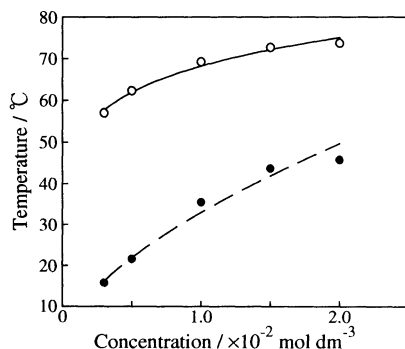


Figure 3. Sol-gel transition temperatures for a TSA-TDAB/benzonitrile gel as a function of concentration: (○) from gel to solution; (●) from solution to gel.

Morphologies of Gels

In order to obtain information about the morphologies of gels, we have observed the SEM images of xerogels obtained by evaporating the solvent incorporated in gels. Figure 4 shows the SEM images of the xerogels obtained from TSA-TDAB/benzonitrile, TSA-TDAB/benzene, TSA-TDATA/benzonitrile, and TSA-TDATA/benzene gels. As seen in Figure 4 (a), the xerogel obtained from a TSA-TDAB/benzonitrile gel showed a fibrous bundle structure. The TSA-TDAB xerogels obtained from gels containing 1,2-dichloroethane, nitrobenzene, ethanol, 1-propanol, and 2-propanol also showed similar fibrous bundle structures. Likewise, all the TSA-TDATA xerogels also showed fibrous structures (Figure 4 (c), (d)). It should be noted, however, that fibers observed for the present TSA-TDAB and TSA-TDATA xerogels are shorter, finer, and more branched than those observed for the TSATA xerogels. Furthermore, the TSA-TDAB xerogels obtained from the gels containing nonpolar solvents such as benzene, toluene, and decalin did not exhibit fibrous bundle structures even under conditions of higher magnification, as shown in Figure 4 (b). These differences in the morphologies of three-dimensional networks may be due to the size of the core moiety based on π -electron systems.

Electrochemical Properties

Cyclic voltammetry was carried out in order to obtain information about the redox behavior of TSA-TDAB and TSA-TDATA. Figure 5 shows the cyclic voltammograms for the anodic oxidation of TSA-TDAB and TSA-TDATA in benzonitrile. The results show that while the anodic oxidation process of TSA-TDAB is irreversible, TSA-TDATA undergoes reversible anodic oxidation, exhibiting two anodic waves and the corresponding cathodic waves. The oxidation potential of TSA-TDATA was determined to be 0.08 V ($E_{1/2}^{\text{ox}}$) vs. Ag/Ag⁺ (1.0×10^{-2} mol dm⁻³).

Ionic Conductivity

Gels, which take the form of a solid, but contain a large amount of solvent within, are thought to behave like a liquid microscopically. It is expected that in the presence of an inorganic salt, low molecular-weight organic gels should exhibit high ionic conductivity.

As shown for TSTA and TSATA/organic solvent gels,^{19,20} a TSA-TDATA/benzonitrile gel containing tetra-*n*-butylammonium perchlorate also exhibited a high ionic conductivity of ca. 10^{-3} S cm⁻¹, which is comparable to that of the corresponding solution.

Electrochromic Properties

We have previously reported that a TSATA gel functions as a new type of potential electrochromic material.²⁰ The TSA-TDATA gels containing tetra-*n*-butylammonium perchlorate as a supporting electrolyte are also expected to function as electrochromic materials owing to the presence of a π -electron redox system and to their high ionic conductivities.

The electrochromic behavior of a TSA-TDATA/benzonitrile gel containing tetra-*n*-butylammonium perchlorate was examined using the cell described in the experimental section. It was found that the gel exhibits a reversible color change from yellow to dark green on electrochemical oxidation and vice versa on reduction when +3V and -3V were applied to the ITO electrode, respectively. Figure 6

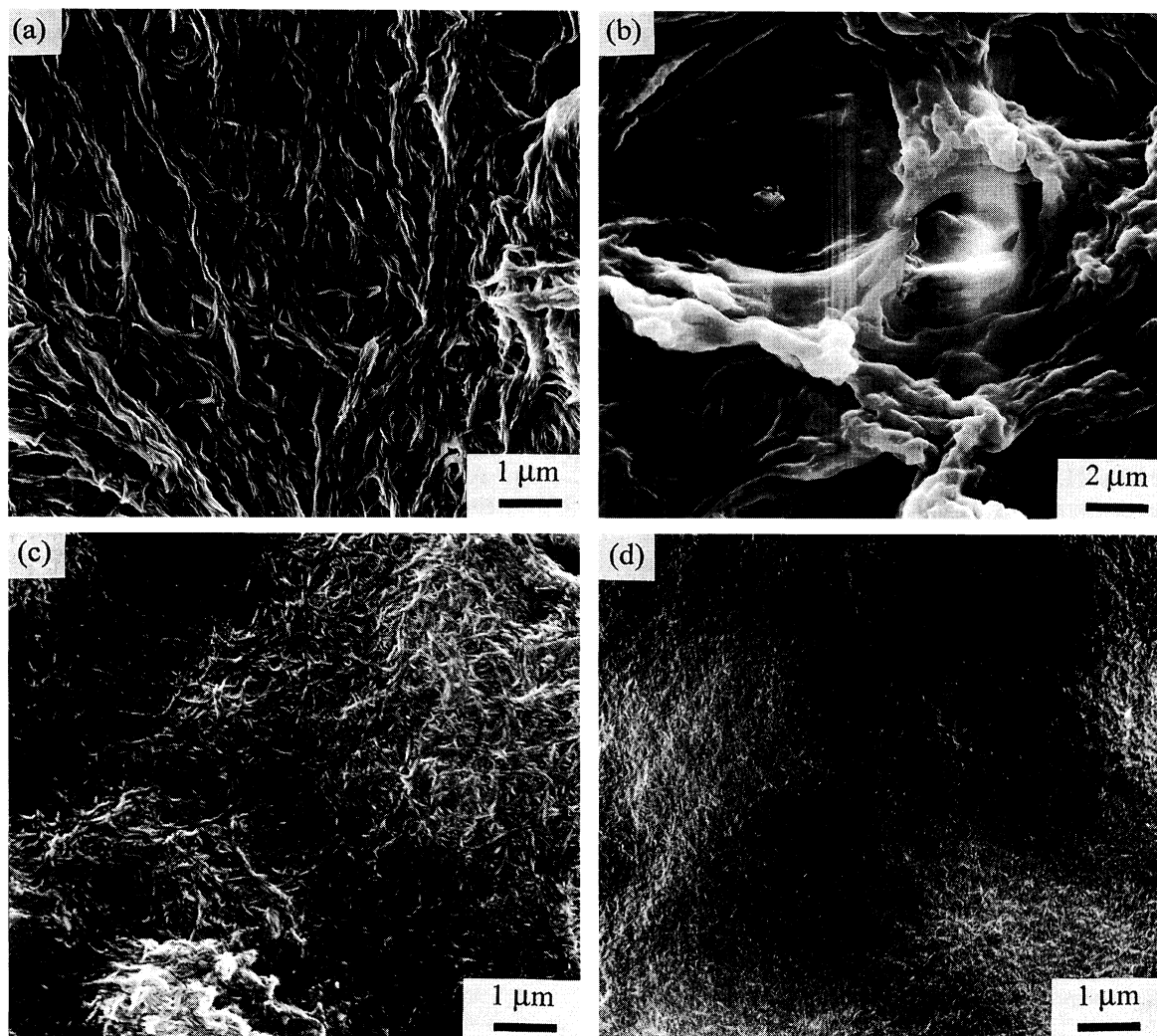


Figure 4. SEM images of the xerogels obtained from the gels of (a) TSA-TDAB/benzonitrile, (b) TSA-TDAB/benzene, (c) TSA-TDATA/benzonitrile, (d) TSA-TDATA/benzene. Concentration of TSA-TDAB or TSA-TDATA for gel formation: $1.0 \times 10^{-2} \text{ mol dm}^{-3}$.

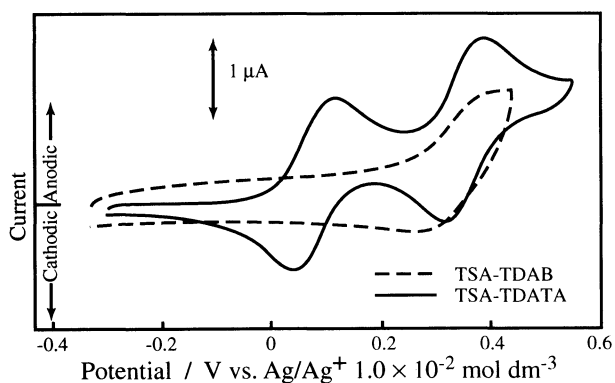


Figure 5. Cyclic voltammograms of (a) TSA-TDAB and (b) TSA-TDATA in benzonitrile ($5.0 \times 10^{-3} \text{ mol dm}^{-3}$) containing $n\text{-Bu}_4\text{NClO}_4$ ($1.0 \times 10^{-1} \text{ mol dm}^{-3}$) at 40°C .

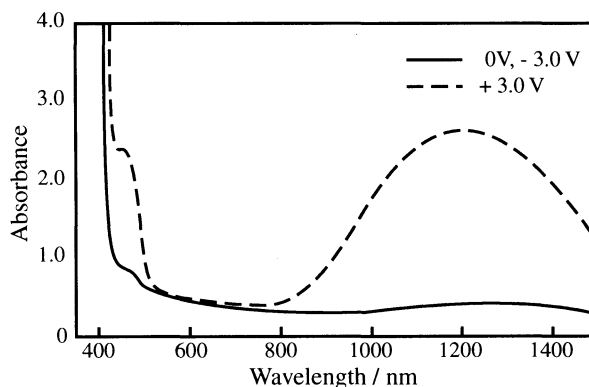


Figure 6. Electronic absorption spectra of neutral, electrochemically-doped and dedoped TSA-TDATA/benzonitrile gel ($1.3 \times 10^{-2} \text{ mol dm}^{-3}$) containing $n\text{-Bu}_4\text{NClO}_4$ ($1.0 \times 10^{-1} \text{ mol dm}^{-3}$).

shows the electronic absorption spectral change of the TSA-TDATA/benzonitrile gel on electrochemical oxidation and reduction. The electronic absorption spectrum of the anodically oxidized species shows new absorption bands

with λ_{max} at 450 and 1200 nm ascribable to the TSA-TDATA radical cation, which disappears upon electrochemical reduction.

It is shown that low molecular-weight organic gels

having a redox moiety function as a new type of potential electrochromic materials. In electrochromic devices consisting of a polymer-gel electrolyte and a dissolved organic electrochromic compound,²⁸ diffusion inhibits optical memory effects. Low molecular-weight gels functioning both as electrolyte and as electrochromic material therefore have the advantage of absence of diffusion of the electrochromic moiety due to its covalent attachment to the gel structure. The electrochromic properties depend on the redox moiety of the gel-forming compound. It is expected that further new electrochromic systems can be developed by designing new redox moieties.

CONCLUSION

In the present study, we have developed a new class of compounds, TSA-TDAB and TSA-TDATA, for low molecular-weight organic gels and found that both TSA-TDAB and TSA-TDATA readily form thermoreversible gels with various organic solvents. It is shown that the intermolecular hydrogen bonding is responsible for the formation of gels and that the morphologies of resulting gels depend on the solvent and the molecular structure of the gel-forming compound. The TSA-TDATA/benzonitrile gel exhibits a high ionic conductivity and electrochromic properties.

Acknowledgment. This work was supported by a Grant-in Aid for Scientific Research on Priority Areas, "New Polymers and Their Nano-Organized Systems" (No. 277/09232240), from The Ministry of Education, Science, Sports and Culture, Japan.

REFERENCES

1. Y. Osada, "Advances in Polymer Sciences", Springer, Berlin 1987, Vol. 82, p 1.
2. "Polymer Gels", D. DeRossi, K. Kajiwara, Y. Osada, and A. Yamauchi, Ed., Plenum, New York, 1991.
3. J.-M. Guenet, "Thermoreversible gelation of polymers and biopolymers", Academic Press, New York, 1992.
4. Y. Osada, H. Okuzaki, and H. Hori, *Nature.*, **355**, 242 (1992).
5. Y. Osada and J. P. Gong, *Adv. Mater.*, **10**, 827 (1998).
6. P. Terech and R. G. Weiss, *Chem. Rev.*, **97**, 3133 (1997).
7. P. Terech, *Ber. Bunsenges. Phys. Chem.*, **102**, 1630 (1998).
8. T. Tachibana, T. Mori, and K. Hori, *Bull. Chem. Soc. Jpn.*, **53**, 1714 (1980).
9. P. Terech and R. H. Wade, *J. Colloid Interface Sci.*, **125**, 542 (1988).
10. Y.-C. Lin, B. Kachar, and R. G. Weiss, *J. Am. Chem. Soc.*, **111**, 5542 (1989).
11. T. Brotin, R. Utermöhlen, F. Fages, H. Bouas-Laurent, and J. Desvergne, *J. Chem. Soc., Chem. Commun.*, 416 (1991).
12. K. Hanabusa, K. Okui, K. Karaki, T. Koyama, and H. Shirai, *J. Chem. Soc., Chem. Commun.*, 1371 (1992).
13. E. J. Vries and R. M. Kellogg, *J. Chem. Soc., Chem. Commun.*, 238 (1993).
14. K. Hanabusa, J. Tange, Y. Taguchi, T. Koyama, and H. Shirai, *J. Chem. Soc., Chem. Commun.*, 390 (1993).
15. K. Hanabusa, Y. Naka, T. Koyama, and H. Shirai, *J. Chem. Soc., Chem. Commun.*, 2683 (1994).
16. S. Yamasaki and H. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **67**, 2053 (1994).
17. K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda, and S. Shinkai, *J. Am. Chem. Soc.*, **116**, 6664 (1994).
18. C. S. Snijer, J. C. Jong, A. Meetsma, F. Bolhuis, and B. L. Feringa, *Chem. Eur. J.*, **1**, 594 (1995).
19. Y. Yasuda, E. Iishi, and Y. Shirota, *Chem. Lett.*, 575 (1996).
20. Y. Yasuda, Y. Takebe, M. Fukumoto, H. Inada, and Y. Shirota, *Adv. Mater.*, **8**, 740 (1996).
21. R. Mukkamala and R. G. Weiss, *Langmuir*, **12**, 1474 (1996).
22. L. Lu and R. G. Weiss, *J. Chem. Soc., Chem. Commun.*, 2029 (1996).
23. G. T. Crisp and J. Gore, *Synth. Commun.*, **27**, 2203 (1997).
24. R. J. H. Hafkamp, B. P. A. Kokke, I. M. Danke, H. P. M. Geurts, A. E. Rowan, M. C. Feiters, and R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.*, 545 (1997).
25. C. M. Garner, P. Terech, J. J. Allegraud, B. Mistrot, P. Nguyen, A. de Geyer, and D. Rivera, *J. Chem. Soc., Faraday Trans.*, **94**, 2173 (1998).
26. T. Kamiyama, Y. Yasuda, and Y. Shirota, *Polym. Prepr., Jpn., Eng. Ed.*, **46**, E37 (1997).
27. T. Kamiyama, Y. Yasuda, and Y. Shirota, *Polym. Prepr., Jpn., Eng. Ed.*, **47**, E549 (1998).
28. H. Tsutsumi, Y. Nakagawa, K. Miyazaki, M. Morita, and Y. Matsuda, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 1725 (1992).