Application of a Furan-Containing Polymer/Fullerene System to Photolithography

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ABSTRACT: A furan-containing polymer turned to a gel and then solidified in 1,1,2,2-tetrachloroethane solution in the presence of fullerene C₆₀ under visible light irradiation. The reaction mechanism involved the polycondensation of furan units via singlet oxygen generated from the excited triplet state of C₆₀. This photo-crosslinking process was applied to a photoresist having sensitivity in the visible region. The first example was demonstrated for the micron size photolithographic patterning using the furan-containing polymer/fullerene system.

KEY WORDS Fullerene / Furan-Containing Polymer / Singlet Oxygen / Photooxygenation / Gelation / Photoresist / Photolithography /

Fullerenes have been introduced into polymers by various methods such as the [1,3]-dipole cycloaddition to azido-substituted polystyrene¹ or the addition to amino-containing polymers.^{2–4} The introduction of fullerenes into polymers through photochemical methods is especially useful because it can be applied to the radiation-curing of resins or photoresists. The [2+2]-cycloaddition with substituted cyclohexenones⁵ and the addition through photoinduced electron transfer with triethylamine⁶ are reported examples of the photochemical reaction of fullerene. Fullerene has been used as a useful sensitizer of recently discovered photofunctional polymers such as a photoconductive⁷ or photorefractive polymer.⁸ We have reported that fullerene C₆₀ can be used as an effective photo-gelling agent for furan-containing polymers.⁹ Since C₆₀ absorbs light over the visible region, the photo-gelling should proceed by visible light irradiation. This can be applied to a photoresist having sensitivity in the visible region. In this report, we investigated the mechanism of the photogelation process. We also demonstrate the first example of photolithographic patterning using the furan-containing polymer/fullerene system.

EXPERIMENTAL

Materials

Fullerene C₆₀ was purchased from the Term Co. and was of the >99.98% grade. Poly(2-hydroxyethylmethacrylate) (PHMA) was synthesized by the free radical polymerization of 2-hydroxyethylmethacrylate (30 wt%) in 300 ml of 2-propanol using an α,α' -azobis(isobutyronitrile) (AIBN) initiator (1.0 $\times 10^{-3}$ wt%) at 80°C for 12 h under a N₂ atmosphere. The polymer was obtained as a white powder at 88% yield after being purified by reprecipitation from hexane and dried under vacuum. The PHMA was then treated with 2-furoic chloride by dropping 15 g of 2-furoic chloride into 20 ml of pyridine solution containing 20 g of PHMA while stirring for 6 h at 30°C. The product was purified by reprecipit-

ation from hexane and dried under vacuum, yielding 18 g (51% yield) of poly(2-furoic acid [2-(methacryloyl-oxy)-ethyl] ester) (PFMA) as a white powder (see Scheme 1). The furan unit was introduced into the side chain at *ca.* 90% as determined by ¹H NMR and FT-IR spectra. From the gel permeation chromatography (GPC) analysis, the *M_n* and *M_w/M_n* were determined to be 5.77 $\times 10^4$ and 3.5, respectively. ¹H NMR of PFMA (C₂D₂Cl₄) δ 8.84 (2H, d, *J* = 4.4 Hz), 8.45 (1H, m), 7.97 (2H, m), 7.63 (2H, d, *J* = 11.7 Hz), 7.23 (2H, s), 6.53 (2H, s), 6.02 (2H, s), 4.42 (3H, broad), 4.20 (3H, broad), 1.90 (2H, broad), 1.80 (2H, broad), 1.26 (2H, broad), 1.00, 0.87 (2H, m); ¹³C NMR of PFMA (C₂D₂Cl₄, 400MHz) δ 178.42, 177.65, 161.74, 159.78, 159.75, 148.52, 148.24, 147.14, 146.02, 145.56, 145.48, 142.55, 128.61, 120.35, 120.26, 113.74, 113.71, 64.30, 63.47, 55.74, 46.51, 46.20, 24.26, 20.26, 18.45.

Irradiation Method

PFMA and C₆₀ were dissolved in distilled 1,1,2,2-tetrachloroethane (TCE) in the dark at 23°C. The solution was then irradiated through a Pyrex filter using a 150 W xenon arc lamp as the light source.

Gelation Method

The reaction between PFMA and C₆₀ was carried out as follows. Fifteen mg of C₆₀ (>99.98%, Term Co.) was added to 50 ml of distilled TCE containing 500 mg of PFMA stirred at 23°C. The solution was then irradiated using a 150 W xenon arc lamp with its broad spectrum output filtered using a Pyrex filter. As the reaction proceeded, the color of the solution changed from the

PFMA

Scheme 1.

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Figure 1. Schematic diagram of viscoelastorecorder (VER).

light purple of C_{60} to a dark red after 5 min, and the viscosity of the solution increased. When it became a gel after 10 h, it shrank by *ca.* 10% in volume relative to the initial solution. The gel completely solidified upon further irradiation.

Measurements

Differential scanning calorimetry (DSC) analysis of a PFMA/ C_{60} mixture and its gel was conducted using a Rigaku Thermoflex TG8110 by increasing the temperature at 5°C min^{-1} under an argon atmosphere. The ^1H NMR spectra were recorded on a JEOL JMN- α -400 (400 MHz) instrument. Tetramethylsilane (TMS) was used as the internal reference in 1,1,2,2-tetrachloroethane- d_2 . GPC analysis was performed in a Shimadzu LC-6A equipped with a RI detector (Shodex SE-51) using a Shodex column (AD-80M/S). The IR spectra were obtained using a Shimadzu FT-IR-4200 spectrophotometer. The UV-Vis spectra were obtained with a Hitachi UV-2000 spectrophotometer using a quartz cell with a 1-cm light path. *In situ* measurement of the dynamic viscoelasticity during gelation of the PFMA- C_{60} solution during irradiation was performed using a viscoelastorecorder (VER) with a quartz cell.¹⁰ A schematic diagram of the VER is shown in Figure 1. A 1.0-ml portion of the sample solution was placed in a cell of which both sides were made of two parallel quartz plates. A metal inner plate was then immersed in the solution. The cell was vertically oscillated by a vibrator cam at a frequency of 1 Hz so that the sample was sheared between the inner plate and the quartz walls of the cell. The force acting on the inner plate was detected by a strain gauge. The output signal from the strain gauge was amplified and led to the phase sensitive detectors, from which both the real and imaginary parts of the rigidity moduli, G' and G'' , were derived and recorded as a function of time. The gap width between the inner plate and the quartz walls of the cell was 1 mm and the shear strain was 0.002.

RESULTS AND DISCUSSION

The photographs in Figure 2 demonstrate the changing of the PFMA- C_{60} solution into a gel. A TCE solution containing 1000 g dm^{-3} (about 5 mol dm^{-3} in monomer units) of PFMA and 0.072 g dm^{-3} ($1 \times 10^{-3}\text{ mol dm}^{-3}$) of C_{60} was placed in a Petri dish and irradiated from the top of the solution (a). The color of the solution changed from the initial purple of C_{60} to a dark brown

Figure 2. Photographs of TCE solution containing 1000 g dm^{-3} of PFMA and $1 \times 10^{-4}\text{ mol dm}^{-3}$ of C_{60} before irradiation (a) and after 48 h visible light irradiation (b).

Figure 3. Absorption spectra of a PFMA- C_{60} solution in TCE before (---) and after (—) irradiation for 2 h.

after 5 min. As the reaction proceeded, the viscosity of the solution increased and it turned to a gel after 10 h (b). The volume of the gel was *ca.* 90% of the initial volume of the solution. The gel was completely solidified further irradiation.

Figure 3 shows the absorption spectra of the PFMA- C_{60} solution before and after the irradiation. The spectrum before irradiation showed a prominent absorption band centered at 420 nm and a broad band around 650 nm both of which are characteristic of the absorption spectrum of C_{60} . Upon irradiation, the band at 420 nm decreased and a broad band appeared around 500 nm. As the reaction proceeded, the band around 420 nm disappeared while the broad band ranging from 450 to 700 nm increased monotonically. Figure 4 shows the DSC curves of the PFMA- C_{60} gel and a PFMA/ C_{60} mixture. The PFMA- C_{60} gel showed a new peak around 330°C , suggesting that a new chemical bond was formed by visible light irradiation.

In order to investigate the gelation process of the

Figure 4. Differential scanning calorimetry traces for the PFMA- C_{60} before irradiation (a) and after irradiation for 24 h (b) (scan rate, $10^{\circ}\text{C min}^{-1}$).

Figure 5. Dynamic rigidity modulus G' (■) and loss modulus G'' (□) during gelation of PFMA- C_{60} solution with light irradiation.

PFMA- C_{60} solution, we have measured the dynamic viscoelasticity using VER during the irradiation. Figure 5 shows variations in the storage modulus, G' , and the loss modulus, G'' , with the irradiation time for a TCE solution containing 1000 g dm^{-3} of PFMA and $1 \times 10^{-3} \text{ mol dm}^{-3}$ of C_{60} . The intersection of the G' and G'' curves corresponds to the gelation point. The rapid increase in G' passing G'' indicates that the PFMA- C_{60} solution changed into the gel after 24 h. Both the G' and G'' values consistently increased with the concentration of C_{60} , and the swelling ratio decreased with the increase in the C_{60} concentration (Figure 6). These results suggest that C_{60} works to create the crosslinking points which construct the polymer network. Unfortunately, any change in the NMR spectrum of C_{60} could not be detected in both the ^1H and ^{13}C NMR measurements, because the concentration of C_{60} was quite low compared to that of PFMA.

In our previous paper, we have reported that the main products of the photochemical reaction of methyl

Figure 6. Swelling ratio of PFMA- C_{60} gel in TCE as function of C_{60} concentration. The swelling ratio is defined as the mass of absorbed solvent (TEC) per mass of dried polymer disk (M_s/M_p).

2-furoate (MFA) and C_{60} in the presence of oxygen were a furan resin and $C_{60}O_n$ ($n=1-10$).¹¹ We concluded that the reaction mechanism yielding the furan resin was the polycondensation of MFA *via* oxygenation by singlet oxygen generated with the function of C_{60} as a photosensitizer. We considered that the endperoxides of MFA underwent polycondensation to form the conjugated polymer, namely, the furan resin, as shown in Scheme 2. The gelation of the PFMA- C_{60} solution can be considered to proceed in the same way. First, the photo-excited C_{60} generates singlet oxygen, which migrates to the furan units of PFMA and oxygenates them. The oxygenated furan units turn to the endperoxides and undergo a thermal polycondensation reaction. The network was constructed as a result of the intermolecular binding between the furan units on different PFMA chains.

In order to verify this proposed gelation mechanism, the irradiation was carried out in the presence of

Scheme 2.

Scheme 3.

Figure 7. Photograph of a fine pattern image using PFMA- C_{60} {thickness, 1.5 μm ; exposure dose, 1 J cm^{-2} ($> 530 nm$); development, dipping for 1 min using TCE}.

1,3-diphenyl-*i*-benzofuran (DBF) or triphenylphosphine (TPP). The DBF works as a quencher of singlet oxygen and the TPP acts as a reducing agent for the furan peroxide.¹² The addition of a small amount of these reagents inhibited the increase in G' and G'' of the PFMA- C_{60} solution during the visible irradiation. These results clearly support the proposed mechanism.

As a conclusion, the gellation mechanism is summarized in Scheme 3. The furan units of the PFMA were oxidized by singlet oxygen and undergo polymerization to construct the polymer network. The brown color of the PFMA- C_{60} gel is ascribed to the conjugated structure of the polycondensates of the furan units.¹³

Finally, we applied the PFMA- C_{60} system to a photoresist. A cast film of PFMA- C_{60} formed on a glass substrate was exposed to a 400 W high pressure mercury lamp equipped with a Pyrex filter through a photomask. After 1 min, the pattern was developed with TCE and dried at 80°C in a clean oven. A fine pattern image of a micron size was obtained as shown in Figure 7. This is the first example of the application of fullerene to photolithography. Since the PFMA- C_{60} system has a high sensitivity to visible light and its reaction is not inhibited by oxygen, it has advantages over the usual negative type resist using free radicals. Especially, it would be suitable for such use as a pigment-dispersed resist which can not appreciably transmit ultraviolet light.⁸ In addition, this system guarantees excellent cost performance because it requires only a small quantity of expensive fullerene.

CONCLUSIONS

We demonstrated that fullerene C_{60} works as a sensitizer involving singlet oxygen for the photocrosslinking of furan-containing polymers. The furan-containing polymer/fullerene system can be applied to negative type photolithography forming micron size patterning with high sensitivity in the visible region. A high efficiency is also expected in the use of fullerene as a sensitizer of radiation curable resins.

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