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Formation of composite microspheres comprising a 2,2′-bipyridyl iron(II/III) complex and acrylamide by UV irradiation

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Formation of the $[Fe(bpy)_3]^{2+}$ complex from $FeCl_3$ and bpy, and compounding with acrylamide (AA) took place simultaneously upon irradiation with a UV beam at 355 nm in an ethanolic solution of AA. We observed composite microspheres with $[Fe(bpy)_3]^{2+}$ confined in the acrylamide (AA) matrix with a simultaneous color change from yellow to red, due to metal-to-ligand charge transfer (MLCT) of the complex ion. The UV beam induces an $^2e \leftarrow t_1$ transition from Cl to Fe(III) in $[FeCl_4]^-$, resulting in the reduction of Fe(III) to Fe(II). Photolysis of $[Fe(III)Cl_4]^-$ is mediated by ethanol *via* a transition state comprising $[Fe(II)Cl_4]^{2-}$ with a solvated layer of C_2H_5OH after donating an electron to the $[Fe(III)Cl_4]^-$ complex. The reduction, in turn, causes decomposition of $[FeCl_4]^-$ to liberate a Cl radical, which changes the state of AA. The pink-colored microspheres are *ca.* 1 μm in average diameter, water-soluble, well dispersed in ethanol, and are stable even after one year.

Introduction

Photo-induced reactions are diverse and associated with a number of rational methods of preparing composite materials. One of the most interesting processes is photo-induced polymerization with other simultaneous reactions.[1] These processes are also attractive from ecological viewpoints since they reduce the consumption of organic solvents and elimination of remaining radicals in the wastes.[2,3] Transition metal complexes gather increasing interests in this context.[4] Their functions as an initiator of polymerization have, however, been little explored.

We previously reported on the irreversible dissociation of the tris(2,2′-bipyridyl)iron(II) complex [Fe(II)-bpy] doped into silica sol.[5] We further found the formation of Fe(II)-bpy by UV irradiation (365 ± 25 nm) on the mixture of $FeCl_3$ and bpy with and without the presence of silica sol.[6] Formation of the complex by the processes mentioned above parallels the change in the color and the electron spin states, enabling the preparation of photo-responsive silica microspheres by adding $FeCl_3$ and bpy to silica sol.[6] During our serial studies, we suspected an important role of $[FeCl_4]^-$ as an intermediate. The complex ion $[FeCl_4]^-$ is capable of photo-reduction with a simultaneous formation of a chlorine radical to serve as a photo-catalyst.[7] We may, therefore, anticipate simultaneous photo-polymerization of appropriate monomers by UV irradiation of the mixture containing these complex ions. This will give us the possibility of preparing composites comprising various metal oxides confined in the polymeric matrices. We therefore aim in this study at *in situ* composite formation to obtain microspherical composites with the complex ion confined in the matrix by UV irradiation. Emphasis is laid on the related mechanisms of competitive reactions involved.

Experimental

Preparation

Starting materials, acrylamide (Wako Chemicals), $FeCl_3$ (97 %, Aldrich) and 2,2′-bipyridyl (Junsei Chmicals) were used as received. We prepared 2.0 mol L^{-1}solutions of AA (the solvent was dehydrated ethanol unless otherwise stated) and gave sources of Fe and bpy at the molar ratio Fe:bpy = 1:3. Freshly prepared AA solution (0.8 mL) was placed in a quartz photo cell of 2 × 10 × 45 mm. The mixed solution was irradiated by a Nd^{3+}/YAG laser (Quanta-Ray GCR 6300) at a constant distance of 25 cm at the intensity of *ca.* 0.048–0.050 W for 30 min at room temperature in air. The irradiation wavelengths were chosen to be either 266, 355 or 532 nm. The resulting polymer microspheres were recovered after washing with ethanol several times, centrifuging and then drying in air at 50 °C for 24 h.

Characterization

Main tools of the characterization were spectroscopic methods. UV-Vis diffuse reflectance spectra were measured using a spectrometer V-550 (JASCO). FT-IR spectra were obtained by a conventional KBr disk method (FTS-60, DIGILAB). EPR spectra were observed at the X-band by a spectrometer JES-RE3X (JEOL). We calibrated the spectra by using a pure iron foil. Microspherical products were insoluble in ethanol and hence were easily separated from the non-reacted AA. They were subjected to a centrifugal sedimentation size distribution analysis (CAPA 500, Horiba) and scanning electron microscopy (SEM, JSEM5200 JEOL). The weight fraction of the isolated microspheres with respect to the initial weight of AA is adopted as a measure of the state change of AA. Mössbauer spectra were obtained at room temperature from a driver (Wissel, MR-250) and a multi-channel analyzer (Norland, 5500) with the beam source ^{57}Co in a Pd matrix (Radiochemical Centre, Amersham, UK).

Results and discussion

Formation of Fe(III)-bpy by UV irradiation

UV-Vis spectra are shown in Fig. 1 on the samples obtained after irradiation with a 355 nm beam for 30 min on the solution containing AA (2.0 mol L^{-1}) and $FeCl_3$ (5.7×10^{-4} mol L^{-1}) with and without bpy. The molar ratio of Fe:bpy was kept constant at 1:3. Without irradiation, no color change occurred [Fig. 1(a)]. Addition of $FeCl_3$ to the AA solution, irradiation using the 355 nm beam and subsequent addition of bpy did not result in appreciable reaction either [Fig. 1(b)]. Irradiation after simultaneous addition of $FeCl_3$ and bpy, however, resulted in a new absorption peak at around 525 nm, as shown in Fig. 1(c).

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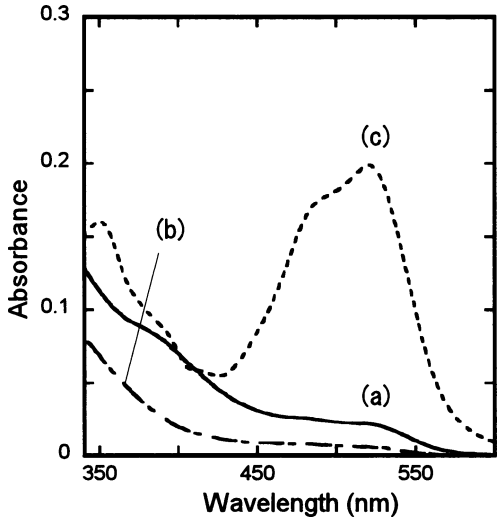

Fig. 1 Visible absorption spectra of Fe(II)-bpy doped AA: (a) Fe + bpy, (b) Fe + UV + bpy, and (c) Fe + bpy + UV.

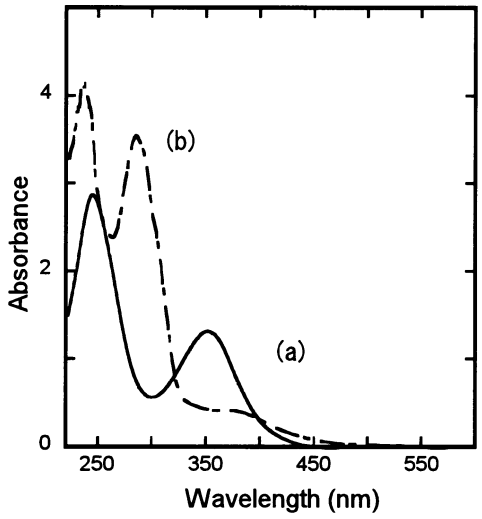

Fig. 3 UV-Vis spectra of (a) $FeCl_3$, and (b) addition of bpy to (a).

At the same time, the color of the solution changed from orange to dark red. Formation of the microspheres was primarily recognized by bare eye observation as an opaque white spot in the area corresponding to the beam diameter.

The opaque portion was much less soluble in absolute ethanol so that it was easily separated to obtain microspheres, as shown in Fig. 2. Although we did not perform gel permeation chromatography (GPC) analysis, the state change of AA strongly suggests the possibility of polymerization. We discuss this point further below. The pink-colored microspheres are *ca.* 1 μm in average particle diameter. These are water-soluble, well dispersed in ethanol, and stable even after one year.

The broad absorption at around 525 nm in Fig. 1(c) is typical for the metal [Fe(II)] to ligand (bpy) charge transfer (MLCT) of Fe(II)-bpy.[8] This indicates that we observe two photo-induced reactions, *i.e.* formation of the $[Fe(bpy)_3]^{2+}$ complex and the state change of AA by the 355 nm UV beam. Further evidence of Fe(II)-bpy will be shown below.

Since we used $FeCl_3$ as a sole Fe source, formation of Fe(II)-bpy indicates the reduction of ferric ions to ferrous ions. Photo-reduction of ferric ions requires the coexistence of bpy and is also associated with the state change of AA.

Interaction between Fe and bpy

Absorption spectra of the mixture of $FeCl_3$ and bpy are shown in Fig. 3. When bpy is added in an amount three times higher than Fe on a molar basis, the absorption peaks specific to $FeCl_3$ at 250 and 360 nm [Fig. 3(a)] disappeared and new three peaks appeared at 243, 282, and 375 nm [Fig. 3(b)]. They are assigned to the electron transitions, $^4t_2 \leftarrow {}^3t_2$, $^4t_2 \leftarrow t_1$ and $^2e \leftarrow t_1$, respectively.[9] They correspond to ligand (Cl) to metal [Fe(III)] charge transfer (LMCT). These spectral changes are only possible when a complex ion is formed, *i.e.*

$$2FeCl_3 + 2bpy \rightarrow [FeCl_4]^- + [Fe(bpy)_2Cl_2]^- \qquad (1)$$

While the reduction potential from free Fe(III) to free Fe(II) amounts to 0.77 V, that of photo-reduction of $[FeCl_4]^-$ to $[Fe(II)Cl_3]^-$ is 0.34 V, being much lower. This indicates that photo-reduction of the $[FeCl_4]^-$ ion is easier than the normal chemical reduction of free ferric ions.[10,11]

Once the LMCT absorption of the $[FeCl_4]^-$ complex is excited, the complex tends to dissociate to give a chlorine radical and ferrous ion.[10] It is known that the transition $^2e \leftarrow t_1$ possesses the energy band gap 364 nm, being the smallest of all the three transitions given above. Hence, it is only the possible transition by 355 nm UV irradiation.

We now discuss the availability of the electron necessary for the reduction from Fe(III) to Fe(II). Since it is reported that the rate of photolysis of the complex $[FeCl_4]^-$ is sensitive to the solvent, we examined the role of the solvent. As we changed the solvent from ethanol to acetone or tetraethoxysilane, we observed neither formation of the complex nor the state change of AA by UV irradiation. This necessarily indicates the important role of ethanol.

Brealey and Uri reported the mechanisms of electron transfer between the complex ion and the solvated layer.[11] As Farkas *et al.*[12,13] pointed out, the electrons spread out over the solvation layer are capable of transferring to the central complex ion $[Fe(III)Cl_4]^-$ as the consequence of UV irradiation, *i.e.*

$$[Fe(IIICl_4]^- + (C_2H_5OH \xrightarrow{355nm} [Fe(IICl_4]^{2-} + (C_2H_5OH^+ \qquad (2)$$

where (C_2H_5OH) and $(C_2H_5OH)^+$ denote the solvation layer of ethanol before and after donating an electron to the $[Fe(III)Cl_4]^-$ complex.

It is reported that the photo-reduction of the Fe(III) ion in the $[Fe(III)Cl_4]^-$ complex produces the $[Fe(II)Cl_4]^{2-}$ ion.[11,14] The latter ionic species is unstable and easily dissociates to give a chlorine radical, $Cl^{\bullet}$, as

$$[Fe(IICl_4]^{2-} \xrightarrow{355nm} [Fe(IIICl_3]^- Cl^{\bullet} \qquad (3)$$

The Fe(II)-bpy complex ion is then formed by reassociation of

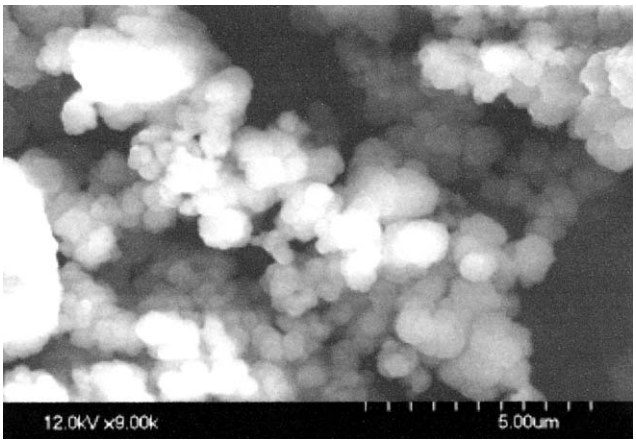

Fig. 2 Scanning electron micrograph of AA-based composite microspheres, prepared after irradiation with 355 nm UV for 30 min. The initial concentrations of $FeCl_3$ and AA were 0.57 mM and 2.0 M, respectively.

$[Fe(II)Cl_3]^-$ with bpy, as

$$[Fe(II)Cl_3]^- + 3bpy \rightarrow Fe^{2+}(bpy)_3 + 3Cl^- \quad (4)$$

Simultaneous polymerization of AA can then occur by the Cl radials liberated by reaction (3).

Role of $FeCl_3$ and bpy on the state change of AA

The percentage yield of complex microspheres, $(AA)_C$, determined from the weight ratio $(AA)_C/AA$, after irradiation with the 355 nm beam for 30 min is plotted in Fig. 4 as a function of $FeCl_3$ concentration. Since the value of the vertical axis in Fig. 4 is determined after a constant time for the reaction (30 min), we may interpret it as a measure of the rate of the state change of AA. When bpy was added simultaneously, the molar ratio Fe:bpy was kept constant at 1:3. As we added $FeCl_3$ without bpy, we did not observe any microspheres at all. It is therefore obvious that the state change of AA is initiated by the coexistence of bpy, as in the case of the photo-reduction of Fe(III). As shown in Fig. 4, the rate of the state change exhibits a sharp maximum at $[FeCl_3] = 5.7 \times 10^{-4}$ mol L^{-1}.

Increasing the rate of the AA state change with increasing the concentration of $FeCl_3$ up to 5.7×10^{-4} mol L^{-1} is explained by the formation of Cl radicals by charge transfer after a photo-induced reaction of $FeCl_3$ with bpy.[11] The apparent minimum concentration for a significantly observable rate of reaction depends upon the arbitrary choice of the reaction time, 30 min in this case. Conversely, further increase in the $FeCl_3$ concentration (above 5.7×10^{-4} mol L^{-1}) suppressed the rate of the state change of AA. This might be attributed to dimerization of $FeCl_3$, preventing formation of the complex ion $[FeCl_4]^-$, as reported by Brealey and Uri in their study on the kinetics of the photolysis of $[FeCl_4]^-$.[11]

Interaction between the microspheres and Fe(III)/Fe(II) complexes

EPR spectra were taken from the microspheres comprising the Fe(II) complex and AA. From the film-like solid obtained by careful heating with an evaporator without UV irradiation, we observe two signals peaking at 200 and 470 mT, as shown in Fig. 5(a). The broad peak at around 200 mT is attributed to the species containing the Fe(III) ion.[15,16] As we already discussed previously, $FeCl_3$ reacts entirely with bpy to form the complex ionic species $[FeCl_4]^-$. It is therefore reasonable to assume that all of the EPR signals from Fe(III) are associated solely with $[FeCl_4]^-$ to indicate coexistence with the Fe(II)-bpy complex.

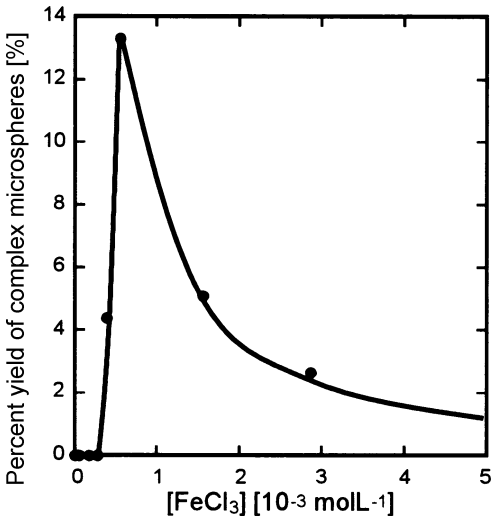

Fig. 4 Change in percentage photo-polymerization with $FeCl_3$ concentration in AA. [AA] = 2.0 mol L^{-1}, Fe:bpy = 1:3 (molar ratio), by irradiation at 355 nm for 30 min.

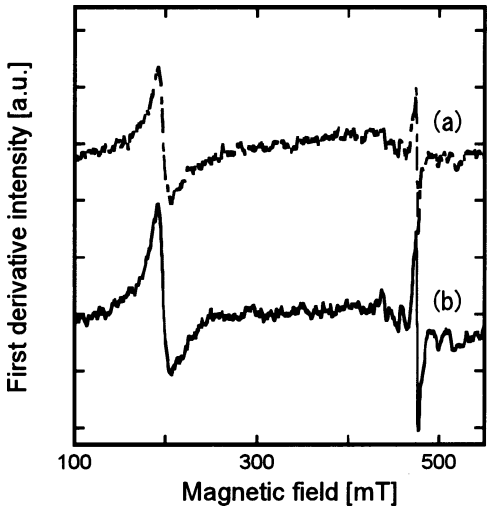

Fig. 5 EPR spectra of Fe(II)-bpy doped AA: (a) before, and (b) after 355 nm UV irradiation.

We also observe a very similar EPR spectrum on the sample after UV irradiation.

The effect of UV irradiation upon the state of the Fe species was further examined by Mössbauer spectroscopy. We observe a clear change in the spectra before and after UV irradiation, as shown in Fig. 6(a) and 6(b), respectively. The spectrum before irradiation [Fig. 6(a)] is very similar to those observed by Witten *et al.* on $[Fe(bpy)_2Cl_2][FeCl_4]$.[17] In contrast, the spectrum after UV irradiation [Fig. 6(b)] exhibits close similarity with those of $[FeCl_4]^-$ doped in poly(aniline) or poly(thiophene).[18,19] If the $Fe(bpy)_3^{2+}$ ions were isolated, quadruple splitting would be much larger.[20] We therefore interpret that the doublet peak is attributed to the octahedral complex formation between Fe(II) and AA. Consequently, we conclude that the complex ions $[FeCl_4]^-$ are confined in the AA-based composite microspheres.

When the AA-based microspheres are subjected to UV irradiation, we observed a very broad band peaked at around 240 nm as shown in Fig. 7(a). The band is ascribed to the π–π^* transition in AA. Those microspheres with the complex compound exhibit a red shift by *ca.* 20 nm, as shown in the UV absorption spectrum, Fig. 7(b). The observed red shift then implies the delocalization of the π-electrons in the AA-based microspheres to decrease the energy band for this transition.

Infrared spectra of the PAA microspheres are displayed in Fig. 8. We assign the band at around 2930 cm^{-1} in Fig. 8(a) and 8(b) to $\nu(CH_2)$ stretching.[21] Large bands ranging from 3100 to 3500 cm^{-1} are attributed to the stretching vibration of NH_2 associated with intra- or inter-molecular N–H···O=C hydrogen bonds of PAA, respectively. We further assign the peaks at 3330 and 3190 cm^{-1} to asymmetric and symmetric vibrations, respectively, of NH_2. By comparing the spectra from the microspheres without doping [Fig. 8(a)] and those doped with Fe(II)-bpy [Fig. 8(b)], we notice that the relative intensity of the peak at 3150 cm^{-1} increases by doping. This might imply the interaction between the electrons in the AA-based microspheres and the complex Fe(II)-bpy toward the formation of bridging bonds, Fe···O=C.

Conclusion

By irradiating with a 355 nm UV beam, $[Fe(bpy)_3]^{2+}$ was formed from $FeCl_3$ and bpy in an ethanolic solution of acrylamide with its simultaneous state change to form microspheres. This was visualized by the color change from yellow to red, due to metal-to-ligand charge transfer (MLCT) of the complex ion. In the resulting AA-based microspheres, the

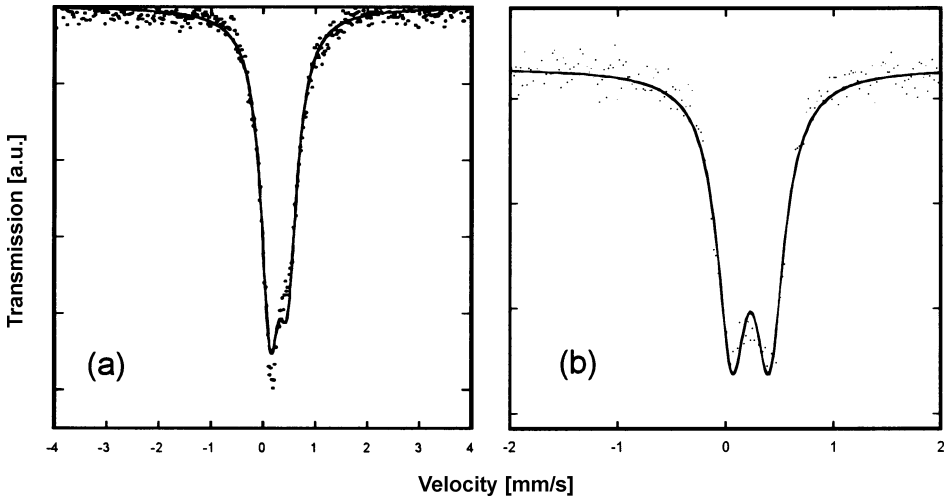

Fig. 6 Mössbauer spectra of (a) Fe-bpy complex without UV irradiation, and (b) Fe-bpy doped PAA (polyacrylamide) obtained after UV irradiation.

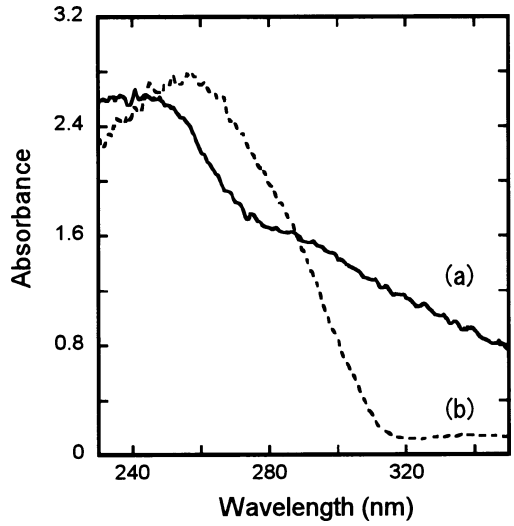

Fig. 7 UV absorption spectra of PAA: (a) without doping, and (b) doped with Fe(II)-bpy.

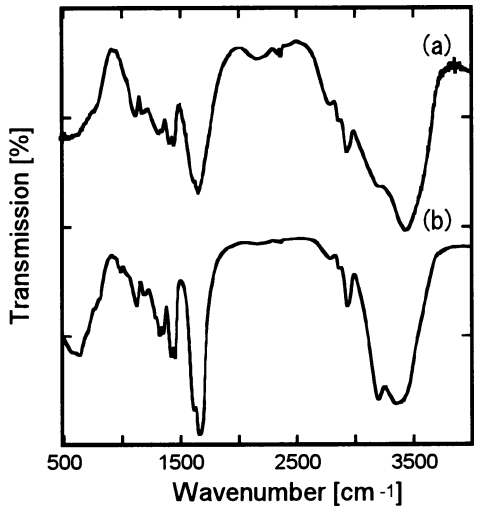

Fig. 8 FT-IR spectra of PAA: (a) without doping, and (b) doped with Fe(II)-bpy.

coexistence of $[Fe(bpy)_3]^{2+}$ was confined. The UV beam induces a $^2e \leftarrow t_1$ transition from Cl to Fe(III) in $[FeCl_4]^-$, resulting in the reduction of Fe(III) to Fe(II). Photolysis of $[FeCl_4]^-$ is observed in an ethanolic solution but not in a solution of acetone or tetraethoxysilane. We therefore conclude the active participation of ethanol in the present complex photochemical reaction. The pink-colored microspheres are *ca.* 1 μm in average particle size, water-soluble, well dispersed in ethanol, and are stable even after one year.

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References

1 J. Hu, H. Zhao, Q. J. Zhang and W. D. He, *J. Appl. Polym. Sci.*, 2003, **89**, 1124–1131.
2 C. Grotzinger, D. Burget, P. Jacques and J. P. Fouassier, *Macromol. Chem. Phys.*, 2001, **202**, 3513–3522.
3 C. Billaud, M. Sarakha and M. Bolte, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 3997–4005.
4 C. R. Rivarola, S. G. Bertolotti and C. M. Previtali, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 4265–4273.
5 C. Nakanishi, S. Ikeda, T. Isobe and M. Senna, *MRS Bull.*, 2002, **37**, 647–651.
6 C. Nakanishi, S. Ikeda, T. Isobe and M Senna, *J. Sol-Gel Sci. Technol.*, 2003, **26**, 103–106.
7 R. Zhang, P. E. Mallon, H. Chen, C. M. Huang, J. Zhang, Y. Li, Y. Wu, T. C. Sandreczki and Y. C. Jean, *Prog. Org. Coat.*, 2001, **42**, 244–252.
8 G. M. Bryant, J. E. Fergusson and J. H. K. Powell, *Aust. J. Chem.*, 1971, **24**, 257–274.
9 ABP review, Inorganic electronic spectroscopy, *Stud. Phys. Theor. Chem.*, 1984, **33**, pp. 203–591.
10 A. Kakui, D. Takada and H. Watanabe, *Chem. Soc. Jpn.*, 2000, **5**, 323–327.
11 G. J. Brealey and N. Uri, *J. Chem. Phys.*, 1952, **20**(2), 257–262.
12 A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 1938, **34**, 1113–1120.
13 L. Farkas and F. S. Klein, *J. Chem. Phys.*, 1948, **16**, 886–893.
14 G. A. Kraus and B. S. Fulton, *J. Org. Chem.*, 1985, **50**, 1784–1786.
15 J. Wang and M. X. Wan, *Synth. Met.*, 1999, **101**, 848–849.
16 T. Masui, T. Ishiguro, J. Tsukamoto and A. Takahashi, *Synth. Met.*, 1997, **84**, 867–868.
17 E. H. Witten, W. M. Reiff, K. Lázár, B. W. Sullivan and B. M. Foxman, *Inorg. Chem.*, 1985, **24**, 4585–4591.
18 N. Kumar, S. R. Vadera and P. C. Jana, *Polymer*, 1992, **33**, 2424–2426.
19 S. Kitao, M. Seto, Y. Maeda, T. Matsuyama, S. Masubuchi and S. Kawama, *J. Phys. Soc. Jpn.*, 1997, **66**, 1195–1200.
20 H. Sano and M. Katada, in *Mössbauer Spectroscopy, Theory and Application*, Spectroscopical Society of Japan, Methodology Series No. 31 (in Japanese), Gakkai Shuppan Center, Tokyo, 1996, vol. 31, pp.71–145.
21 M. E. Rinaudo, J. C. Lassegues, J. Portier, J. Salardenne, J. Grondin and R. Cavagnat, *J. Mater. Chem.*, 1997, **7**, 1549–1555.