Enhanced Photopolymerization of Diacetylene in Colloidal Gold Solution

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The diacetylene $Me(CH_2)_{11}C{\equiv}C{-}C{\equiv}C(CH_2)_8CO_2H$ (12,8-DA) can be photopolymerized in aqueous colloidal gold solution owing to attraction between the surface of the Au particles and the 12,8-DA molecules which reduces the distance between adjacent DA molecules.

Polydiacetylenes (PDAs) have attracted much attention owing to their physical, chemical and material properies. In particular their optical properties such as non-linear optical effects[1] have been investigated in solution and as Langmuir–Blodgett (LB) films.[2,3]

Recently, the production of controlled nanosize materials or nanocomposite materials has been a interesting branch of advanced materials research.[4,5] In this area many remarkable characteristics, which result from the quantum-size effect, and which can not be observed in the bulk materials, appear and can be utilized in new electronic and photonic devices. For instance, organic diacetylene nanocrystals of bis(butoxycarbonylmethylurethane) have been synthesized[6] in aqueous solution by UV irradiation. Nanosize core-shell structured metal–organic materials with non-linear optical properties have potentially interesting properties such as low scattering and possible enhanced susceptibility.

In this work, we report an enhanced photopolymerization of a diacetylene monomer (10,12-pentacosadiynoic acid, $Me(CH_2)_{11}C{\equiv}C{-}C{\equiv}C(CH_2)_8CO_2H$ (12,8-DA) in an aqueous colloidal gold solution. The thermochromic properties of PDA in such solutions is also investigated.

An aqueous colloidal gold solution was prepared according to Frens' method.[7] Aqueous solutions of chloroauric acid ($HAuCl_4{\cdot}4H_2O$) (5×10^{-3} mass%; Solution 1) and citric acid (1 mass%; Solution 2) were prepared. Solution 1 (400 cm^3) was heated to boiling, and Solution 2 (10 cm^3) added. Initially the boiling mixture turns faintly blue and then finally red. This colour results from the surface plasma absorption band of colloidal gold particles. The size of the spherical gold colloidal particles is *ca.* 20 nm with a narrow size distribution according to transmission electron microscopy. The colloidal gold solution is stable over several months. The Au particles within the colloid are sufficiently large to act as a template for polymerization of DA attracted to their surface.

The diacetylene monocarboxylic acid 12,8-DA is commercially available and was used without purification. An ethanol solution of 12,8-DA monomer (5.0×10^{-3} mol dm^{-3}, 1.5 cm^3), was added dropwise to the colloidal gold solution (300 cm^3) at room temperature and the resulting mixture (Au–DA) was exposed to UV irradiation using a high-pressure mercury lamp (Ushio Electric Co. Ltd., 100 W) to initiate photopolymerization. Similarly an ethanol solution of 12,8-DA (5.0×10^{-3} mol dm^{-3}, 1.5 cm^3) was also added dropwise to water (300 cm^3) and irradiated as above for comparison.

The optical spectra of the Au colloidal solution and the Au–DA mixture, which were measured during the UV irradiation process, are shown in Fig. 1. The absorption band at *ca.* 530 nm results from the surface plasma resonance of gold particles. The intensity of the surface plasma absorption bond increases and the peak position shifts slightly to longer wavelength on addition of the 12,8-DA–ethanol solution to the aqueous colloidal gold suspension. This change results from interaction between the hydrophilic $-(CH_2)_8CO_2^-$ group of 12,8-DA and the gold particle which leads to an altered dielectric constant of the capped DA shell layer according to the electromagnetic resonance effect.

The optical spectra of Au–DA solution before and after UV irradiation for 1,2,4 and 6 h are shown in Fig 1. The excitonic absorption band of the π-conjugated polymer backbone of 12,8-DA at 650 nm[8] starts to appear after *ca.* 30 min irradiation, and increases with time. This establishes that 12,8-DA can be photopolymerized in an aqueous colloidal gold solution.

Fig. 2 shows the difference between absorption spectra of Au–DA before and after UV irradiation. The resulting spectrum is as expected for a π-conjugated 10,12-PDA[8,9] polymer, with a main peak at 650 nm and a broad secondary peak at *ca.* 600 nm.

For the H_2O–DA solution, UV irradiation did lead to some polymerisation but at a much reduced rate. A very weak peak indicative of the π-conjugated PDA polymer of *ca.* one-tenth intensity of that in Au–PDA appears after extended UV irradiation, but was too weak to be clearly observed even after 3 or 4 hours. This indicates that there is an enhancement in photopolymerization of diacetylene in aqueous colloidal gold solution. This effect is due to the 12,8-DA molecules being attracted to the surface of the Au particles so leading to an effective increase in local concentration of the 12,8-DA molecules by formation of a 'capped shell layer'.

Thermochromism of PDA in solution and in Langmuir–Blodgett (LB) films has been investigated.[3] We also investi-

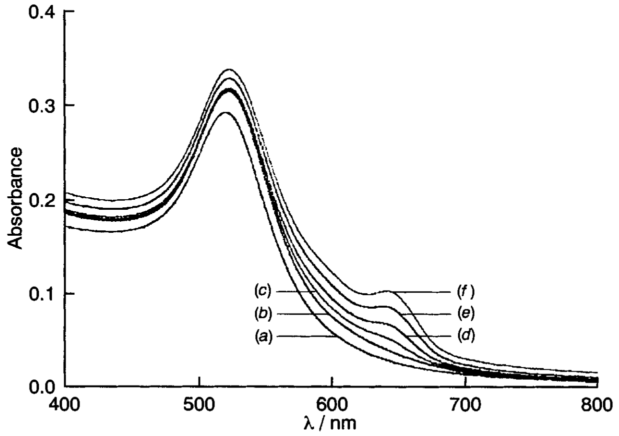

Fig. 1 The optical spectra of Au colloidal particles (*a*) and Au–DA solution before (*b*) and after UV irradiation for 1 (*c*), 2 (*d*), 4 (*e*) and 6 h (*f*)

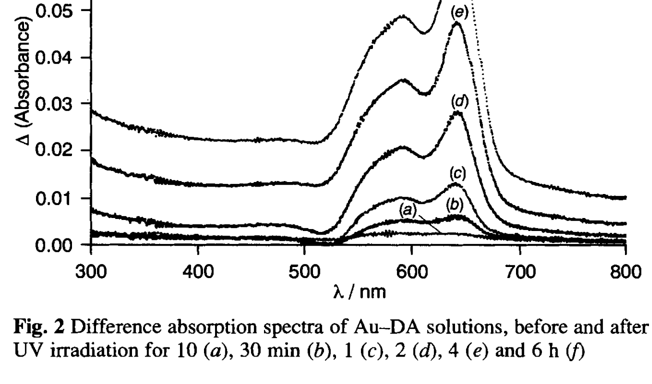

Fig. 2 Difference absorption spectra of Au–DA solutions, before and after UV irradiation for 10 (*a*), 30 min (*b*), 1 (*c*), 2 (*d*), 4 (*e*) and 6 h (*f*)

gated such phenomena in the Au–PDA solution. Fig. 3 shows changes of the spectra of Au–PDA upon warming to 55, 70 and 90 °C over 5 min intervals using a water-bath. The excitonic absorption band shifts by *ca.* 100 nm (from 650 to 550 nm) and increases in intensity upon raising the temperature. This colour change is believed to result from a conformational transition.[3,9,10] The same effect is also observed in H_2O–DPA solution, albeit with much reduced intensity.

In conclusion, photopolymerization of 12,8-DA is enhanced in the presence of colloidal gold as a consequence of attraction between gold particles and the 12,8-DA monomers which leads to high local concentration of the molecules. The resulting polymer is a composite containing nanometre sized gold particles.

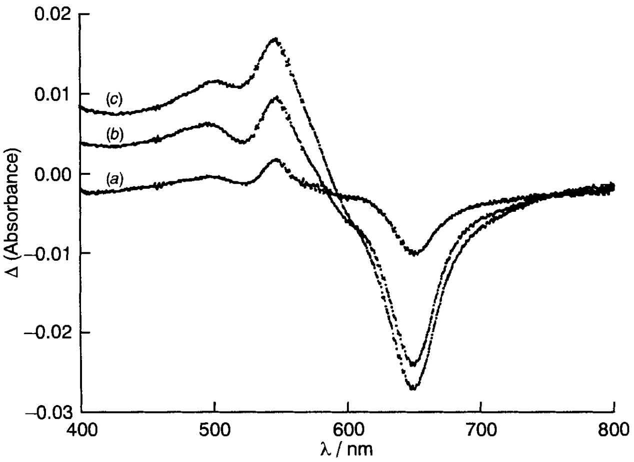

Fig. 3 Difference absorption spectra of Au–PDA solutions before and after heating to 55 (*a*), 70 (*b*) and 90 °C (*c*) for 5 min

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