

Preparation of the Composite Consisting of Nano-Sized Gold Particles and Nylon-11 Oligomer

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Received 24 November 1998; accepted 27 April 1999

ABSTRACT: Nylon-11 oligomer was utilized as a matrix to prepare a composite containing nano-sized gold particles. Nylon-11 oligomer was prepared by a thermal degradation of a commercial nylon-11 in vacuum. Weight-average molecular weight of the oligomer was in a range from 500 to 800. Nylon-11 oligomer was formed into a film, and then gold was vapor-deposited onto the oligomer film. The gold-colored oligomer film turned a transparent red after a heat treatment at 120°C. Transmission electron microscopy showed an isolated distribution of nano-sized gold particles in the red film of the oligomer. The gold particles were stable in the oligomer for more than a year, and they were dissolved in CH₂Cl₂ to produce a stable colloidal solution. These results suggest that the gold particles were not only dispersed in the oligomer film, but they were stabilized by the nylon-11 oligomer to form a composite. IR spectrum of the composite showed that N—H groups of the nylon-11 oligomer were responsible for the interaction between the gold particles and the oligomer. Pulse ¹H-NMR measurement suggested that an active molecular motion of the nylon-11 oligomer caused the dispersion of the gold particles. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1654–1661, 1999

Key words: nylon-11 oligomer; nano-sized gold particles; dispersion; composite

INTRODUCTION

Methods for preparing nano-sized metal particles have attracted much interest because the nano-sized particles are one of the mesoscopic materials for future devices.¹ Their properties are different from those of bulk materials. This phenomenon is called the size effects.^{2–6} Evaporation technique has been one of the most effective methods for preparing isolated nano-sized particles on a solid substrate.⁷ Chemical reduction of inorganic salts was also used extensively to prepare nano-sized particles dispersed in solutions,

and surfactants or polymers are used to prevent aggregation or coagulation of the particles.

We have previously reported on the thermal relaxation technique to prepare nano-sized metal particles dispersed in a polymer film.^{8,9} Structural relaxation of polymer caused dispersion of metal particles from a metal film formed on the polymer film. In this technique, a nylon-11 film formed by vapor deposition was used as a matrix because nylon-11 is a unique polymer exhibiting ferroelectric or piezoelectric property,^{10,11} and their structure is well characterized.^{12,13} However, the vapor-deposited film is not adequate for dispersing a great amount of the nano-sized metal particles because the thickness of the film is very thin.

In this article, we present a new material, nylon-11 oligomer, which was utilized as a matrix

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Journal of Applied Polymer Science, Vol. 74, 1654–1661 (1999)

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CCC 0021-8995/99/071654-08

for preparing a composite containing nano-sized gold particles. A great deal of the nylon-11 oligomer was prepared in one batch by the thermal degradation of nylon-11 polymer. The nylon-11 oligomer was formed into a film, and isolated gold particles were dispersed in the film to give a composite. The gold particles were stable in the composite, and it was dissolved in CH_2Cl_2 to give a stable colloidal solution of gold.

EXPERIMENTAL

Preparation of Nylon-11 Oligomer

Degradation of nylon-11 was carried out by using a reaction apparatus consisting of a quartz flask (reactor) equipped with a storage flask and another flask in which products were collected (collector). One hundred grams of nylon-11 pellets (Rilsan BMN0, ELF Atochem S.A., France; sold by Toray Industries, Tokyo, Japan) were introduced into the storage flask, and then the reaction apparatus was evacuated to ca. 200 Pa. The reactor was heated to a temperature ranging from 450 to 550°C, and then the nylon-11 pellets were transferred into the reactor. To suppress an excessive degradation of nylon-11 in the reactor, the transfer of the pellets was carried out intermittently. The pellets soon fused and began to degrade thermally. Degraded species evaporated and condensed at the collector cooled with liquid nitrogen. The condensates were heated again at 200°C in vacuum to remove oily product, and 93 g of nylon-11 oligomer was obtained.

Products were characterized by infrared spectroscopy (IR), gel permeation chromatography (GPC), and thermal analysis (DTA). IR spectra were obtained by Jeol FTIR JIR-6000 spectrometer. GPC was carried out by a Waters 600E system equipped with Shodex K-801 and K-802 GPC columns (Showa Denko K.K., Tokyo, Japan) at a flow rate of 1 mL/min. Chloroform (Wako Pure Chemicals Industries, Ltd., Osaka, Japan) was used as a solvent and an eluent. Polystyrene standards (Showa Denko), the molecular weights of which were in a range from 580 to 66,000, were used for calibration of GPC. For a GPC measurement of nylon-11 polymer, a 4 : 1 mixture of chloroform and *m*-cresol (Wako) was used as a solvent and an eluent. DTA measurement was carried out in air with Rigaku TAS-300 system.

Preparation of Nano-Sized Gold Particles/Nylon-11 Oligomer Composite

The nylon-11 oligomer (10 g) was dissolved in chloroform (190 g), and the solution (60 g) was cast on a glass plate. After evaporating chloroform by heating at 40°C for 60 min in air, a thin film with thickness of ca. 15 μm was obtained. In an evaporator (ULVAC EBH-6) evacuated to ca. 6.7×10^{-3} Pa, gold (99.99%, Tanaka Kikinokogyo K.K., Tokyo, Japan) was vapor deposited from a tungsten basket onto the thin film of the nylon-11 oligomer. Deposition rate of ca. 6 nm min^{-1} was monitored by a quartz-crystal microbalance. Thickness of the deposited gold was 20 nm. Temperature of the nylon-11 oligomer film was kept at 20°C. After the vapor deposition of gold, the gold/nylon-11 oligomer film was heated at 120°C for 10 min in air to disperse gold particles into the interior of the film.

Samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and visible spectroscopy (VIS). XRD patterns were measured by 2θ method by using $\text{CuK}\alpha$ radiation on a Rigaku RINT1000 system equipped with a thin film attachment. Incident angle of X rays to a sample was 1°. TEM images were observed by using a Jeol JEM-2010 TEM operated at 200 kV. The samples were dissolved in CH_2Cl_2 (Wako). Then, drops of the solutions were put on carbon-coated Cu grids and dried. VIS spectra were measured by Shimadzu PC-3100 UV-VIS spectrophotometer.

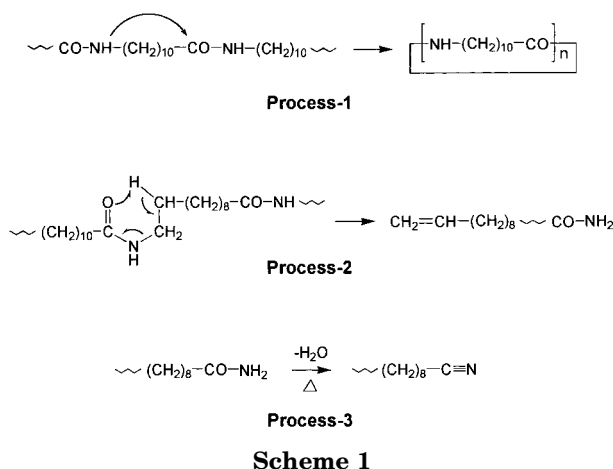
Measurement of T_2 for the Nylon-11 Oligomer

To estimate the molecular motions of the nylon-11 oligomer, T_2 (spin-spin relaxation time) measurements were carried out by pulse ^1H -NMR spectrometer (Jeol HMN-MU-25). Free-induction decays were recorded for total ^1H of the nylon-11 oligomer in a temperature range from -70 to 100°C and analyzed by using a personal computer. Solid-echo method was used for the measurement $< 0^\circ\text{C}$. Carr-Purcell-Meiboom-Gill method was used for the measurement $> 0^\circ\text{C}$. A measurement for nylon-11 polymer was carried out in a temperature range from -70 to 150°C by using the solid echo method.

RESULTS AND DISCUSSION

Characterization of Degradation Products

When an intact nylon-11 film was used as a substrate, vapor deposition of gold formed a gold-



colored film. On the other hand, when a melted nylon-11 was rapidly quenched to room temperature and the metastable nylon-11 film thus formed was used as a substrate, some of vapor-deposited gold was dispersed into the film to form nano-sized particles.¹⁴ An excessive heating of the nylon-11 melt caused the favorable dispersion of the gold particles. This indicated that a thermally degraded nylon-11 was effective for preparing the nano-sized gold particles. Therefore, we first examined thermal degradation of nylon-11 and characterized the degraded products.

Degradation of nylon-11 began around 350°C, and nylon-11 was completely decomposed above 600°C.¹⁵ It was reported that various kinds of compounds were produced by the thermal degradation of nylon-11 in nitrogen (Scheme 1).^{16,17} These compounds were considered to be effective for dispersing gold particles because the compounds had NH or CN groups which were considered to have affinity for gold.¹⁸ However, the degradation in nitrogen was unsuitable because it gave a mixture consisting of various compounds. Therefore, to obtain a product having a definite structure, we adopted a thermal degradation in vacuum. In vacuum, the product produced by the degradation was immediately evaporated, and it was subject to no further degradation.

Nylon-11 pellets were cloudy white solids, but they turned waxy solid after the degradation. Figure 1 shows the IR spectra of the products. The product prepared by the degradation at 525°C showed a similar spectrum to that of the nylon-11 polymer. The bands at 3311 and 1633 cm^{-1} were assigned to the NH and C=O group of amide, respectively. Also, bands assigned to C—H were observed at 2929 and 2854 cm^{-1} . In addition, the

degradation product showed the bands at 3082 and 2247 cm^{-1} , which were assigned to C—H of unsaturated hydrocarbon (C=C) and C≡N group, respectively. The $\text{CH}_2=\text{CH}-$ group was generated in the process-2, and the CN group was generated in the process-3 shown in Scheme 1. Degraded products obtained by the degradation at 450 and 550°C showed similar spectra to that of the product degraded at 525°C, but the spectra was broad because mixtures were generated.

GPC measurement for the degradation product at 525°C indicated that the distribution of the molecular weight was a little broad (weight-average molecular weight/number-average molecular weight was ca. 1.3). Weight-average molecular weight measured at the maximum of the GPC chart was 652. Weight-average molecular weight of the initial nylon-11 polymer was ca. 25,000. Therefore, the nylon-11 polymer was considered to be degraded to an oligomer.

From the results described above, we concluded that the product prepared by the degradation at 525°C in vacuum was nylon-11 oligomer with CN and $\text{CH}_2=\text{CH}-$ terminal groups.

Preparation of Nano-Sized Particles Using Nylon-11 Oligomer

When gold (20 nm in thickness) was deposited on a nylon-11 oligomer film, the surface of the film

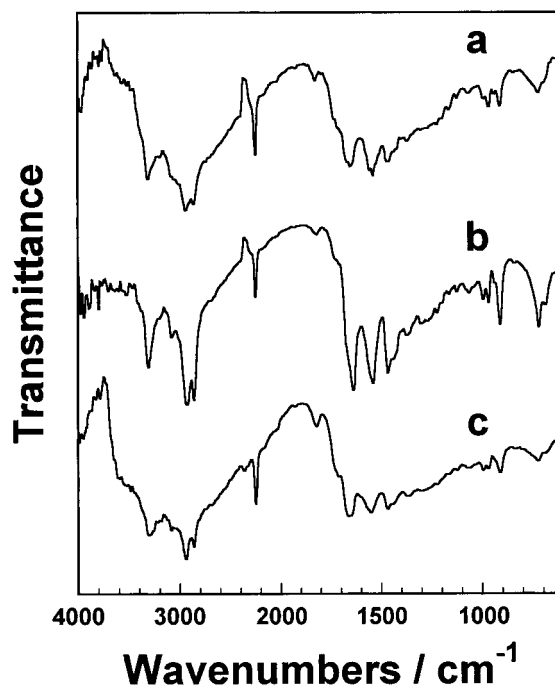


Figure 1 IR spectra of nylon-11 oligomers prepared at (a) 450°C, (b) 525°C, and (c) 550°C in vacuum.

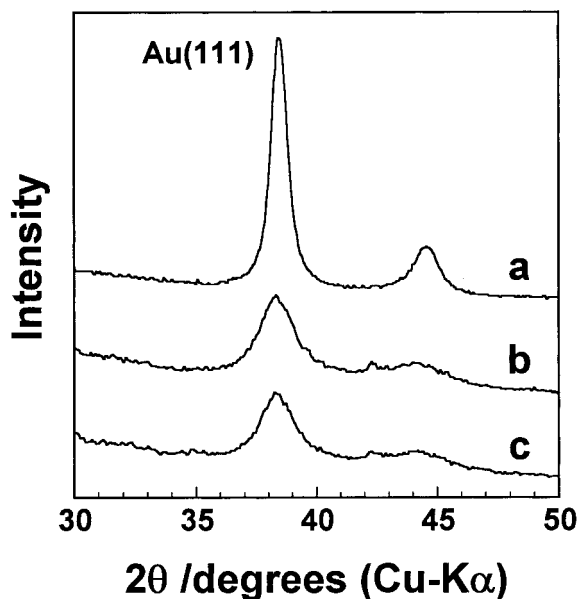


Figure 2 XRD patterns of gold vapor deposited on (a) glass plate, and nylon-11 oligomer film (b) before and (c) after heat treatment at 120°C for 10 min in air. Thickness of deposited gold was 20 nm.

exhibited a gold color. After a heat treatment at 120°C, which was chosen as a point where the nylon-11 oligomer begins to melt partially, the gold color thoroughly disappeared on the surface of the oligomer film, and the transmitted color turned ruby red. The ruby-red color of the oligomer film indicated a formation of nano-sized particles of gold because the ruby-red color was characteristic of nano-sized gold particles.¹⁹ The ruby-red color also suggested that the gold particles fell apart in the nylon-11 oligomer by the heat treatment.

Figure 2 shows XRD patterns of gold vapor deposited on a glass plate and on the nylon-11 oligomer films, respectively. The gold film deposited directly on the glass plate showed a sharp Au(111) peak at $2\theta = 38.3^\circ$. On the other hand, the gold deposited on the oligomer film showed a broad and weak Au(111) peak at $2\theta = 38.5^\circ$ before the heat treatment. A broad linewidth of an XRD peak indicates that crystallite size is very small.²⁰ Before the heat treatment, crystallite size of the gold deposited on the oligomer film, which was calculated by means of Scherrer's equation by using the width of Au(111) peak, was ca. 6 nm. This result suggested that the gold deposited on the nylon-11 oligomer did not form a continuous film, but produced nano-sized particles, which aggregated on the surface of the oligomer film so that the film exhibited the gold color.

After the heat treatment, the oligomer film showed almost the same XRD pattern as that before the heat treatment. This indicated that the nano-sized particles of gold did not increase their size in the oligomer film. Therefore, the particles were considered to be stabilized by the nylon-11 oligomer, and the gold particles and the nylon-11 oligomer formed a composite.

Figure 3 shows VIS spectra of the gold/nylon-11 oligomer films. Before the heat treatment, the film showed a little broad absorption band at 528 nm. After the heat treatment, the absorption band shifted only slightly to 524 nm, and a profile of the band became a little sharper accompanying a decrease in absorbance. These bands were both assigned to plasmon absorption of nano-sized gold particles according to the previous results.⁹ Therefore, the band at 528 nm for the oligomer film before the heat treatment suggested that isolated gold particles were also present on the film in addition to the aggregate of the gold particles, which showed the gold color. The gold color gave an almost flat absorption in a VIS spectrum, and thus the disappearance of the gold color brought about the decrease in the absorbance.

Maxwell-Garnett (MG) theory explains a plasmon absorption of nano-sized metal particles.²¹ The MG theory predicts that when a volume fraction of nano-sized particles in a matrix decreases, a plasmon absorption band shows a blue shift. According to the MG theory, the slight blue shift

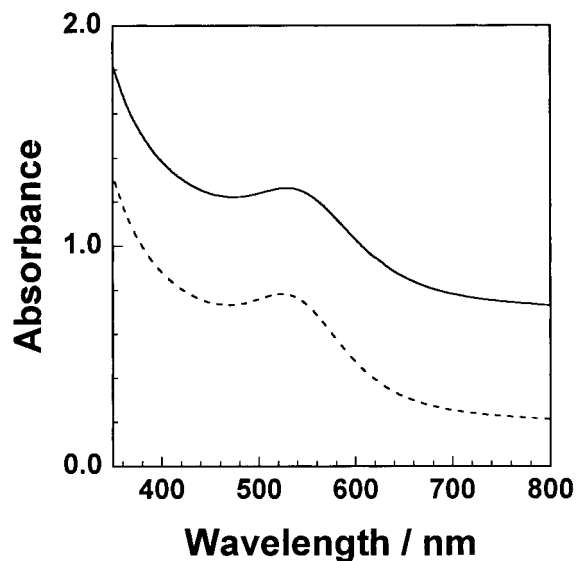


Figure 3 VIS spectra of gold/nylon-11 oligomer film before (solid line) and after (dotted line) heat treatment at 120°C for 10 min in air.

of the plasmon band observed in Figure 3 suggests that the aggregate of the gold particles on the oligomer film are dispersed into the film, and a volume fraction of the gold particles per unit volume is decreased. However, the absorption band at 524 nm was still high for fairly isolated gold particles.⁷ This indicated that the gold particles did not come apart from each other enough to lose dipole interactions between their plasmon electrons.

The gold particles/nylon-11 oligomer film was very stable at room temperature for long periods exceeding a year, and any separation of gold from the composite was not observed. The film was dissolved easily into dichloromethane or other organic solvents to produce a ruby red-colored solution with no precipitates. A TEM image of a specimen collected from the solution was shown in Figure 4. A number of nano-sized particles were observed, and a selected-area diffraction of the specimen showed a clear diffraction pattern of gold. The size distribution of the gold particles dispersed in the oligomer film, also shown in Figure 4, gave the mean size of ca. 4.5 nm.

Interaction Between Gold and Nylon-11 Oligomer

The stable dispersion of gold particles not only in the nylon-11 oligomer but also in the solution confirmed again that each particle was stabilized by nylon-11 oligomer molecules. The previous article reported that polymers having functional groups such as CN, SH, and NH₂ contributed to the formation of colloidal gold.¹³ The nylon-11 oligomer prepared by the degradation of nylon-11 polymer also had CN and NH₂ groups, as shown in Figure 1.

An interaction between the gold particles and the nylon-11 oligomer was examined by IR spectroscopy. A composite containing 13.8 wt % of gold particles was prepared by the vapor deposition of 600 nm of gold in thickness onto a film of the nylon-11 oligomer, followed by a heat treatment at 120°C. The mean size of the gold particles dispersed in the composite was ca. 5.5 nm. The composite was washed with methanol, and the majority of the nylon-11 oligomer, which was not bound to the gold particles, was removed. This operation gave a concentrated composite. The content of the gold particles became 79.8 wt %, but the mean size of the gold particles (ca. 5.6 nm) was almost the same as that of the gold particles before the concentration. Figure 5 shows a TEM image of the concentrated composite. The gold

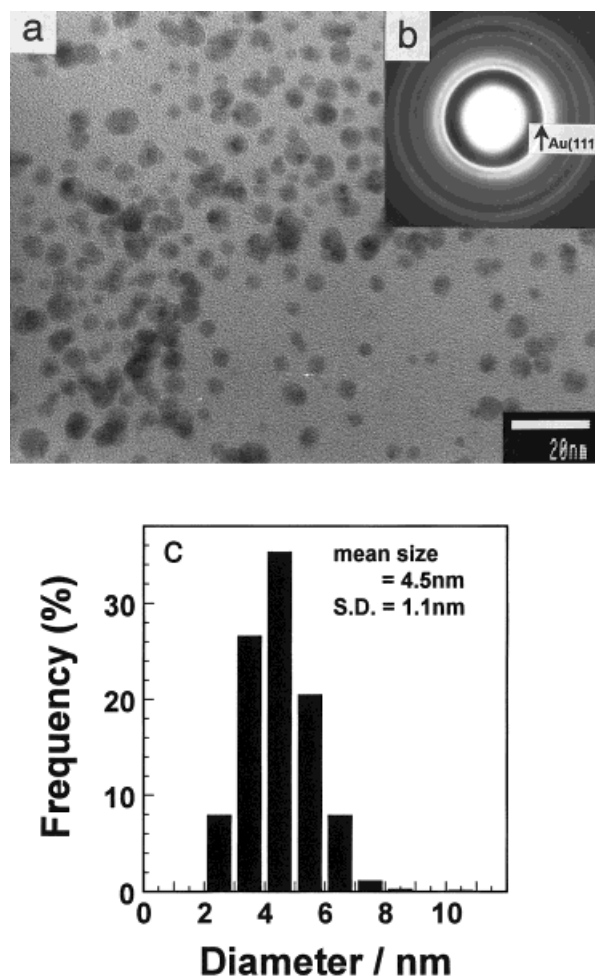


Figure 4 (a) TEM image, (b) electron diffraction, and (c) size distribution of gold particles dispersed in nylon-11 oligomer.

particles exhibited an organized structure, and they were kept adequate distances apart. Figure 6 shows an IR spectrum of the concentrated composite. The band at 2929 and 2854 cm⁻¹ (C—H) was clearly observed for the concentrated composite, but the N—H band (3303 cm⁻¹) became broad and decreased its intensity. Intensity of the band at 2245 cm⁻¹ (C≡N) and 1650 cm⁻¹ (C=O, amide) also decreased. These results suggested that the oligomer molecules were adsorbed on the gold particles through the interaction between the gold and the functional groups (N—H, C≡N, and C=O) of the nylon-11 oligomer. The interaction was strong so that the adsorbed oligomer was not removed from the surface of the gold particles by washing with methanol. Therefore, the gold particles did not show the increase in their size, and the gold particles were separated from each

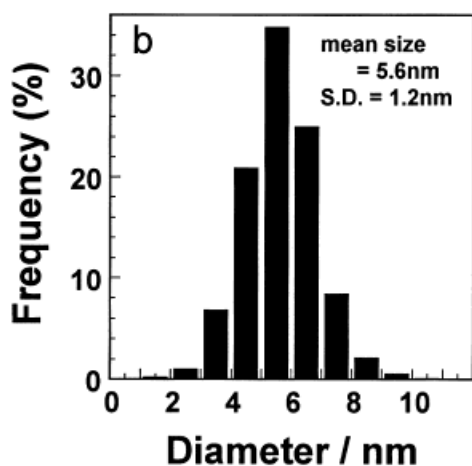
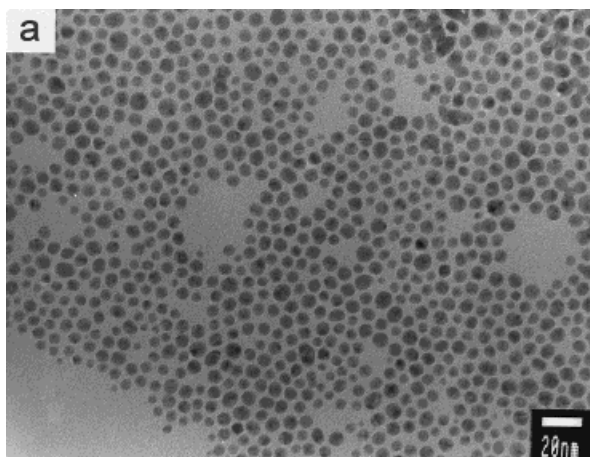


Figure 5 (a) TEM image and (b) size distribution of concentrated gold particles/nylon-11 oligomer composite.

other because of the steric repulsion of the adsorbed oligomer as observed in particles stabilized by polymer.²²

Molecular Motion of Nylon-11 Oligomer

Faupel et al. reported the details of a metal diffusion in polymers.²³ They suggested that reactive metals, which interacted strongly with a polymer, were fixed on the surface of the polymer, but less reactive metals like noble metals, were diffused into the inside of the polymer. In this case, the polymers caused a structural relaxation in a solid state, but they did not exhibit self-diffusion in the solid.

In this study, the nylon-11 oligomer was the waxy solid so that a molecular motion of the nylon-11 oligomer was supposed to be more active

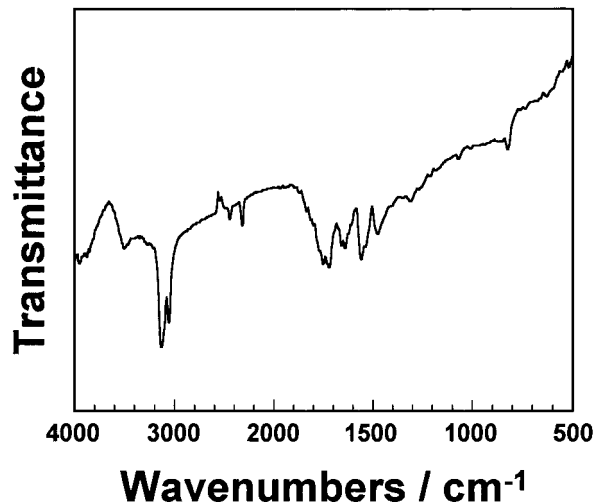


Figure 6 IR spectrum of concentrated gold particles/nylon-11 oligomer composite.

than that of the nylon-11 polymer. DTA analysis for the nylon-11 oligomer indicated that several endo peaks were observed below the heat-treatment temperature of 120°C.

A measurement of spin-spin relaxation time (T_2) of ^1H is very useful to evaluate a mobility of polymer molecules in a solid state.^{24,25} A polymer solid usually consists of various phases such as crystal, amorphous phase, and the interface of a crystal and an amorphous phase, and in these phases, molecules give different T_2 values.²⁶ T_2

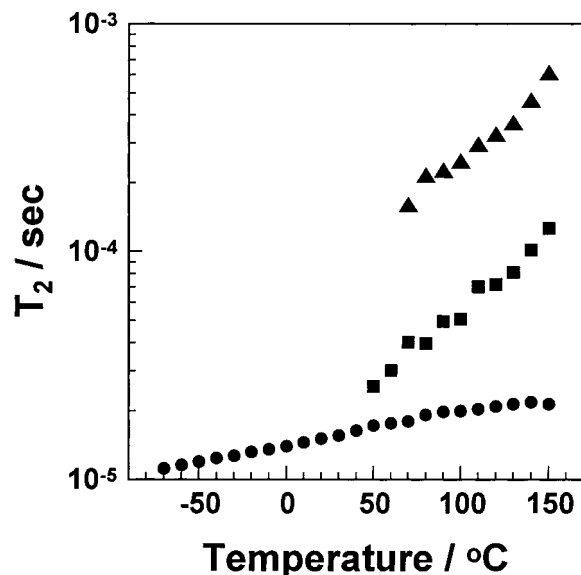


Figure 7 Temperature dependence of T_2 of nylon-11 polymer measured by pulse ^1H -NMR.

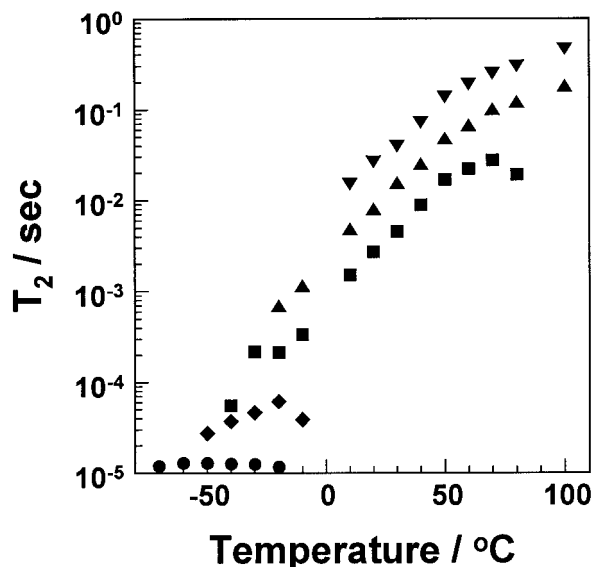


Figure 8 Temperature dependence of T_2 of nylon-11 oligomer measured by pulse $^1\text{H-NMR}$.

values were on the order of 10^{-5} s for molecules forming a crystal phase, in a range between 10^{-3} and 10^{-2} s in an amorphous phase, 10^{-4} and 10^{-5} s in an interface between a crystal and an amorphous phase, and $>10^{-2}$ s in a melt, respectively.

Figure 7 shows a temperature dependence of T_2 for nylon-11 polymer. The nylon-11 polymer had a single component giving $<2 \times 10^{-5}$ s of T_2 below a glass transition point ($T_g = 46^\circ\text{C}$). This corresponded to a T_2 value arising from a motion of nylon-11 molecules in a crystal phase so that the molecular motion of the nylon-11 polymer was restricted around room temperature.

On the other hand, the nylon-11 oligomer had three components of T_2 in a range of 10^{-3} to 5×10^{-2} s around room temperature (Fig. 8). The oligomer did not show T_2 which corresponded to a crystal phase even at 0°C . These results indicated that the molecular motion of the nylon-11 oligomer became more active than that of the nylon-11 polymer even at room temperature, at which gold was vapor-deposited. The molecules of the nylon-11 oligomer were considered to migrate in the film at higher temperatures. Therefore, the vapor-deposited gold was easily trapped by the oligomer molecules and increased their size to form nano-sized particles. The gold particles trapped by the oligomer molecules were then dispersed into the interior of the oligomer film at elevated temperatures.

CONCLUSION

Nylon-11 oligomer was produced by a degradation of nylon-11 polymer. The nylon-11 oligomer was utilized to prepare a composite consisting of nano-sized gold particles and the oligomer. The nano-sized particles of gold were formed on the oligomer film by vapor-deposition of gold and then were dispersed into the interior of the oligomer film by a heat treatment at 120°C . The composite was very stable not only in a solid but also in a solution. The nylon-11 oligomer stabilized the gold particles through an interaction between the gold particles and functional groups of the oligomer. Around room temperature, a molecular motion of the nylon-11 oligomer was very active so that the oligomer molecules easily interacted with gold and trapped gold as the nano-sized particles on the surface of the oligomer film. Then, the trapped gold particles were considered to disperse into the interior of the film when the oligomer molecules diffused into the film by the heat treatment.

REFERENCES

- Schön, G.; Simon, U. *Colloid Polym Sci* 1995, 273, 101.
- Eto, M.; Kawamura, K. *Phys Rev B* 1995, 51, 10119.
- Apell, S. P.; Giraldo, J.; Lundqvist, S. *Phase Transitions* 1990, 24–26, 577.
- Aktsipetrov, O. A.; Elyutin, P. V.; Nikulin, A. A.; Ostrovskaya, E. A. *Phys Rev B* 1995, 51, 17591.
- Lo, K. Y.; Lue, J. T. *Phys Rev B* 1995, 51, 2467.
- Nehasil, V.; Stará, I.; Matolín, V. *Surf Sci* 1996, 352–354, 305.
- Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer-Verlag: Berlin, 1995.
- Noguchi, T.; Gotoh, K.; Yamaguchi, Y.; Deki, S. *J Mater Sci Lett* 1991, 10, 477.
- Akamatsu, K.; Deki, S. *J Mater Chem* 1997, 7, 1773.
- Mathur, S. C.; Newman, B. A.; Scheinbeim, J. I. *J Polym Sci, Part B: Polym Phys* 1988, 26, 447.
- Scheinbeim, J. I.; Lee, J. W.; Newman, B. A. *Macromolecules* 1992, 25, 3729.
- Kim, K. G.; Newman, B. A.; Scheinbeim, J. I. *J Polym Sci, Part B: Polym Phys* 1985, 23, 2477.
- Mathias, L. J.; Powell, D. G.; Autran, J.-P.; Porter, R. S. *Macromolecules* 1990, 23, 963.
- Noguchi, T.; Goto, K.; Yamaguchi, Y.; Deki, S. *J Mater Sci Lett* 1992, 11, 797.
- Svoboda, M.; Schneider, B.; Štokr, J. *Collect Czech Chem Commun* 1991, 56, 1461.
- Lefievre, V. M.; Sallet, D.; Martel, B. *Polym Degrad Stab* 1989, 23, 327.

17. Ballistreri, A.; Garozzo, D.; Giuffrida, M.; Impalomeni, G.; Montaudo, G. *Polym Degrad Stab* 1988, 23, 25.
18. Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal Chem* 1995, 67, 735.
19. Williams, J. A.; Rindone, G. E.; McKinstry, H. A. *J Am Ceram Soc* 1981, 64, 709.
20. Klug, H. P.; Alexander, L. E. *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*; Wiley: New York, 1974.
21. Gehr, R. J.; Boyd, R. W. *Chem Mater* 1996, 8, 1807.
22. Birdi, K. S. *Surface and Colloid Chemistry*; CRC Press: New York, 1997.
23. Faupel, F.; Willecke, R.; Tjran, A. *Mater Sci Eng* 1998, R22.
24. Tanaka, H.; Nishi, T. *J Chem Phys* 1986, 85, 6197.
25. Folland, R.; Cherlesby, A. *Polymer* 1979, 20, 207.
26. McCall, D. W. *Acc Chem Res* 1971, 4, 223.