

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Syntheses and Electronic Behaviors of Binary Hybrid Copolymers having Phenylene-Selenium, -Nickel, and -Strontium Units

Hideo Matsui^a; Hideyuki Hasegawa^a; Masakuni Yoshihara^{ab}

^a Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Higashiosaka, Osaka, Japan ^b Molecular Engineering Institute, Kinki University, Higashiosaka, Osaka, Japan

To cite this Article Matsui, Hideo , Hasegawa, Hideyuki and Yoshihara, Masakuni(2005) 'Syntheses and Electronic Behaviors of Binary Hybrid Copolymers having Phenylene-Selenium, -Nickel, and -Strontium Units', Journal of Macromolecular Science, Part A, 42: 7, 869 – 876

To link to this Article: DOI: 10.1081/MA-200063129

URL: <http://dx.doi.org/10.1081/MA-200063129>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Syntheses and Electronic Behaviors of Binary Hybrid Copolymers having Phenylene-Selenium, -Nickel, and -Strontium Units

HIDEO MATSUI,¹ HIDEYUKI HASEGAWA,¹
AND MASAKUNI YOSHIHARA^{1,2}

¹Department of Applied Chemistry, Faculty of Science and Engineering,
Kinki University, Higashiosaka, Osaka, Japan

²Molecular Engineering Institute, Kinki University, Higashiosaka, Osaka, Japan

Several binary hybrid copolymers having phenylene-selenium, -nickel, and -strontium units were synthesized, and their electronic behaviors were examined. UV-VIS and ESR spectral analyses and ab-initio calculations showed that an electron transfer from phenylene moiety to metals takes place and its ability vary by changing metals.

Keywords selenium, nickel, strontium, alternative framework, hybrid copolymers, electron transfer

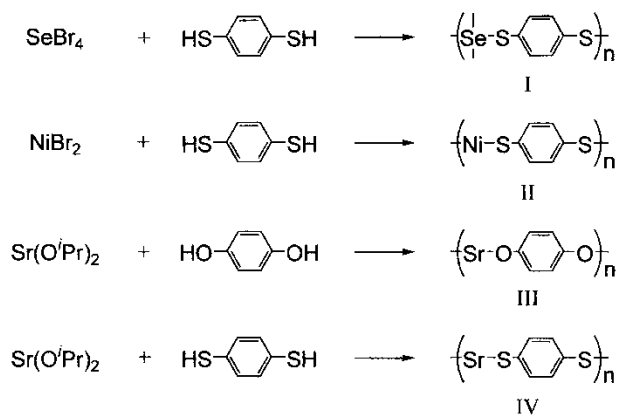
Introduction

Combinations of organic and inorganic units have been expected to afford new types of materials having unique properties, and many works on coordination polymers have been reported (1–7). We have considered that an organic–inorganic hybrid copolymer with covalent bonding will exhibit electronically and/or photochemically unique natures, because a covalent bonding electron will spread beyond an organic–inorganic bond, while a coordination bonding electron may be localized at a ligand–metal bond. Previously, we reported the syntheses of covalent-bonded metal-organic moiety binary hybrid copolymers, in which an electron transfer from organic moieties to metals takes place and an aryl moiety exhibits the effective electron transfer (8–12).

In this paper, we wish to describe the electronic behaviors of binary hybrid copolymers with a selenium-phenylene unit, a nickel-phenylene unit, and a strontium-phenylene unit (Scheme 1). These metals have different electronegativities, e.g. Se = 2.4, Ni = 1.8, and Sr = 1.0, and the change of metals in the copolymers are expected to affect their electronic natures.

Received November 2004; Accepted January 2005.

Address correspondence to Masakuni Yoshihara, Department of Applied Chemistry, Faculty of Science and Engineering and Molecular Engineering Institute, Kinki University, 3-4-1, Kowakae, Higashiosaka, Osaka, 577-8502, Japan. Tel.: +81-6-6721-2332; Fax: +81-6-6727-4301; E-mail: m-yoshi@apch.kindai.ac.jp



Scheme 1. Syntheses of hybrid copolymers.

Experimental

Reagents

Commercially available metal halides and strontium isopropoxide were used. Other reagents and solvents were purified by the standard procedures.

Apparatus

UV-VIS spectra were taken using a Hitachi U-4000 apparatus, and ESR spectra were taken using a Jeol Jes-TE200 ESR spectrometer.

Calculation

Ab-initio calculations were performed using copolymer models by the RHF/MINI calculation method.

Syntheses of Copolymers

Selenium-S-phenylene hybrid copolymer I was prepared by the reaction of selenium bromide (0.3 mmol) and 1,4-benzenedithiol (0.6 mmol) in anhydrous ethanol (80 mL) with the use of magnesium oxide (15 g) as a base under refluxing for 6 h. Similar treatment of nickel bromide (0.3 mmol) and 1,4-benzenedithiol (0.3 mmol) gave a nickel-S-phenylene hybrid copolymer II. A mixture of strontium isopropoxide (0.3 mmol) and 1,4-hydroquinone in anhydrous ethanol (80 mL) was refluxed for 6 h to give a strontium-O-phenylene hybrid copolymer III. Similar treatment of strontium isopropoxide (0.3 mmol) with 1,4-benzenedithiol (0.3 mmol) gave a strontium-S-phenylene hybrid copolymer IV. The copolymers obtained above were washed with anhydrous ethanol by using a Soxhlet extractor and dried by heating under *vacuo*.

Results and Discussion

Selenium bromide was found to react with 1,4-benzenedithiol with the use of magnesium oxide as a base for giving the corresponding binary copolymer I (orange-colored), while no reaction took place with 1,4-hydroquinone. Nickel bromide did not react with 1,4-hydroquinone but smoothly reacted with 1,4-benzenedithiol to give the corresponding binary copolymer II (brown-colored). Strontium isopropoxide reacted with both 1,4-hydroquinone and 1,4-benzenedithiol to give binary copolymers III (green-colored) and IV (light yellow-colored), respectively.

In order to see the sizes and forms of the copolymers, their TEM images were taken (Figure 1). Copolymer I was found to have a spherical form with the diameter of 150 nm, and copolymers II and III had amorphous forms.

The formations and the compositions of copolymers were examined. First, FT-IR spectra measurements showed the presences of a phenylene group for every copolymer, a C–S bond for I, II, and IV, and a C–O bond for III (Table 1). The ICP and elemental analyses of copolymers were performed. From metal and carbon contents, the ratios of the composition units were calculated, and the results are summarized in Table 2.

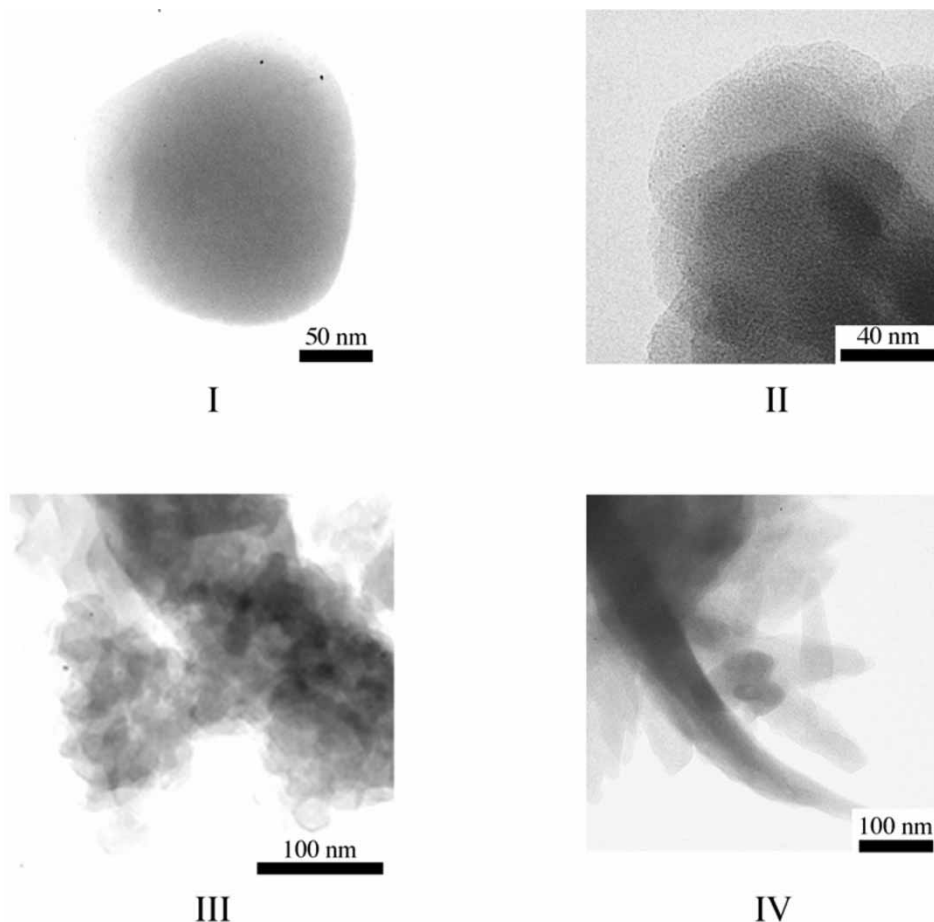


Figure 1. TEM image of copolymers.

Table 1
FT-IR spectra of copolymers

Copolymer	Wave number (cm ⁻¹)		
I	1490 (ν C ₆ H ₄)	839 (δ C ₆ H ₄)	669 (ν C-S)
II	1468 (ν C ₆ H ₄)	815 (δ C ₆ H ₄)	646 (ν C-S)
III	1488 (ν C ₆ H ₄)	1085 (ν C-O)	839 (δ C ₆ H ₄)
IV	1467 (ν C ₆ H ₄)	811 (δ C ₆ H ₄)	645 (ν C-S)

Table 2
ICP and elemental analyses of copolymers and ratios of composition units in copolymers

Copolymers	Elemental analyses (%)				Ratios of composition units			
	Se	Ni	Sr	C	Units	Ideal	Found	%
I	16.41	—	—	40.98	Se:C ₆ H ₄	1:2	1:2.73	73
II	—	23.45	—	36.60	Ni:C ₆ H ₄	1:1	1:1.27	79
III	—	—	30.68	32.15	Sr:C ₆ H ₄	1:1	1:1.28	78
IV	—	—	29.79	29.57	Sr:C ₆ H ₄	1:1	1:1.20	83

Composition ratios over 73% were obtained in every copolymer, suggesting that nearly alternative hybrid structures were formed.

The electronic behaviors of the copolymers were examined. The colors of the copolymers were found to vary by changing the metals, and their UV-VIS spectra were thus taken (Figure 2). Copolymers II and III showed absorption bands over the whole

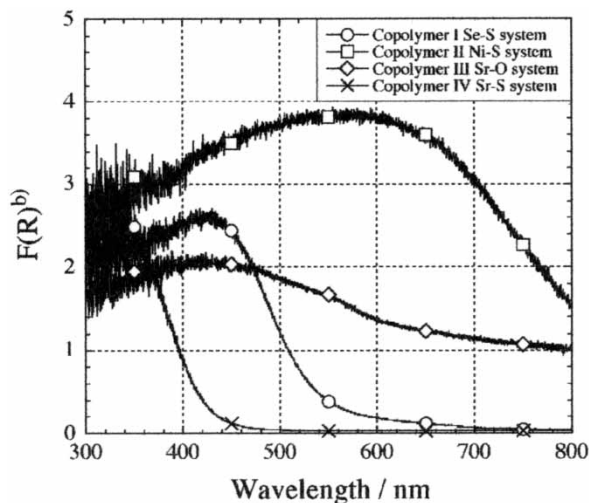


Figure 2. UV-VIS spectra of hybrid copolymers. a) Spectra were taken by using diffusion reflecting method. b) $F(R)$ is a coefficient of diffusion reflecting which is calculated by the following equation: $F(R) = \{1 - R(\lambda)\}^2 / 2R(\lambda)$, $R(\lambda)$: reflection rate of sample.

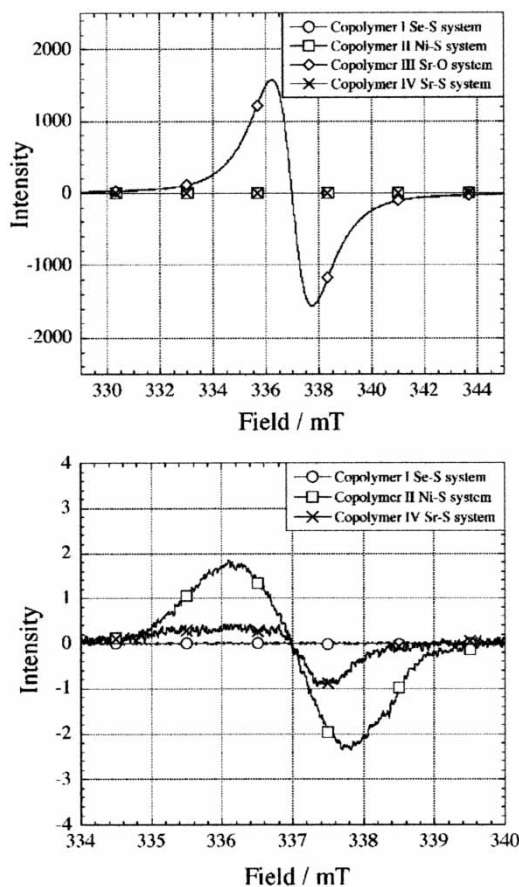


Figure 3. ESR spectra of hybrid copolymers. Spectra were taken by using 10 mg of sample. The measurement conditions: C.field; 337.0 mT, power; 1.00 mW, sweep width; 10 mT, modulation width; 0.5 mT, time constant; 0.1 s, temp.; room temp.

wavelengths with high intensities, and the intensities were in the order of $II > III > I > IV$. The ESR spectra of the copolymers were taken (Figure 3), indicating that a signal at 337 mT ($g = 2.004$) due to an organic free radical was observed except for I, and the intensities were in the order of $III > II > IV$. Our understanding is that an electron transfer

Table 3
Results of *ab-initio* calculations of copolymer models

Copolymers	HOMO (eV)	LUMO (eV)	ΔE (eV)
I	-1.225	1.034	2.259
II	-7.975	1.034	9.009
III	-5.934	0.735	6.669
IV	-6.887	0.191	7.078

$$\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$$

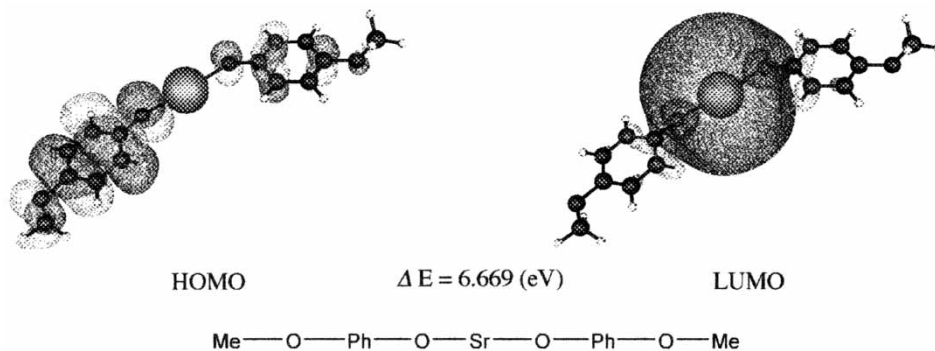


Figure 4. HOMO/LUMO of copolymer III model.

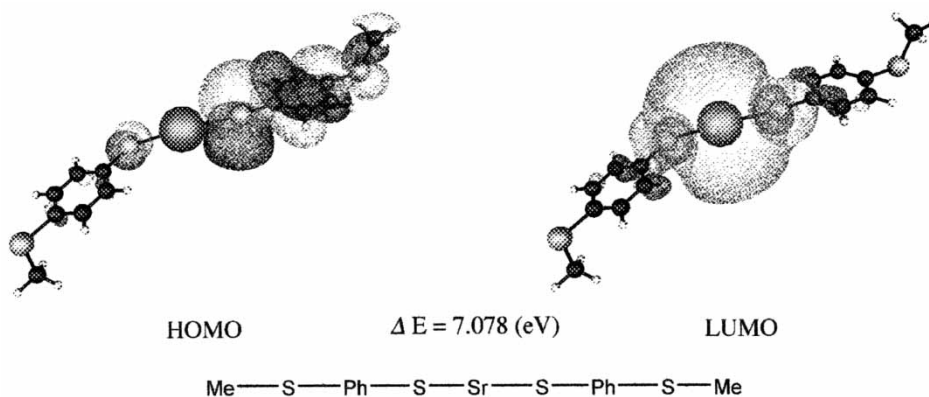


Figure 5. HOMO/LUMO of copolymer IV model.

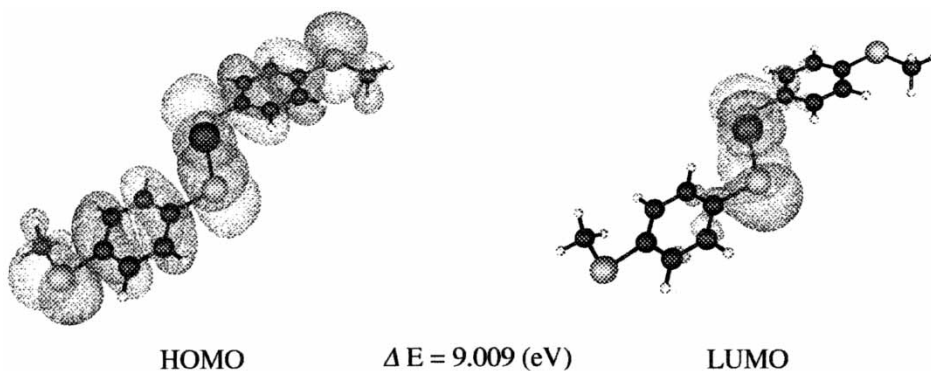


Figure 6. HOMO/LUMO of copolymer II model.

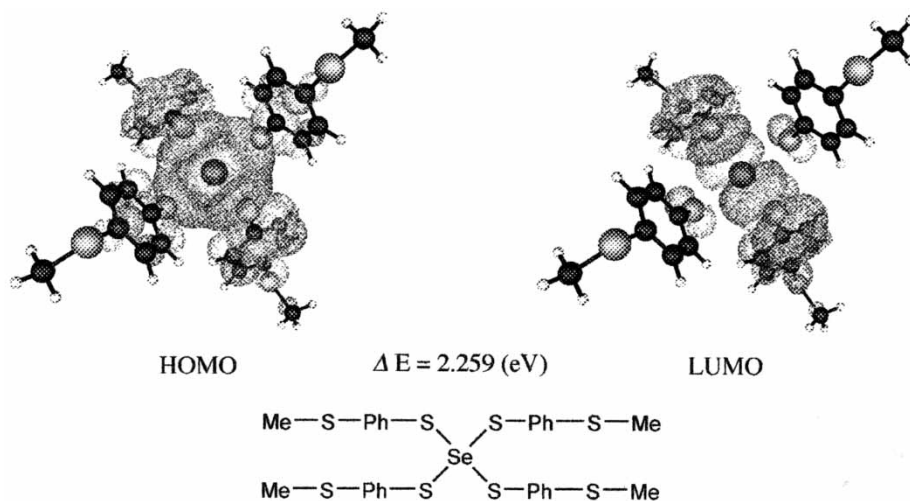


Figure 7. HOMO/LUMO of copolymer I model.

between the phenylene group and metals takes place, and its mode and/or degree may be affected by metals.

In order to examine the electron transfer process theoretically, *ab-initio* calculations by using copolymer models were performed (Table 3 and Figures 4–7). In a III's model (Figure 4), HOMO mainly uses the phenylene group and LUMO is completely localized at the strontium atom with the HOMO-LUMO energy difference (ΔE) of 6.805 eV, suggesting that the electron transfer from the phenylene group to the strontium atom takes place to localize the transferred electron on metal forming a cation radical species on the phenylene group, and thus the strongest ESR signal may be detected. In a IV's model (Figure 5), HOMO uses partly the phenylene group and LUMO is rather weakly localized on the strontium atom with $\Delta E = 7.077 \text{ eV}$, suggesting the occurrence of a small electron transfer. Almost similar trend is observed in a II's model (Figure 6). In a I's model (Figure 7), both HOMO and LUMO use the phenylene and the selenium atom with $\Delta E = 2.450 \text{ eV}$, suggesting that the transferred electron is not localized on the phenylene group and the selenium atom, and, thus, an ESR signal may not be detected.

Conclusions

In this work, we have examined electron movement in several phenylene-metal hybrid copolymers, and it was found that metals affected the mode of electron transfer. Such an electron transportation will be achieved by various metals and will provide a valuable source for electronically and/or magnetically useful materials.

References

- Burch, Robert, R. (1990) Oxidation-reductions for preparation of $(\text{Ti}(\text{OC}_6\text{H}_4\text{O}_2))_n$ and related metalloquinone polymers: hybrid inorganic–organic metal oxides. *Chem. Mater.*, 2: 633–635.
- Psheshetsky, V.S., Lishinsky, V.L., Kokorin, A.I., Tsarkova, L.A., Rakhnianskaja, A.A., and Pertsov, N.V. (1992) Coordination properties of polymeric azacrown ethers. *Makromol. Chem., Macromol. Symp.*, 59: 163–182.

3. Hao Encai, Wang Liyan, Zhang Junhu, Yang Bai, Zhang Xi, and Shen Jiacong, (1999) Fabrication of polymer/inorganic nanoparticles composite films based on coordinative bonds. *Chem. Lett.*, 5–6.
4. Badruz Zaman, Md, Smith Mark D., Ciurtin Delia M., and zur Hans-Conard, (2002) New Cd(II)-, Co(II)-, and Cu(II)-containing coordination polymers synthesized by using the rigid ligand 1,2-bis(3-pyridyl)ethyne(3,3-DPA). *Inor. Chem.*, 4895–4903.
5. Seki, K. and Mori, W. (2002) Syntheses and characterization coordination polymers with open frameworks. *J. Phys. Chem. B*, 106: 1380–1385.
6. Kitagawa Susumu, Kitaura Ryo, and Noro Shin-ichiro, (2004) Functional porous coordination polymers. *Angew. Chem. Int. Ed.*, 43: 2334–2375.
7. Larionova Joulia, Willemin Stephanie, Donnadiou Bruno, Henner Bernard, Guerin Cheistian, Gillon Beatrice, and Goujon Antoine, (2004) Cryatal engineering in two- and three-dimensional systems based on cyanomolybdates: structures, magnetism and intercalation properties. *J. Phys. Chem. Sol.*, 65: 677–691.
8. Matsui Hideo, Okada Akira, and Yoshihara Masakuni, (2001) Syntheses of novel networked alternative titanium-organic hybrid copolymers. *M. J. Mater. Sci. Lett.*, 20: 1151–1153.
9. Yoshihara Masakuni, Takeuchi Takeshi, Matsui Hideo, and Ito Seishiro, (2001) Synthesis of novel particles with alternative organic-zirconium hybrid structures. *J. Jpn. Soc. Color Mater.*, 74: 229–231.
10. Yoshihara Masakuni, Oie Hiroaki, Okada Akira, Matsui Hideo, and Seisaku Ohshiro, (2001) Synthesis of yttrium-organic hybrid networks. *Macromolecules*, 35: 2435–2436.
11. Kudo Ryoichi, Matsui Hideo, and Yoshihara Masakuni, (2002) Syntheses of novel networked hybrid copolymers with alternative tantalum-organic moieties. *J. Chem. Soc. Jpn, Chem. and Indus. Chem.*, 3: 371–375.
12. Yoshihara Masakuni, Sino Tatsuya, Otsuki Keigo, Matsui Hideo, and Seisaku Ohshiro, (2002) Syntheses of novel network alternative ytterbium-organic moieties hybrid copolymers. *J. Mater. Sci. Lett.*, 21: 1051–1053.