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New materials which respond to visible light: functional polymers containing zirconium

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Photoresponsive polymers which change their magnetic properties when illuminated by visible light have been found. n-Butyl zirconate was polymerized in tetrahydrofuran and other solvents. The polymer, when illuminated, changes its conformation and a new spin–nuclear interaction in the electron spin resonance spectrum is observed. These polymers, when 1 wt% Pt was added, exhibited photocatalytic activities and photolysed a 1:1 methanol–H_2O mixture and a 0.24 M Na_2S aqueous solution, using visible light of wavelength 480 to 730 nm.

1. Introduction

The needs for polymer materials are changing from structural materials to functional materials. This trend will continue until molecular functional devices are developed. One of the molecular functional materials is stimulation-responsive polymer which responds to external stimulation such as light, electric field, magnetic field, or heat. There are two types of photoresponsiveness which are exhibited by living organisms. One is to use light as an energy source, so that biological material is synthesized using light energy. Another is to use light as an information source for the surrounding environment. Some examples are phototaxis, heliotropism, and the visual process.

Some of the photoresponsive polymers already studied are those which change their conformation when illuminated by light [1]. When the conformation changes, the bulk polymer is elongated or contracted reversibly. Such light-induced morphological changes can be used for light-driven chemical valves, light-induced porous filters etc.

The present authors have studied polymers of n-butyl orthotitanate polymerized in various solvents. Those polymers show light-induced electron spin resonance (ESR) spectra in which n-butyl coupling of the unpaired electron is observed [2]. The polymers obtained by their procedures have proved to be polymer radicals [2]. The polymer radicals absorb visible light and in the conformation of the excited state of the polymer radical the coupling between n-buthoxy groups and the unpaired electron becomes strong.

The light-induced ESR spectra seem to indicate a light-induced polarization of the polymer molecule. If so, a redox reaction caused by the polarization process may be expected. For this reason, photocatalytic properties were tested using a 1 : 1 methanol–H_2O mixture and a 0.24 M Na_2S solution in water as substrates.

2. Experimental procedure

Zirconate polymers were prepared by the following method. 6.1. g of n-butyl zirconate (Mitsubishi Metal Corporation, Omiya, Japan) was dissolved in 500 ml of several solvents (tetrahydrofuran (THF) benzene, ethanol, CS_2, and acetone) with which 2.0 g of freshly crushed silica gel (Koso Chemical Co.) was mixed, which was then illuminated by flourescent lamps. The particle size of the silica gel was less than 100 mesh. In acetone solution the polymerization immediately started after mixing and white precipitates were observed. In other solvents, the polymer as well as the monomer was soluble in the solvent and a sol state of the polymer solution was first observed. When approximately 50% of the solvent was evaporated, the gel state was observed. When all of the solvent was evaporated, the gel changed to solid particles of the polymer.

The reflectance spectra of the polymer powders were recorded by a Shimadzu Type 240 spectrometer using an integral-sphere attachment Type 180/190. ESR absorption spectra were taken by a Type JES ME3X spectrometer (Japan Electron Optics Co.) using a 100 kHz magnetic field modulation frequency. The light illumination of the sample in the ESR cavity was provided by a 100 V 150 W JCR halogen lamp (Iwasaki Electric Co.) which was guided by a Type SLS-150 glass fibre cable (Sumita Optics Co.). IR spectra were recorded with a Type 102 IR spectrometer (Japan Spectroscopic Co.).

The catalytic activiy was measured by a flow-through type cell. The amount of light absorbed by the catalyst was measured by a chemical actinometer using $K_3Fe(C_2O_4)_3$ [3]. The hydrogen envolved by the solution was mixed with N_2 gas, which flowed at the rate of 50 ml min^{-1} in the cell. The H_2–N_2 mixture was led to the sampler of a gas chromatograph (type 701, Okura Electric Co.). A Porapak-Q column was used at 140° C. As the substrate for the photocatalytic activity test, 1:1 methanol–H_2O mixture and 0.24 M Na_2S aqueous solution were used. To see the effect of some additives, 2-propanol was also used as a substrate.

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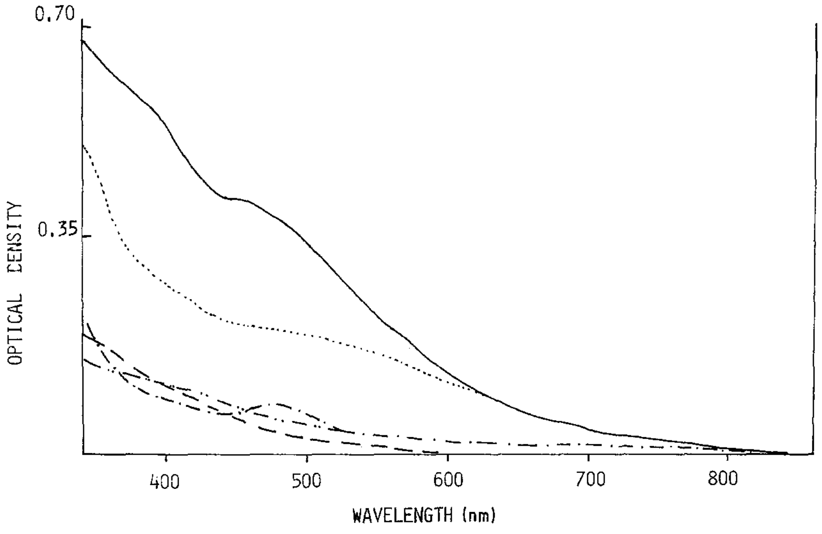

Figure 1 The reflectance spectra of the polymers obtained in several solvents: (——) C_48_8O, (···) C_6H_6, (–·–) C_2H_5OH, (–··–) C_2H_6O, (– – –) CS_2.

3. Results and discussion

The reflectance spectra of powders of the polymers obtained from various solvents are shown in Fig. 1. The spectra in Fig. 1 show that the zirconium-containing polymers absorb visible light. The ESR spectra of the polymer obtained from tetrahydrofuran as a solvent is shown in Fig. 2. When the sample tube is illuminated by visible light (400 to 700 nm) the spectrum of Fig. 2a was obtained. In this spectrum, spin nuclear coupling between the unpaired electron and the protons of the $-CH_2CH_3$ group of the n-butyl group is found. The methyl splitting observed is 31.99 MHz and the methylene splitting observed is 4.77 MHz. The dark spectrum (Fig. 2b) has no hyperfine structure. The difference seems to show that the polymer radical, if no light excitation occurs, exhibits little spin nuclear coupling between the unpaired electron and the n-buthoxy group. But, if once the polymer free radical is excited by light, a new conformation of the n-buthoxy chain is induced by it and spin nuclear coupling between the unpaired electron and the n-buthoxy group can be observed. The lifetime of the excited state of the radical may be short, but the lifetime of the induced comformation for which the spin nuclear coupling is observed can be long. The IR spectra (Fig. 3) indicate that the polymer obtained has a Zr–O bond (1060 cm^{-1}) and an alkyl side chain (1300 to 1700 cm^{-1}) [4, 5].

The polymers obtained in ethanol and benzene as solvents show different ESR spectra which are shown in Fig. 4. In both polymers the ESR component is due to the structure in which the unpaired spin density is on the oxygen atom to some considerable extent. Many oxygen-containing radicals have *g*-factor values larger than 2.01 [6]. In the cases of the polymers obtained in CS_2 and acetone, the ESR absorption with $g = 2.004$ is intensified by visible light, too, as shown in Fig. 5.

These results seem to indicate that both the structure and the conformation of the polymer vary according to the solvent in which the polymerization is conducted.

The results of photocatalytic activity tests are shown in Table I. The effect of the addition of CH_3COOH was studied using 2-propanol which contains 2% of CH_3COOH and polymer obtained in THF. The efficiency for H_2 production decreased to 64% of the value without CH_3COOH. Also, the effect of the addition of THF was studied using 2-propanol which contained 2% THF and the polymer obtained in benzene. The efficiency for H_2 production decreased to 77% of the value without THF. These results indicate that the adsorption of substrate by the catalyst is important

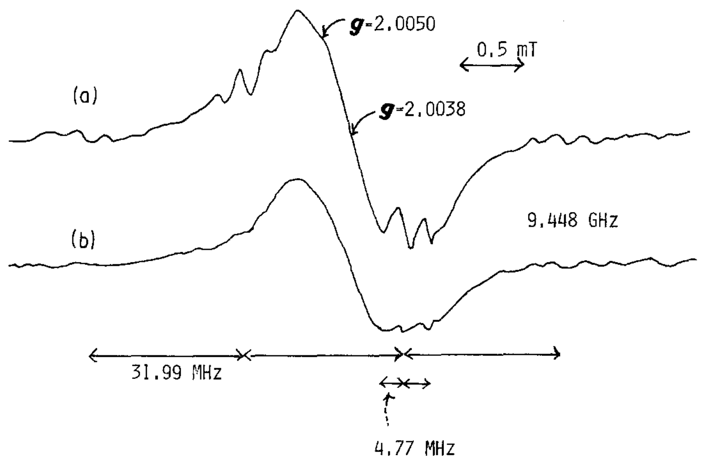

Figure 2 The ESR spectra of the polymer obtained from tetrahydrofuran as a solvent: (a) illuminated by visible light, (b) dark spectrum.

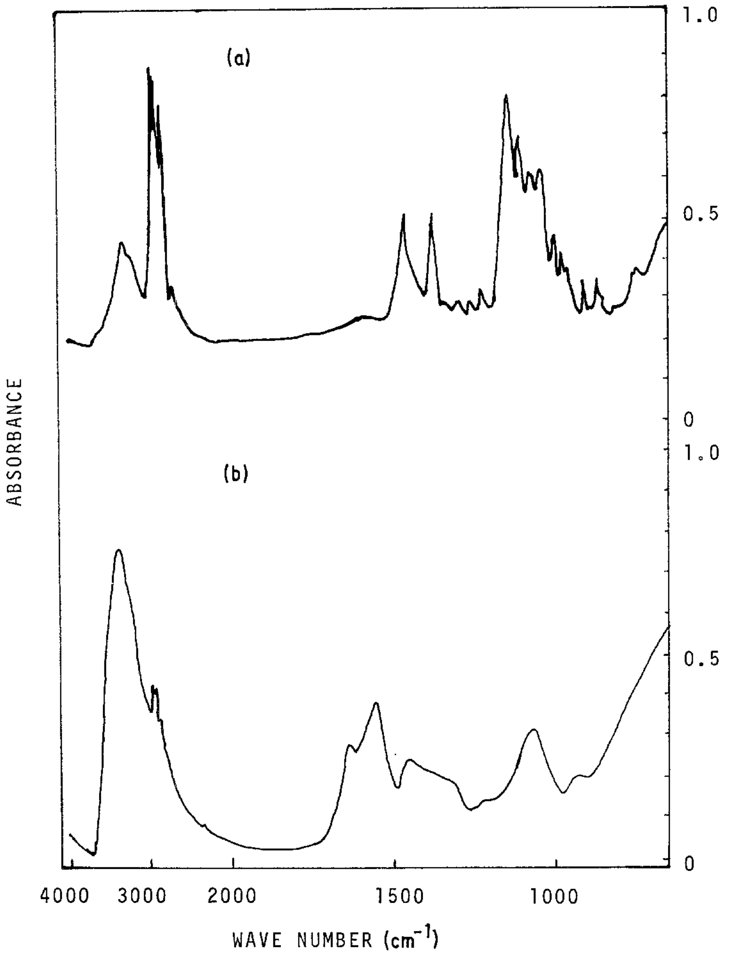

Figure 3 IR spectra of (a) n-butyl zirconate (monomer) and (b) its polymer. Sample 1.0 mg/150 mg KBr disc.

in photocatalytic hydrogen production. The small amounts of additive seems to have a stronger affinity to the catalyst than the solute, and therefore they decrease the H_2 production efficiency far more than the value expected from their concentrations.

The catalytic function of the polymer may be illustrated as in Fig. 6. The original ground-state radical (GR) state of the polymer catalyst is excited by light to the excited radical (ER) state in which some of the free-radical electrons are excited to the lowest unoccupied molecular orbitals (LUMO). In this structure the molecular conformation is the same as GR, and therefore it does not meet the requirement of the newly excited electronic state in the LUMO. The conformation therefore changes to that of an excited and deformed radical (EDR). In this EDR structure the polymer radical will be polarized because there are two types of electric charge accumulated in the molecule. In this structure an oxidation reaction with an electron donor molecule will take place, and also the LUMO electrons will be given to H^+ or other acceptor molecules through platinum. The lifetime of the ER and EDR structures will be short, and the EDR changes to a ground-state deformed radical (GDR) in which the electronic state is identical to GR but the molecular conformation of EDR is still left. The lifetime of

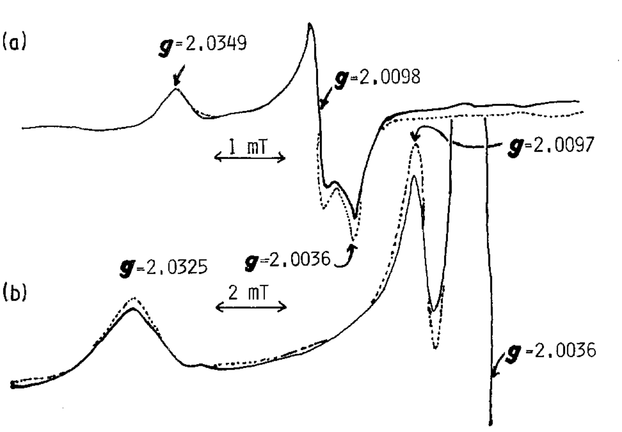

Figure 4 The ESR spectra of the polymer obtained from (a) ethanol and (b) benzene as solvents; (——) dark, (···) light.

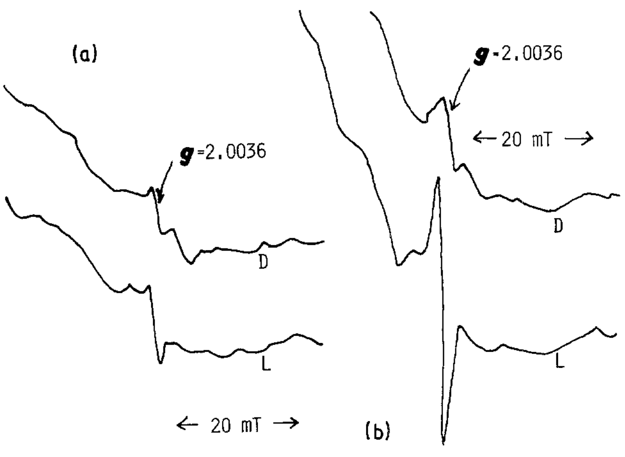

Figure 5 The ESR spectra of the polymer obtained from (a) CS_2 and (b) acetone as solvents; D = dark, L = light.

TABLE I Photocatalytic activities of the polymers

Substrate	Solvent used for obtaining polymer				
	THF[*]	C_6H_6	C_2H_5OH	CS_2	CH_3COCH_3
1:1 CH_3OH/H_2O	6.7[†]	7.4	7.2	3.5	6.3
0.24 M Na_2S	29	19	24[‡]	23	23

[*] Tetrahydrofuran.

[†] Indicating quantum efficiency.

[‡] If 0.024 M of CH_3COONa is added this value decreases to 15.

the GDR is long enough to be observed by the ESR method (some 10 min). The ESR spectrum in Fig. 2a corresponds to this structure.

In the case of the polymers of n-butyl orthotitanate, they were found to be useful as photocatalysts [2]. In other words, they are energy-converter type functional polymers. The results in Fig. 2 and Figs 4 and 5 indicate that the polymer of n-butyl zirconate may be used as a light detector. In other words the zirconium-containing polymer radical prepared in this work has a photoresponsive capacity by which the information concerning the lighting conditions surrounding the polymer can be sensed, especially in the visible region of light. The results in Table I indicate that polymers of n-butyl zirconate have energy-converter type functions as well.

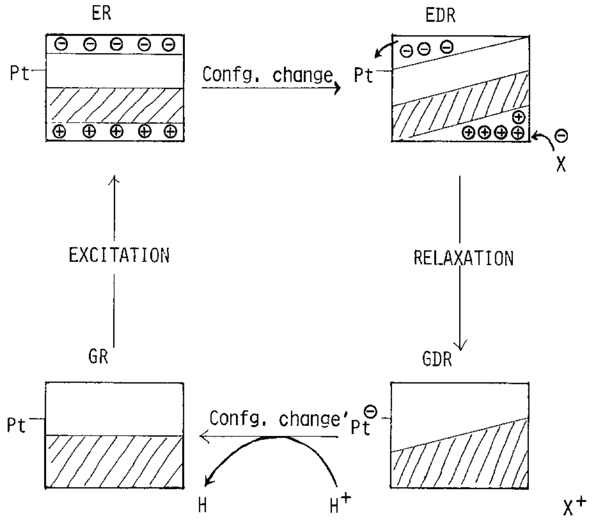

Figure 6 The excitation and relaxation diagram of the photocatalytic polymer molecule. "Confg. change" and "Confg. change'" mean that the configuration of the molecule changes in these processes.

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