

Photo-crosslinking polymers by fullerene

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Photochemical addition of furan derivatives to fullerene C_{60} was applied to the photo-crosslinking of polymers with C_{60} . A polymer having furan units in the side chains was synthesized by the reaction of poly(2-hydroxyethylmethacrylate) with 2-furoic chloride. A 1,1,2,2-tetrachloroethane solution of the polymer was exposed to visible light in the presence of C_{60} . The solution turned to a gel after 10 h and then solidified completely. The photo-crosslinking process was monitored *in situ* by dynamic viscoelasticity measurement. © 1997 Elsevier Science Ltd.

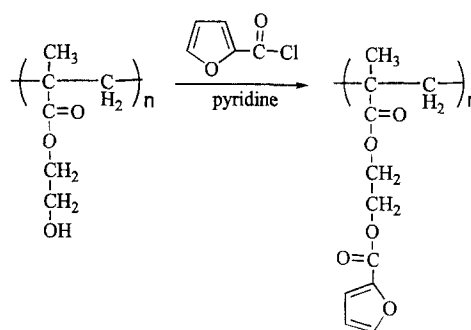
(Keywords: photo-crosslinking; fullerene; furan derivative)

Introduction

Numerous studies on polymers containing fullerene have been carried out for the purpose of applying fullerenes to functional materials^{1–7}. Fullerenes have been introduced into polymers by various methods such as [1,3]-dipole cycloaddition to azido-substituted polystyrene² or addition to amino-containing polymers^{3–5}. Introduction of fullerenes to polymers through photochemical methods is especially useful because it can be applied to radiation-curing of resins or photoresists. [2 + 2]-Cycloaddition with substituted cyclohexenones⁸ and addition through photoinduced electron transfer with triethylamine⁹ have been reported as photochemical reactions or fullerene. We have found that fullerene C_{60} reacted with furan derivatives by u.v. or visible irradiation to form mono- or multi-adducts of furans to C_{60} ¹⁰. Although Nie *et al.* have reported that C_{60} was covalently and reversibly bound to a furan unit attached to a resin¹¹, they did not mention its photochemical reaction. In our experiments, however, furan derivatives did not react with C_{60} in the dark. This indicates that the reaction of C_{60} with furans is not the usual thermal addition such as reactions with cyclopentadiene^{12,13}, anthracene^{14,15} or benzofuran¹⁶, but a photochemical one. Thus, it is expected that a polymer having furan moieties in the side chains forms a network through C_{60} by irradiation. Here, we report the synthesis of a polymer carrying furan units in the side chains and its photo-crosslinking properties, using *in situ* dynamic viscoelasticity measurements.

Experimental

Materials. The polymer having furan units in the side chains was synthesized by the reaction of poly(2-hydroxyethylmethacrylate) (PHMA) with 2-furoic chloride (Scheme 1). The PHMA was synthesized by



Scheme 1

free radical polymerization of 2-hydroxy-ethylmethacrylate (30 wt%) in 300 ml of 2-propanol using an AIBN initiator (1.0×10^{-3} wt%) at 80°C for 12 h under a N_2 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 reprecipitation from hexane and dried under vacuum, yielding 18 g (51% yield) of poly(2-furoic acid [2-(methacryloyloxy)ethyl] ester) (PFMA) as a white powder. From g.p.c. analysis, M_n and M_w/M_n were determined to be 5.77×10^4 and 3.5, respectively. The furan unit was introduced into the side chains at *ca.* 90% as determined by ¹H-n.m.r. and FTi.r. spectra.

Measurements. A viscoelastorecorder (VER) was used for measuring dynamic viscoelasticity *in situ* during the visible light irradiation. A 1.0 ml solution of 1,1,2,2-tetrachloroethane (TCE) was placed in a rectangular quartz cell, and a metal plate was immersed in the solution. The gap between the metal plate and the inside

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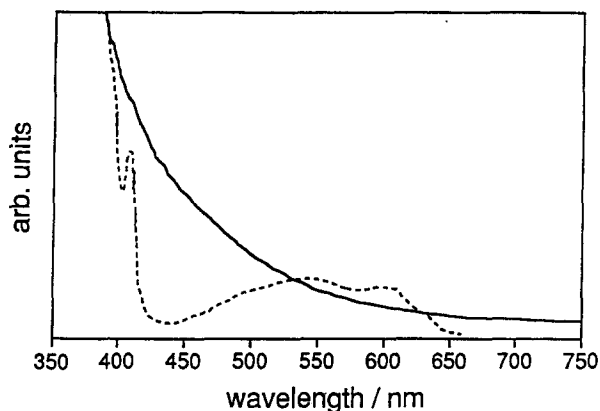


Figure 1 Absorption spectra of a PFMA-C₆₀ solution in TCE before (---) and after (—) irradiation for 2 h

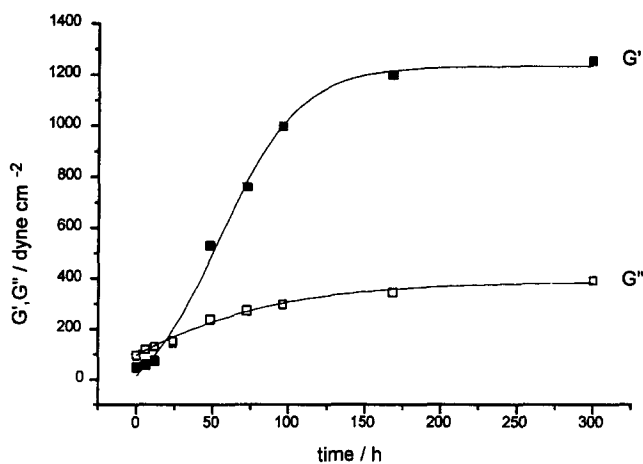


Figure 2 Variation of dynamic rigidity modulus G' (■) and loss modulus G'' (□) of PFMA-C₆₀ solution with irradiation time

wall of the cell was 1 mm. The cell was oscillated vertically with a vibrator cam at a frequency of 1 Hz, so that the solution was sheared between the metal plate and the inside wall of the quartz cell. The shear strain was set to be 0.002. The force acting on the metal plate was detected with a strain gauge. The output signal from the strain gauge was amplified and fed to the phase-sensitive detectors, from which both real and imaginary parts of the rigidity modulus, G' and G'' , respectively, were derived and recorded using a computer.

The visible light irradiation was performed with a 150 W xenon arc lamp equipped with an u.v.-cutting filter, O-52 (Toshiba), which cut wavelengths shorter than 530 nm. U.v.-vis spectra were obtained with spectrophotometer, UV-2000 (Hitachi), using a 1.0 cm path-length quartz cell.

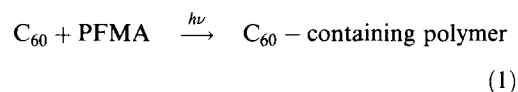
Results and discussion

When a TCE solution containing 1000 g dm⁻³ of PFMA (about 5 mol dm⁻³ in monomer units) and 0.072 g dm⁻³ (1.0 × 10⁻³ mol dm⁻³) of C₆₀ in a 10 ml petri dish was exposed to visible light, the PFMA-C₆₀ solution changed its colour from the purple of C₆₀ to dark brown after 10 min. As the reaction proceeded, the solution increased in viscosity and became a gel after 10 h. It shrank by ca. 10% in volume relative to the initial solution. The gel solidified completely on further irradiation.

Figure 1 shows the absorption spectra of a PFMA-C₆₀ solution in TCE before and after the irradiation.

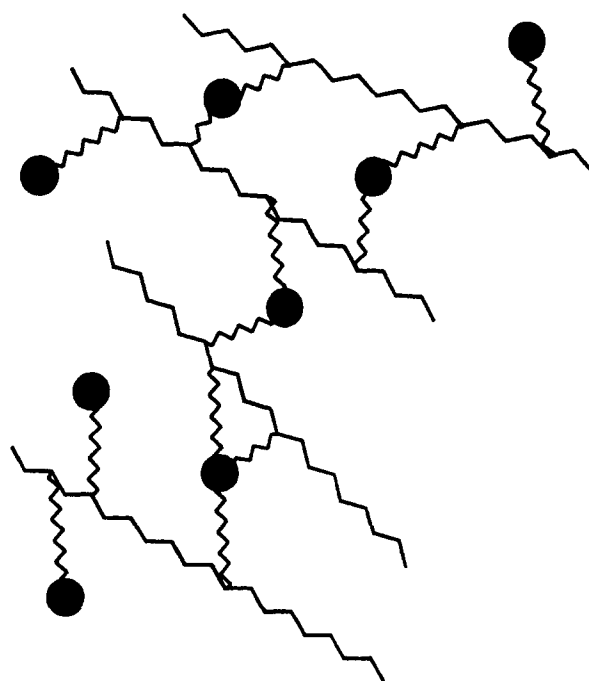
The spectrum before the irradiation showed a prominent absorption band centered at 420 nm and a broad band at around 550 nm. These are characteristic of the absorption spectrum of C₆₀. When the solution was exposed to the visible light, the peak at 420 nm decreased and a broad band appeared at around 450 m, which were characteristic of C₆₀-adducts. As the reaction proceeded, the band in the visible region increased monotonically.

In order to monitor the process of the gelation and the following solidification, we measured the dynamic viscoelasticity of the solution during the visible light irradiation. Figure 2 shows variations in the storage modulus G' and the loss modulus G'' with the irradiation time for the TCE solution containing 1000 g dm⁻³ of PFMA and 0.072 g dm⁻³ of C₆₀. The gelation point corresponds to the cross point between G' and G'' . The rapid increase in G' passing G'' indicates that the PFMA/C₆₀ solution was coagulating as the time proceeded. The typical sigmoidal change in G' indicates that the gelation process occurred as



In the first step, the excited C₆₀ binds to one furan unit of PFMA, as a result of which a C₆₀-containing polymer is formed. The C₆₀ moiety in the C₆₀-containing polymer subsequently binds to a furan unit of the other PFMA, and consequently, a C₆₀-containing network is constructed.

Because the gelation proceeded in a nonpolar solvent and was not inhibited by oxygen, the photochemical addition of C₆₀ to the furan unit in the polymer side chain can be widely applied to radiation-curing of resins and photoresists.



Scheme 2 PFMA-C₆₀ network (●: C₆₀)

Several experiments are now in progress to examine the structure of the network by measuring the concentration dependence of C_{60} on G' and G'' , the swelling ratio, and the dynamic light scattering (DLS).

Conclusions

We demonstrated that fullerene C_{60} can be used as an effective photo-crosslinking reagent for furan-substituted polymers because of its high photosensitivity and multiple functions. Although numerous functional materials utilizing specific properties of fullerenes have been reported, most of them are still far from ready for practical use because they use expensive fullerenes as a major component. Use of the fullerene as a crosslinking reagent does not involve this problem, and thus it can be applied to radiation-curing of resins and photoresists.

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References

- Samulski, E. T., DeSimone, J. M., Hunt, M. O., Menciloglu, Y. Z., Jarnagin, R. C., York, G. A., Labat, K. B. and Wang, H., *Chem. Mater.*, 1992, **4**, 1153.
- Hawker, C. J., *Macromolecules*, 1994, **27**, 4836.
- Geckeler, K. E. and Hirsch, A., *J. Am. Chem. Soc.*, 1993, **115**, 3850.
- Manalova, N., Rashkov, I., Beguin, F. and van Damme, H., *J. Chem. Soc., Chem. Commun.*, 1993, 1725.
- Patil, A. O., Schriver, G. W., Carstensen, B. and Lundberg, R. D., *Polymer Bull.*, 1993, **30**, 187.
- Guhr, K. I., Greaves, M. D. and Spurling, T. H., *J. Phys. Chem.*, 1995, **99**, 17302.
- Dai, L., Mau, A. W. H., Griesser, H. J. and Spurling, T. H., *J. Phys. Chem.*, 1995, **99**, 17302.
- Wilson, S. R., Kaprinidis, N., Wu, Y. and Schuster, D. I., *J. Am. Chem. Soc.*, 1993, **115**, 8495.
- Glenn, B. M., Lawson, E., Bunker, C. E., Kitaygorodskiy, A. and Sun, Y., *Chem. Phys. Lett.*, 1995, **247**, 51.
- Tajima, Y., Tezuka, Y., Yajima, H., Ishii, T. and Takeuchi, K., Manuscript in preparation.
- Nie, B., Hasan, K., Greaves, M. D. and Rotello, V.M., *Tetrahedron Lett.*, 1995, **36**, 3617.
- Taylor, R. and Walton, D. R. M., *Nature (London)*, 1993, **363**, 685.
- Meidine, M. F., Roers, R., Langley, G. J., Avent, A. G., Darwish, A. D., First, S., Kroto, H. W., Taylor, R. and Walton, D. R. M., *J. Chem. Soc., Chem. Commun.*, 1993, 1342.
- Schlueter, J. A., Seaman, J. M., Taha, S., Cohen, H., Lykke, K. R., Wang, H. H. and Williams, J. M., *J. Chem. Soc., Chem. Commun.*, 1993, 972.
- Tsuda, M., Ishida, T., Nogami, T., Kurono, S. and Ohashi, M., *J. Chem. Soc., Chem. Commun.*, 1993, 1296.
- Prato, M., Suzuki, T., Foroudian, H., Li, Q., Khemani, K. and Wudl, F., *J. Am. Chem. Soc.*, 1993, **115**, 1594.
- Fukuda, E. and Kaibara, M., *Thrombosis Res., Suppl. II*, 1976, **8**, 49.