

기능성 색소/MMA 공중합체의 합성과 광학적 특성

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Synthesis and Optical properties of Functional Dye/MMA Copolymers

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1. Introduction

In recent years the focus of research in dye chemistry has largely changed from involvement in the traditional chemistry of dyes and pigments to investigations of functional dyes. With the development of the electronics and information industries, the importance of functional dyes has increased. Many research papers have been published concerning new synthetic methods and mechanism of functional dyes. Highly functionalized dicyanopyrazine derivatives can be used as fluorescent dyestuffs, emitters for electroluminescent devices etc. Because of the specific properties of 2,3-dicyanopyrazine derivatives resulted from the two strong electron withdrawing cyanogroup on the pyrazine ring.

Fluorescent chromophores have been generally known to have a planar and rigid π -conjugation system, and many well known fluorescent chromophores have rigid ring systems such as stilbene, coumarin, naphthalimide, perylene, rhodamine, pyrazine etc.

In this study, we designed and synthesized the dicyanopyrazine copolymers by radical polymerization of 5-[2-[4-(6-methacryloyl hexyloxy)-phenyl]-ethenyl]-6-triphenylphosphordiy methyl-2,3-dicyanopyrazine using methyl methacrylate. The polymers have been characterized by gel permeation chromatography, thermogravimetric analysis, infrared, and nmr spectroscopy. The specific properties of resulting polymers have been investigated by UV-visible spectroscopy.

2. Experimental

^1H NMR spectra were taken on a Bruker DRX-300 FT-NMR Spectrometer in chloroform- d_6 . Infrared spectra were taken on a MAGNA-IR 760 spectrometer using KBr pellets. Differential scanning calorimetry (DSC) was obtained using a TA Instrument 2100, under nitrogen flow at a heating rate of $10^\circ\text{C}/\text{min}$. The visible and fluorescence spectra were measured on UNICAM 8700 and SHIMADZU RF-5301PC spectrophotometer, respectively. All chemicals were reagent grade and used without further purification.

2.1. Preparation of monomer

5-[2-[4-(6-hydroxy-hexyloxy)-phenyl]-ethenyl]-6-triphenylphosphordiyl methyl- 2,3-dicyano pyrazine (4)

To a suspension of 2,3-bis(triphenylphosphonium methyl)-5,6-dicyanopyrazine dibromide (**3**) and equivalent amount of 4-(6-hydroxy hexyloxy) benzaldehyde, which was prepared by the Williamson reaction of benzaldehyde with 6-bromohexane-1-ol, in ethanol at room temperature was added sodium ethoxide. The reaction mixture was refluxed for 4hr. After the reaction was complete, the reaction mixture was cooled. The precipitate was filtered, washed with ethanol.

5-[2-[4-(6-methacryloyl hexyloxy)-phenyl]-ethenyl]-6-triphenylphosphordiyl methyl- 2,3-dicyano pyrazine (5)

After the solution containing **4** in THF was cooled with ice-salt bath, triethylamine was added to the solution. Methacryloylchloride(MAC) solution in THF was added dropwise to the solution. The reaction mixture was stirred for 4 hr at room temperature. The mixture was poured into water and extracted with methylene chloride. The organic layer was washed with water, dried with MgSO₄. After the solvent removed, the crude product was purified by column chromatography.

2.2. Preparation of copolymer

The vinylmonomer **5** and methyl methacrylate (MMA) with three different mole ratios of 2.5, 5, 10 % were polymerized using α, α' -azobisisobutyronitrile (AIBN) as initiator. The mixture of **5**, MMA, and AIBN in benzene were heated at 70°C for 12 hr. The resulting polymers were purified by reprecipitation using a chloroform/methanol.

3. Results and Discussion

Synthesis of monomer and copolymers

5-[2-[4-(6-hydroxy-hexyloxy)-phenyl]-ethenyl]-6-triphenylphosphordiyl methyl- 2,3-dicyano pyrazine (**4**) were synthesized by Wittig reaction of **3** and 4-(6-hydroxy hexyloxy) benzaldehyde. And then, we prepare a monomer 5-[2-[4-(6-methacryloyl hexyloxy)-phenyl]-ethenyl]-6-triphenyl phosphordiyl methyl- 2,3-dicyano pyrazine (**5**) by esterification with methacryl chloride and **4**. The resulting monomer was obtained as dark-red powder. The chemical structure of the monomer was confirmed by ¹H-NMR, and IR spectrum. From the ¹H-NMR spectrum of monomer, vinyl protons observed at 5.66(s, 1H) and 6.01(s, 1H). The same monomer showed absorption bands at 2206, 1716, and 1681 cm⁻¹ indicating nitrile, ester, and vinyl groups, respectively.

The **5** and MMA with three different mole ratios (**5**/MMA) of 2.5, 5, 10 % were polymerized in benzene solution with AIBN as initiator to give the copolymers. The polymerization results are summarized in Table 1 and chemical structure is shown in scheme 1.

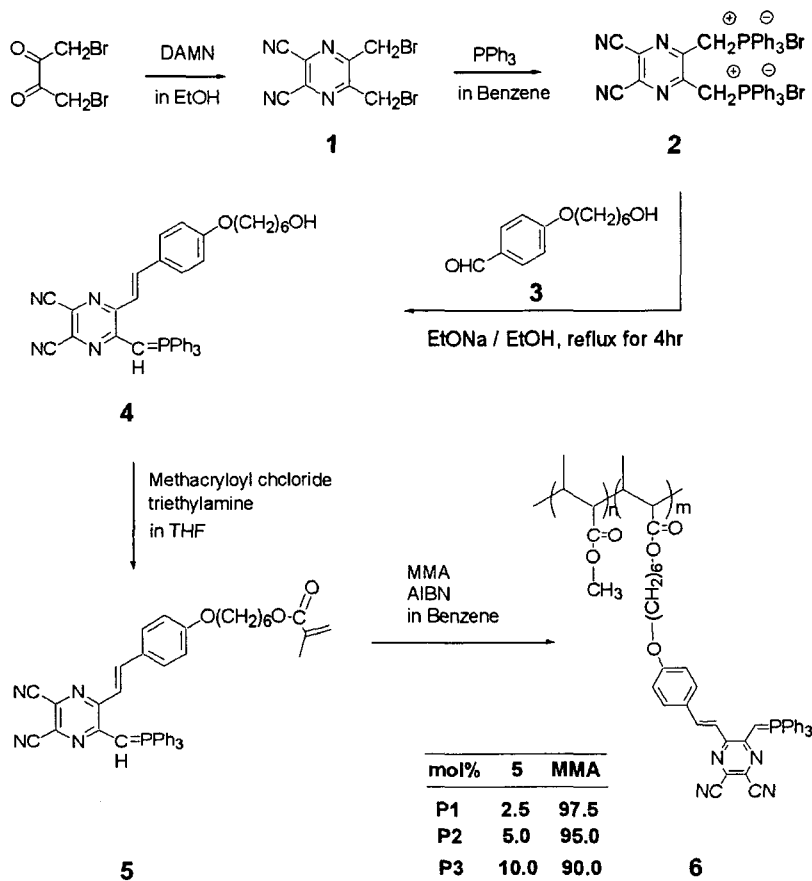
The copolymers were characterized by ¹H-NMR spectroscopy. The terminal vinyl chemical shift of monomer at around 5.66, 6.01 ppm were disappeared completely and small broad aromatic peaks were appeared. The glass transition temperature (T_g) of the copolymers were determined to be 121.5, 122.2, and 124.9°C for **P1**, **P2**, and **P3** respectively from the DSC thermograms. The number average molecular weights of the copolymers were determined to be 21,327 ~ 28,580 by

GPC analysis. The onset decomposition temperature values determined by thermogravimetric analysis (TGA) appear similar above 230 ~ 240 °C.

Optical properties of monomer and copolymers

Figure 1 shows the UV-visible and fluorescent spectra of monomer and copolymer in chloroform. The monomer showed two absorption maxima at 405 nm and 498 nm, because of methylene phosphorous group was introduced at 5-position of the 2,3-dicyanopyrazine chromophore. The methylene phosphorane is usually described as a resonance hybrid. The fluorescent maximum of monomer are obtained at 598 nm, Stokes shift was 200 nm. In the case of copolymer, similar absorption and fluorescent spectra were obtained.

Figure 2 shows the spectral change of the monomer and P3 as increasing p-toluenesulfonic acid in the toluene. Addition of p-toluenesulfonic acid to the toluene solution of monomer produced hypsochromic shifts of the long wavelength absorption band. In the case of P3, same spectral change was observed. It is of interest that pendent functional dye in the polymer side chain remain their own functional properties.



Scheme 1. Reaction route of copolymer

Table 1. The characteristics of copolymers

	Monomer (mole %)	M_n^a	M_w^a	PDI ^a	T_g^b	T_{id}^c
P1	2.5	28,580	46,259	1.6	121.5	244
P2	5	24,386	41,660	1.7	122.2	233
P3	10	21,327	44,383	2.1	124.9	230

a : Determined by gel permeation chromatography (GPC)

b : Determined by (DSC)

c : Temp. of 2% weight loss; Determined by (TGA)

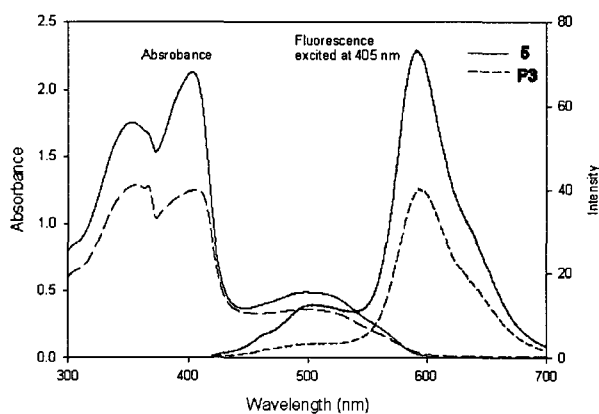


Figure 1. Visible and fluorescent spectra of monomer and P3.

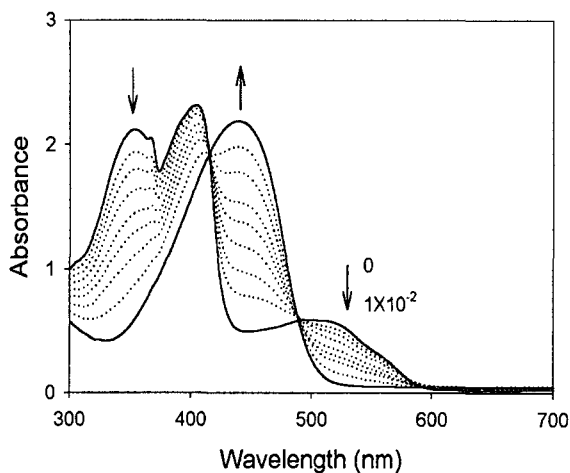


Figure 2. Spectral change of 5 in toluene for various concentration of *p*-toluenesulfonic acid(0 - 1×10^{-2} mol/L).