CHEMISTRY LETTERS, pp. 487-490, 1986.

PHOTORESPONSIVE POLYMERS CONTAINING ZIRCONIUM WHICH RESPONDS TO VISIBLE LIGHT

Michiko YONEMURA, Tadao SEKINE, and Hisashi UEDA*
National Chemical Laboratory for Industry, Tsukuba Research Center,
Yatabemachi, Ibaraki 305

Photoresponsive polymers which change their magnetic properties when illuminated by visible light was 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 ESR spectrum is observed.

The needs for polymer material are changing from structural material to functional material. This trend will continue until molecular functional devices will be developed. One of the molecular functional material 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 organism. One is to use light as an energy source and biological material is synthesized using light energy. Another is to use light as an information source to the surrounding environment. Some of the examples are phototaxis, heliotropism, and visual vision.

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 reversively. Such light-induced morphological changes can be used for light-driven chemical valve, light-induced porous filter, etc.

The present authors have studied polymers of n-butyl orthotitanate polymerized in various solvents. Those polymers show light-induced 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 induced by the photoabsorption by the polymer radical the coupling between n-buthoxy group and the unpaired electron becomes strong.

In the present work photoresponsiveness of zirconium containing polymer is studied. 6.1 g of n-butyl zirconate (Mitsubishi Metal Corporation, offered as a generous gift) was dissolved in 500 ml of several solvents (tetrahydrofuran, benzene, ethanol, CS_2, and acetone) to which freshly crushed 2.0 g of silica gel (koso Chemical Co.) was mixed, which was then illuminated by fluorescent 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 the 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.

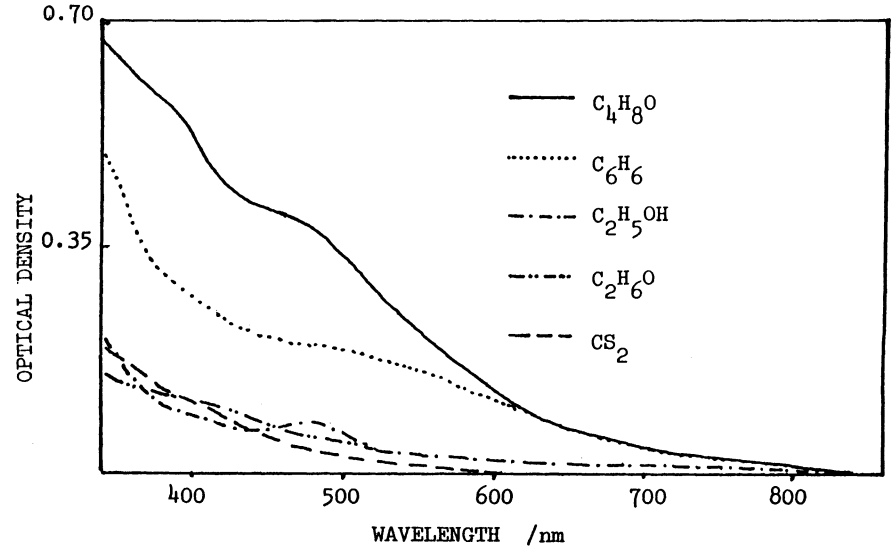

Fig. 1. The reflectance spectra of the polymers obtained in several solvents.

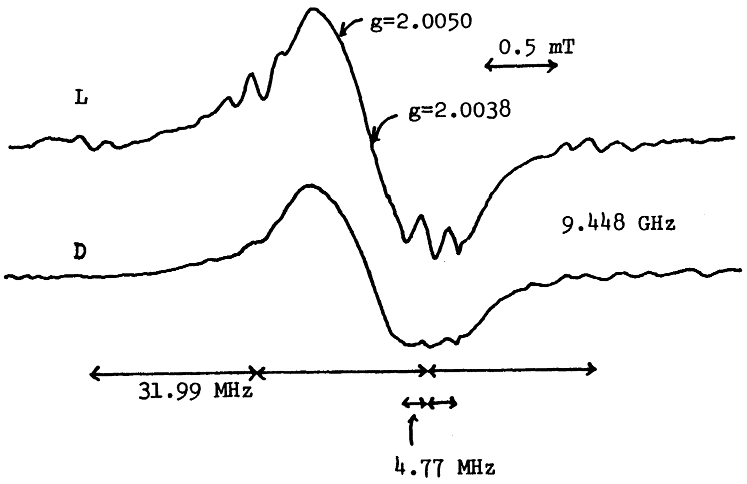

Fig. 2. The ESR spectra of the polymer obtained from tetrahydrofuran as a solvent.

The reflectance spectra of the powders of the polymers obtained from various solvents are shown in Fig. 1. The spectra in

Fig. 1 show that the zirconium containing polymer absorb visible light. The ESR spectra of the polymer obtained from tetrahydrofuran as a solvent is shown in Fig. 2. D denotes the spectrum obtained in the dark. When the sample tube is illuminated by visible light (400 - 700 nm) the spectrum L was obtained. In the spectrum L, the spin nuclear coupling between the unpaired electron and the protons of $-CH_2CH_3$ group of the n-buthoxy group is found. The methyl splitting observed is 31.99 MHz and the methylene splitting observed is 4.77 MHz. The dark spectrum D has no hyperfine structure. This 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-butyl chain is induced by it and the 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 conformation by which the spin nuclear coupling is observed can be long.

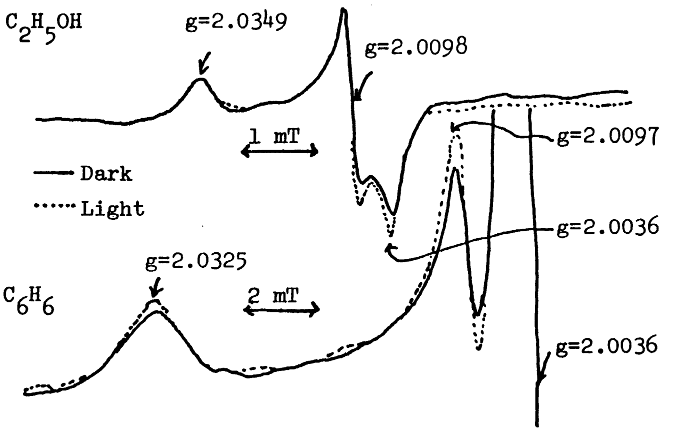

Fig. 3. The ESR spectra of the polymer obtained from ethanol and benzene as solv.

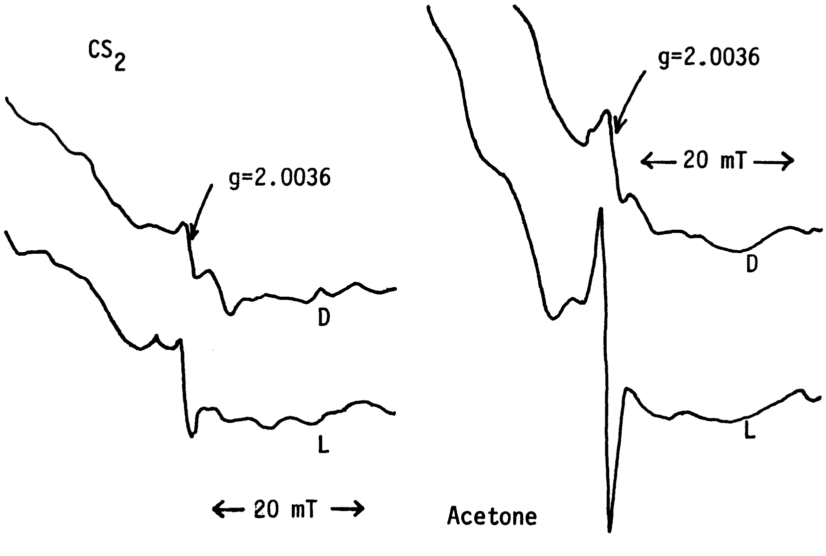

Fig. 4. The ESR spectra of the polymers obtained from CS_2 and acetone as solvents.

The polymers obtained in ethanol and benzene as solvents show different ESR spectra, which are shown in Fig. 3. 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.[3] In the cases of the polymers obtained in CS_2 and acetone, the ESR absorption with g = 2.004 is also intensified by visible light as shown in Fig. 4.

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.

In the case of the polymers of n-butyl orthotitanate, they were found to be useful as photocatalyst.[2] In other words they are energy-converter type functional polymers. In the case of the polymers of n-butyl zirconate, this energy-converting function have not been tested yet. The results in Figs. 2 and 3 indicate that the polymer of n-butyl zirconate may be useful as light detector. In other words the zirconium containing polymer radical prepared in this work has photoresponsive capacity by which the information concerning to the lighting conditions surrounding the polymer can be sensed, especially in the visible region of light.

The present authors thank Dr. Hiroto Uchida of Mitsubishi Metal Corporation for his helpful suggestions in this work.

References

1) M. Irie, Radiat. Chem., 40, 42 (1985); M. Irie,"Molecular Models of Photoresponsiveness," ed by G. Montagnoli and B.F. Erlanger, Plenum Press, New York (1983), p.291.
2) T. Sekine, M. Yonemura, and H. Ueda, Nippon Kagaku Kaishi, 1985, 605.
3) P. B. Ayscough, "Electron Spin Resonance in Chemistry," Methuen & Co. Ltd. London (1967), p.349.

(Received January 9, 1986)