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OPTICAL RECORDING MEDIA FROM POLYMER-TCNQ COMPLEXES

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Abstract Polymer-TCNQ(tetracyanoquinodimethane) charge transfer complexes were synthesized using organic polycations as electron donor. The materials were spin coated on the aluminium deposited polycarbonate substrate and their optical recording effects were tested at 830nm. With the recording power of 8mW and recording speed of 1.2m/s, the maximum CNR(carrier to noise ratio) of 40dB was observed.

INTRODUCTION

The rapid development of the information society demands high speed and high density information storage media. Optical recording media can store enormous amounts of data by laser irradiation, so they have been studied in various forms and formats for past 10 years.

Optical memory effect of metal-TCNQ charge transfer complexes was first suggested by Potember *et al.*[1] They studied the electric swiching effects of metal-TCNQ thin films, and found that lines or patterns can be observed on the surface of the film by intense laser irradiation. E.I. Kamitos *et al.*[2] have prepared Cu-TCNQ and Ag-TCNQ by thermal vacuum evaporation. By using Raman spectroscopy they found that electric field or laser induced phase transition involves the formation of a nonstoichiometric complex salt containing neutral TCNQ accompanying color change :

$$\left[Cu^{+}TCNQ^{-}\right]_{n} \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} Cu_{x} + [TCNQ]_{x} + \left[Cu^{+}TCNQ^{-}\right]_{n-x} \qquad (1)$$

The reaction is reversible and the initial state can be reformed by heat treatment. Since then various metal-TCNQ complexes have been prepared and studied as the WORM(write once read many) or rewritable optical recording media. But metal-TCNQ complexes are insoluble in organic solvents and requires expensive and complicate process such as vaccum deposition or sputtering with heat tretment to prepare optical recording media. Thus, it is difficult to prepare optical disks from these materials.

In this study we synthesized organic polymer-TCNQ complexes which are soluble in organic solvents. Polycations instead of metals were used as the electron donor in the complexes. The materials were spin coated on aluminium deposited polycarbonate disks, and their optical memory effects were tested by using commercial optical disk evaluation system at 830 nm. Thermal treatment to erase the optically recorded marks was also attempted.

EXPERIMENTAL

Synthesis of the polymer-TCNQ complexes

TCNQ was purchased from Taipan Chemical Co. and used after recrystalization by acetonitrile. 4-vinyl pyridine, 2-vinylpyridine, and styrene were purchased from Janssen Chimica and used after distillation. n-butyliodide was purchased from Aldrich Chemical.

Poly(1-butyl-4-vinylpyridinium-TCNQ)

4-vinyl pyridine was polymerized in bulk by using benzoyl peroxide as catalyst. The polymer was quarternized with n-butyl iodide in nitromethane to produce poly(1-butyl-4-vinylpyridiniumiodide). LiTCNQ was prepared by Merby's method.[3] By ion-exchange reaction of the above prepared polymer and LiTCNQ, poly(1-butyl-4-vinylpyridinium-TCNQ) (PBVT) was synthesized.

Copoly(styrene/1-butyl-2-vinylpyridinium-TCNQ)

Equal quantities of styrene and 2-vinylpyridine was mixed and polymerized in bulk by using azobisisobutyronitrile. The polymer was quaternized by n-butyliodide, and by the ion exchange reacion with LiTCNQ, copoly(styrene/1-butyl-2-vinyl pyridinium -TCNQ) (CSVT) was synthesized.

Spectrum Analysis

The polymers synthesized were analyzed by their IR and UV/VIS spectra. IR spectra was obtained using FTS 20/80 FTIR Spectro Photometer of Bio-Rad Co. by KBr pellet methode. UV/VIS spectra of the polymer in acetonitrile was obtained using UV-210 PC UV-VIS Scanning Spectrophotometer of Shimadzu Co.

Preparations of the Optical Recording Media

800 Å of aluminium was coated on 3.5 inch pregrooved polycarbonate disks by thermal vapor deposition as the reflective layer. The polymers were dissolved in 2,2,3,3-tetrafluoro-1-propanol (TFP) in the ratio of 0.2g/ml, filtered by 0.45mm syringe filter (Millipore), and spin coated on the disks. Spin coater P6204 from Integrated Technology Co. was used. The disks were dried in vacuum oven for 12hrs. Figure 1 shows the structure of the optical recording media prepared in this experiment.

Test of Optical Recording Characteristics

The optical recording characteristics of the recording media were evaluated by using Optical Disk Driver DDU-1000 from Pulstec Inc. Figure 2 shows the schematic diagram of the Optical Disk evaluation system. The 830nm laser diode was used as the recording and reading light source. The main unit of DDU-1000 controls the writing and reading power of the laser, focussing, tracking, and disk spin speed. The signals from function generator (Hewlett Packard, 8116A) were recorded through LD-driver on the disks, and the recorded

signals were analyzed by spectrum analyzer (Hewlett Packard, 3589A) to give CNR (carrier to noise ratio). In this study, the writing power and writing velocity were varied and the rectangular pulse with duty ratio of 50% was used as the writing signal. The reading power was set to constant at 0.8mW.

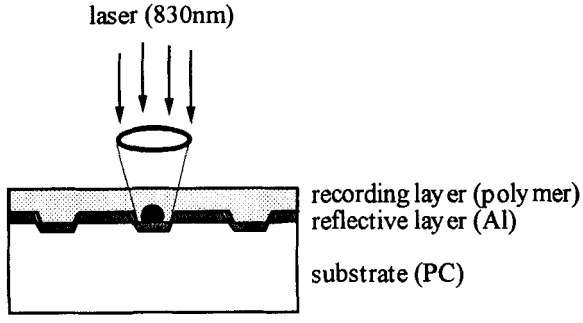

FIGURE 1 The structure of the optical recording media.

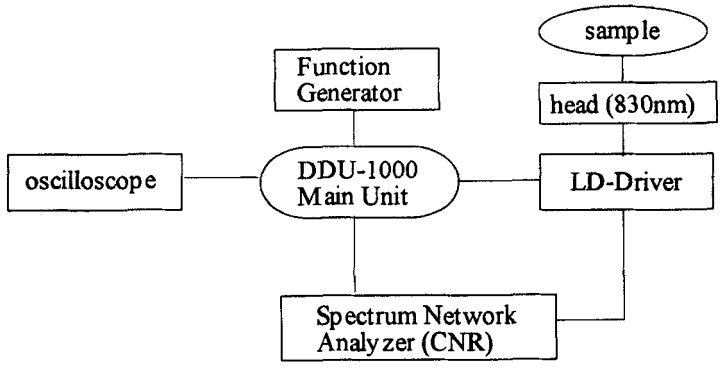

FIGURE 2 Schematic diagram of optical disk evaluation system.

RESULTS AND DISCUSSIONS

Spectrum analysis

The formation of the complexes was confirmed by their UV/VIS and IR spectra.[4] Figure 3

shows the infrared absorption spectra of the polymer-TCNQ complexes. The IR spectra of $TCNQ^-$(simple salt) shows a small bathochromic shift of the -C≡N absorption compared to that observed in neutral TCNQ. Thus neutral TCNQ shows CN absorption peak at 2222cm^{-1}, while $TCNQ^-$(simple salt) shows -C≡N absorption peak at 2164cm^{-1}. Both polymers show the -C≡N absorption peak at 2164cm^{-1}.

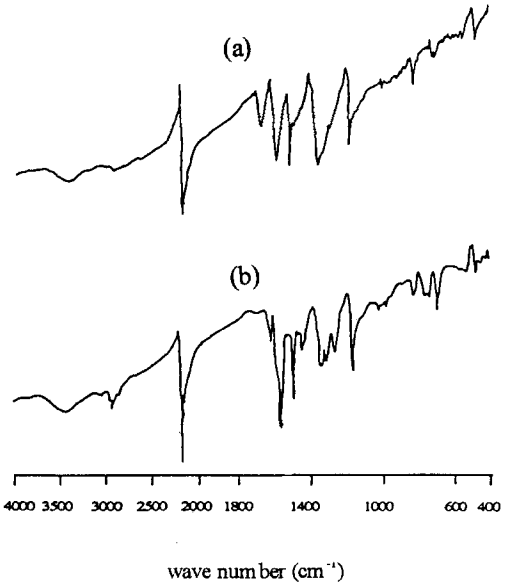

FIGURE 3 Infrared absorption spectra of (a) poly(1-butyl-4-vinylpyridinium-TCNQ) and (b) copoly(styrene/1-butyl-2-vinyl-pyridinium-TCNQ).

Figure 4 shows the ultraviolet absorption spectra of the polymers in acetonitrile. Both polymers show major maxima at 420 and 840nm, and the intensity ratio of the 420 and 840nm bands is about 0.5, which are the characteristics of the $TCNQ^-$.

The above IR and UV/VIS spectra confirm that both polymer-TCNQ complexes synthesized are simple salt which does not contain neutral TCNQ.

Optical Recording Test

The samples with different thickness were prepared by changing the spin speed. So each sample shows different reflectance. The reflectance of the samples ranges about 35-55%. The laser focussing and tracking were possible only for samples with high reflectance.

Figure 5 shows the CNR values of the samples prepared from the polymer-TCNQ complexes. As the recording speed decreases and recording power increases, higher CNR

(carrier to noise ratio) can be observed. With the record ing speed of 1.2m/s and the recording power of 8.9mW, maximum 32dB was obtained from PBVT/TFP sample. The

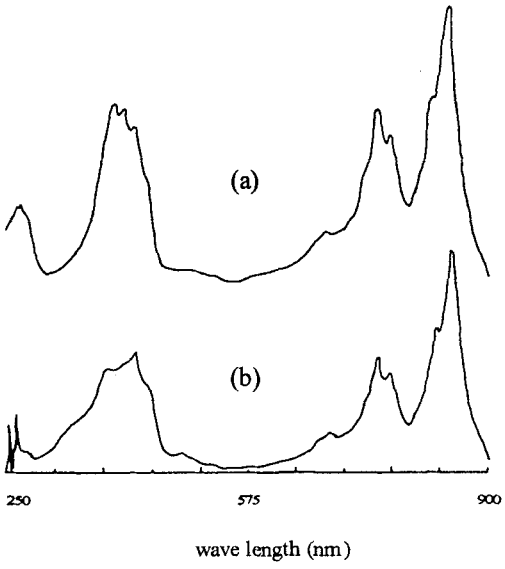

FIGURE 4 UV/VIS absorption spectra of (a) poly(1-butyl-4-vinylpyridinium-TCNQ) and (b) copoly(styrene/1-butyl-2-vinyl-pyridinium-TCNQ).

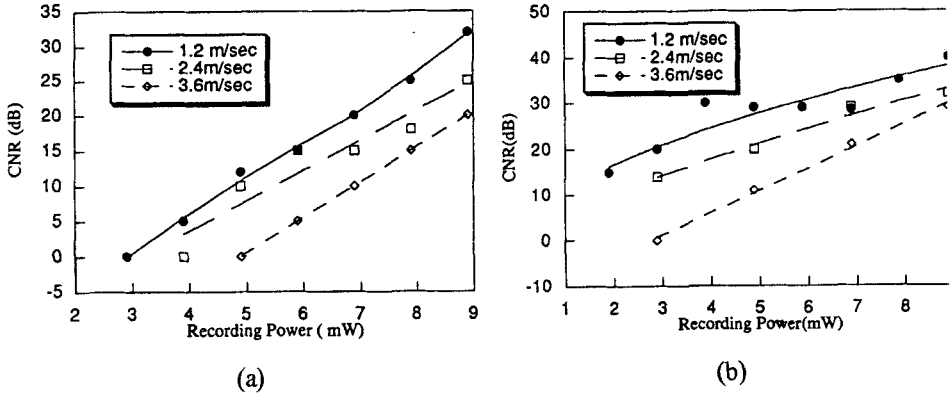

FIGURE 5 The effect of recording speed and power on CNR of the optical media derived from (a) PBVT/TFP and (b) CSVT/TFP.

figure also shows that recording was possible even with very low power(1.9mW) from CSVT/TFP sample. This shows that the media is quite sensible to laser radiation. With the recording power of 8.9mW, maximum 40 dB was obtained for this sample.

Attempts were made to erase the recorded signal by thermal treatment. If the media was recorded by chage transfer induced by laser radiation, the recorded state can go back to the original state by heat treatment. Figure 6 shows the remaining CNR after thermal treatment of the CSVT/TFP sample recorded with 1.2m/s of writing speed and 5.9mW of writing power. At each temperature, the sample was thermally treated for 5min. The CNR decreased with heat treatment, but rewriting was not possible. This tells that the optical recording was made through pit formation instead of charge transfer.

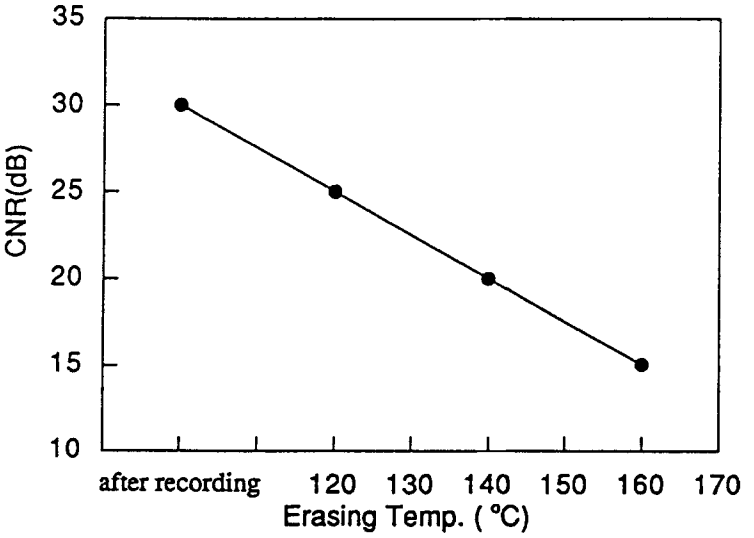

FIGURE 6 CNR after thermal erasing (CSVT/TFP).

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