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Synthesis and photochromism of polyacetylene derivatives containing a spiroxazine moiety

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Abstract

Cyclopolymerization of 1,6-heptadiyne derivatives containing the photochromic spiroxazines was carried out by molybdenium-based transition metal catalyst. The polymer structure was characterized by various instrumental methods such as NMR, IR and UV–visible spectroscopy to have a conjugated polymer backbone structure carrying a spiroxazine moiety. The resulting polymers were found to be photochromic in thin solid film.

Keywords: Spiroxazine; Photochromism; Cyclopolymerization; Dipropargyl derivatives; Polyacetylene

1. Introduction

Organic polymers and oligomers having conjugated π-systems possess a variety of intersesting optical and electrical properties [1,2]. Among the π-conjugated polymers, polyacetylene is structurally the simplist conjugated polymer. The biggest drawbacks of polyacetylene are insolubility, infusibility and instability in oxidation. In order to overcome these problems, substituents are introduced into the polyacetylene backbone. Conjugated polymers obtained from acetylene derivatives have potential as organic semiconductors [3], membranes for gas separation and for liquid-mixture separation [6], materials for enantio separation of racemates by high performance liquid chromatography [4], a side-chain liquid crystal [5], materials for chemical sensors [7], as materials needing nonlinear optical properties [8], and for photoluminescence and electroluminescence properties [9].

1,6-Heptadiyne and its homologues of substituted acetylenes are very interesting examples of substituted acetylenes, which can be susceptible to the ring-forming polymerization to give a new type of conjugated polymer backbone system. The polymerization of 1, 6-heptadiyne using an insoluble Ziegler–Natta catalyst [$TiCl_4$/Al(i-C_4H_9)$_3$] was reported by Stille and Frey [10].

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Recently, photochromic materials have gained much attention and they now constitute an active research area because of their tremendous importance in biological phenomena and in their potential applications in the areas of linear and nonlinear optics [11]. In this article, we report the cyclopolymerization and copolymerization of 1,6-heptadiyne containing photochromic spiroxazine moiety catalyzed by $MOCl_5$.

2. Experimental

Melting points were determined using an Electrothermal IA 900 and are uncorrected. A multichannel photodiode detector (MCPD, Otsuka Electronics., Co., Japan) was used to obtain visible absorption spectra and CHN analyses were carried out with a Carlo Elba model 1106 analyzer. Mass spectra were recorded on a Shimadzu OP-1000 specrometer using an electron energy of 70 eV and the direct probe EI method. ^{1}H-NMR spectra were recorded on a Varian Unity Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. IR spectra were measured with a Galaxy 7020A IR spectrometer. The molecula weight and polydispersity were determined in tetrahydrofuran (THF) solvent by an Alliance GPCV 2000 DAWN PSP calibrated with polystyrene standards. Thermogravimetric analysis (TGA) was performed on a TA 4000 Auto DSC 2910 under a nitrogen atmosphere with a heating rate of 10 °C/min in a temperature range of 20–700 °C.

2.1. Synthesis of intermediates and monomers

Intermediates **4**, **5**, **6**, **9**, **10** and monomers **3**, **11** were prepared according to the literature procedures [12–14].

2.1.1. Synthesis of diethyl dipropargylmalonate *3*

Diethylmalonate **1** (24.47 g, 0.153 mol) was added to the absolute ethanol (160 ml) containing sodium ethoxide (from sodium, 7.7 g, 0.336 mol). After 30 min, propargyl bromide **2** (39.97 g, 0.336 mol) was slowly added to the stirred suspension under 60 °C. Then the mixture was refluxed for 12 h. After removal of the alcohol under reduced pressure, the residue was diluted with water and extracted with ethyl ether. The ether fraction was dried over anhydrous magnesium sulfate. The magnesium sulfate was filter off, and then the ether was removed under reduced pressure. The residue was distilled at 82 °C and 0.12 Torr. to give 3.76 g. Yield; 95%. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.27 (t, $J = 7.00$, 6H), 2.03 (s, 2H), 2.99 (s, 4H), 4.24 (m, $J = 6.08$, 4H). IR (KBr pellet, cm^{-1}): 3302 (≡C–H), 2127 (C≡C), 1735 (C=O).

2.1.2. Synthesis of dipropargylmalonic acid *4*

Diethyl dipropargyl malonate 3 (3 g, 12.7 mmol) was refluxed with 25 ml of 10% alcoholic KOH for 6 h, and then the alcohol was removed under reduced pressure and the residue was acidified with 3N HCl. The residue was extracted with diethyl ether. The ether fraction was dried with $MgSO_4$ and evaporated (vacuum) to give 1.97 g of product. Yield; 85.8%. ^{1}H-NMR (DMSO-d_6, δ ppm): 2.44 (s, 2H), 2.88 (s, 4H), 3.43 (s, 2H)

2.1.3. Synthesis of dipropargylacetic acid *5*

The dipropargyl malonic acid **4** (10 g, 55.5 mmol) was heated in water (20 ml) at 120–130 °C, until no more carbon dioxide was evolved. The cooled solution was extracted with ethyl ether, dried over anhyd $MgSO_4$ and the ether removed under reduced pressure. Distillation of the residual yellow oil at 82 °C/0.12 Torr gave a colourless liquid, which solidified rapidly. Yield; 52.9%. ^{1}H-NMR ($CDCl_3$, δ ppm): 2.05 (s, 2H), 2.69 (s, 4H), 2.84 (t, $J = 6.26$ Hz, 1H).

2.1.4. Synthesis of dipropargyl acetyl chloride *6*

To a flask charged with ethyl ether solution (10 ml) of dipropargylacetic acid **5** (4 g, 29.38 mmol) pyridine was added (2.8 g, 35.26 mmol), under nitrogen atmosphere, dropwise at room temperature. Thionyl chloride (4.19 g, 35.26 mmol) was added dropwise to the reaction mixture which was kept at −78 °C for 30 min, and the reaction mixture was stirred for 24 h at room temperature. The mixture was filtered, evaporated and distilled at 34 °C and 0.12 Torr to give 2.57 g of the product. Yield; 56.6%. ^{1}H-NMR ($CDCl_3$, δ ppm): 2.11 (s, 2H), 2.77 (s, 4H), 3.19 (t, $J = 6.3$ Hz, 1H)

*2.1.5. Synthesis of spiroxazine **9***

Spiroxazine **9** was prepared from 1,3,3-trimethyl-2-methylene-indoline **7** and 1-nitroso-2,7-hydroxy-naphthalene **8** according the method descried in Refs. [13,14]. Yield; 4.33 g (58%), mp 211.5–214 °C. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.36 (s, 6H), 2.76 (s, 3H), 6.58 (d, $J=7.4$ Hz, 1H), 6.84 (d, $J=8.84$ Hz, 1H), 6.90 (t, $J=7.46$ Hz, 1H), 7.02 (d, $J=8.68$ Hz, 1H), 7.22 (t, $J=7.40$ Hz, 1H), 7.58 (d, $J=8.6$ Hz, 1H), 7.65 (d, $J=8.56$ Hz, 1H), 7.71 (s, 1H), 7.88 (s, 1H). Elemental analysis: C, 76.89; H; 5.93; N, 10 $C_{22}H_{20}N_2O_2$, requires: C; 76.72, H; 5.85, N; 8.13

*2.1.6. Synthesis of spiroxazine **10***

A stirred solution of **5** (2 g, 5.81 mmol) and 6-bromo-1-hexanol (1.26 g, 6.96 mmol) in methanol (80 ml) containing suspended powdered potassium carbonate (0.96 g) was refluxed for 12 h. The reaction mixture was cooled to room temperature. The precipitated crude product was separated by filteration and recrystallized with methanol to give 1.26 g of **6**. Yield; 49%, mp: 144–147 °C. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.35 (s, 6H), 1.64 (m, 6H), 1.89 (m, 2H), 2.76 (s, 3H), 3.68 (t, $J=6.24$ Hz, 2H), 4.19 (t, $J=6.32$ Hz, 2H), 6.57 (d, $J=7.52$ Hz, 1H), 6.84 (d, $J=8.8$ Hz, 1H), 6.89 (t, $J=7.48$, 1H), 7.03 (d, $J=8.68$ Hz, 1H), 7.08 (d, $J=6.92$ Hz, 1H), 7.22 (t, $J=7.48$ Hz, 1H), 7.56 (d, $J=8.72$ Hz, 1H), 7.62 (d, $J=8.84$ Hz, 1H), 7.72 (s, 1H), 7.84 (s, 1H). Mass (m/z): 444 (M^+). Elemental analysis: Calcd C, 75.65; H, 7.26: N, 6.3; O, 10.8 $C_{28}H_{32}N_2O_3$, requires C, 75.00; H, 7.68; N, 6.16: O, 10.35.

*2.1.7. Synthesis of monomer **11***

To a solution of **10** (2.36 g, 5.304 mmol) and triethyl amine (0.54 g, 5.336 mmol) in THF (10 ml) was added dipropargyl acetyl chloride **6** (0.82 g, 5.304 mmol) in THF (10 ml) dropwise at 0 °C. The reaction mixture was stirred for 24 h at room temperature, and the solvent was evaporated (vacuum). The residue was partitioned between ethyl acetate and water. The ethyl acetate phase was dried with anhydrous magnesium sulfate, filtered and evaporated under reduced pressure to give a yellow oil. The residual oil was crystallized from ethanol to give brown crystals of **11**. Yield; 50.3%, mp; 58–60 °C.

^{1}H-NMR ($CDCl_3$, δ ppm): 1.35 (s, 6H), 1.51 (m, 4H), 1.72 (m, 2H), 1.87 (m, 2H), 2.03 (s, 2H), 2.65 (s, 4H), 2.76 (s, 3H), 4.18 (m, 4H), 6.58 (d, $J=7.64$ Hz, 1H), 6.84 (d, $J=8.76$ Hz, 1H), 6.90 (t, $J=7.46$ Hz, 1H), 7.03 (d, $J=8.76$ Hz, 1H), 7.08 (d, $J=6.88$ Hz, 1H), 7.22 (t, $J=7.44$ Hz, 1H), 7.57 (d, $J=8.76$ Hz, 1H), 7.63 (d, $J=8.88$ Hz, 1H), 7.72 (s, 1H), 7.84 (s, 1H). Mass (m/z): 562 (M^+). Elemental analysis: Calcd C, 76.84; H, 6.81: N, 4.98; O, 11.37 $C_{36}H_{38}N_2O_4$ requires: C, 74.65; H, 7.04; N, 4.69; O, 11.60. IR (KBr pellet, cm^{-1}): 3292 (≡C–H), 2119 (C≡C), 1737 (C=O)

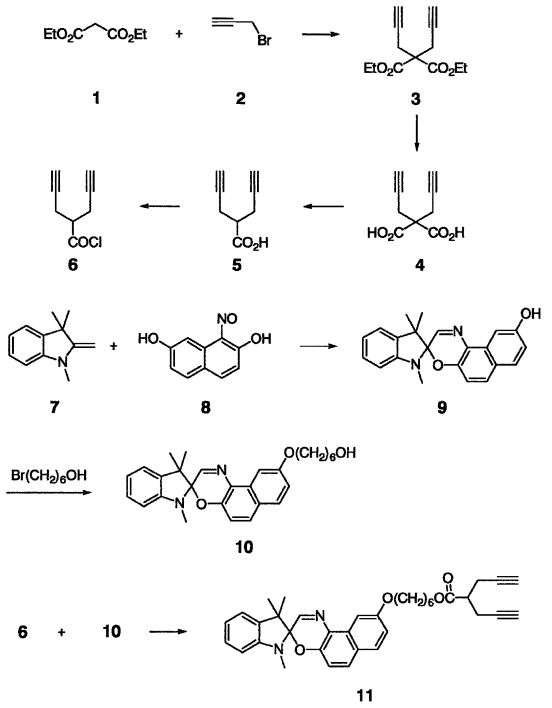
2.2. Polymerization

Polymerization was carried out by nitrogen atmosphere because the active species of the catalyst is very sensitive to oxygen and moisture. The homo- and copolymerization of the monomers (3, 11) were carried out by $MoCl_5$-based metathesis catalyst system. Molybdenium (V) chloride ($MoCl_5$) was dissolved in chlorobenzene as 0.1 M solution before use. A solution of $MoCl_5$ (0.21 ml 0.1 M chlorobenzene solution, 0.0213 mmol), monomer **11** (0.3 g, 0.533 mmol) and THF (3.55 ml) were injected into a polymerization ampoule equipped with rubber septum at room temperature. The reaction mixture was allowed to react at 60 °C for 4 h. After the polymerization, 10 ml of chloroform was added to the ampoule. The resulting polymer solution was precipitated into excess hexane, filtered form the solution and dried under vacuum at 40 °C for 24 h. Copolymerization of **3** with **11** was carried out with similar method for homopolymerization.

3. Results and discussion

The synthesis of intermediates and monomers was carried out according to the synthetic route outlined by Scheme 1. Scheme 2 illustrates homo- and copolymerisation of the monomers by ring-forming metathesis catalyst system. The structure of the polymer was analyzed by ^{1}H-NMR, IR and UV–visible spectroscopies.

The ^{1}H-NMR spectra of monomer **11**, polymer **12**, **14** and copolymer **13** are shown in Fig. 1.



Scheme 1.

While the acetylenic proton peak at 2.02 ppm disappeared, the new broad peak which is assignable to the proton of conjugated double bond appeared in the range of 6.0–6.8 ppm in the ^{1}H-NMR spectrum. The peak at the 2.9–3.6 ppm and the 4.2 ppm are due to the methylene protons adjacent to the conjugated carbons and the methylene protons of ethyl groups, respectively. The methyl protons of N–CH_3 were also observed at 2.8 ppm.

The IR spectra of the polymer showed no absorption peaks at 3300 and 2100 cm^{-1}, which are expected to the present for the acetylenic carbon–hydrogen bond stretching and carbon–carbon triple bond stretching in the monomer, respectively.

In Table 1, the results for the polymerization are summarized. The molecular weights of the resulting polymers were estimated by gel-permeation chromatography (GPC) to be in the range $M_n = 8.94\times10^3$–1.08×10^4 and polydispersity of the resulting polymers were in the range of 1.99–2.62.

The TGA thermogran of polymer **13** and **14** revealed two decomposition process, one peaking at around 270 and 300 °C. The lower temperature process is attributed to decomposition of spiroxazine moiety and the higher temperature process is due to the loss of the backbone configuration.

Table 1
Cyclopolymerization of dipropargyl monomers

Experimental number	Feed ratio of A/B	Yield (%)	M/C[a]	$[M]_o$[b]	GPC[c]	
					M_n	M_w/M_n
12	100/0	73.0	25	0.15	8940	1.99
14	50/50	75.1	25	0.15	13,790	3.85
13	0/100	63.3	25	0.15	10,845	2.62

[a] Monomer-to-catalyst molar ratio.
[b] Initial monomer concentration (M_o).
[c] Values were obtained by GPC analysis with polystyrene standards.

It shows that the polymer **13** retains 95% of its original weight at 274 °C, 70% at 407 °C, and 60% at 700 °C. The thermal properties of copolymer **14**, is similar to those of polymer **13** and do not vary significantly regardless of the molar ratio of monomer in the polymer backbone, as shown in Fig. 2.

To investigate the photochromic effect on the cyclopolymerization of 1,6-heptadiyne derivatives, we introduced the photochromic spiroxazine group in the 4-position of the 1,6-heptadiyne unit. The photochromic reaction in question is caused by the reversible heterolytic cleavage of the C (spiro)–O bond under UV irradiation, yielding the coloured form that can return to the colourless form by ring closure under visible light irradiation or in the dark. Newly synthesized homo- and copolymer were soluble in THF and could afford thin solid film by dip-coating onto the glass substrate. Electronic absorption spectra changes of polymer **13** and **14** upon UV irradiation in thin solid film are depicted in Fig. 3.

The UV–visible spectrum exhibits the characteristic broad absorption peak at the visible region was originated from the π–π^* conjugation band transition of the polyene main chain, which had not been observed at the UV–visible spectra of monomer. The spiroxazine monomer **11** absorbs UV ranges (λ max = 360 nm) light and shows absorption at λ max = 600 nm as a photochromic change caused by ring open isomerization. The visible range absorption increased

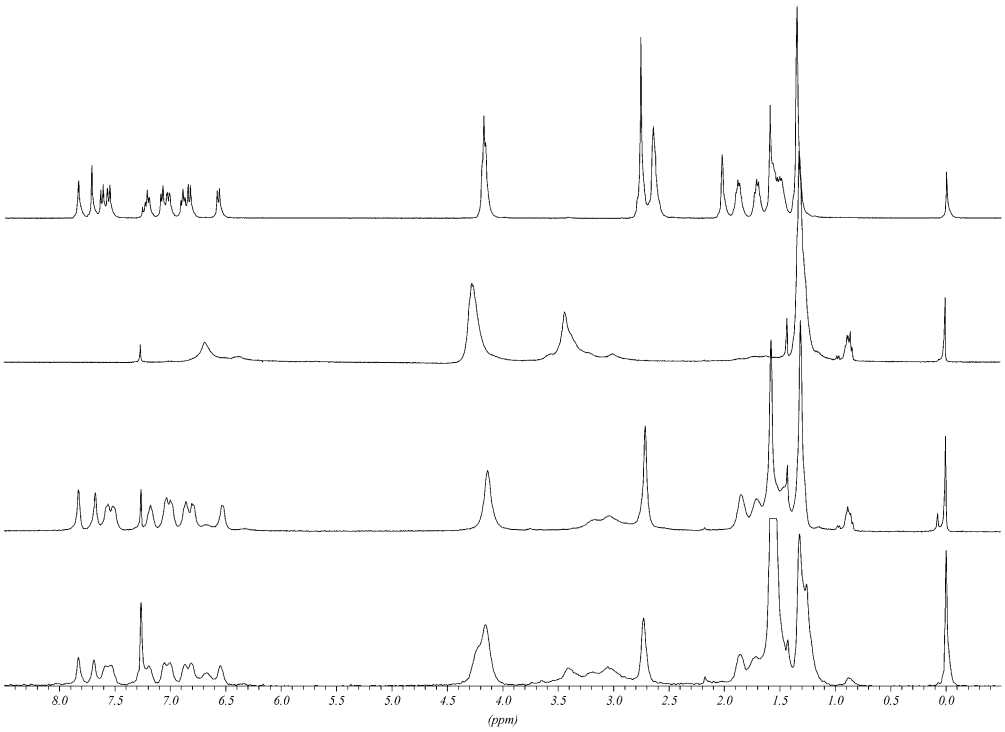


Fig. 1. ^{1}H-NMR spectrum of monomer **11**, polymer **12**, polymer **13** and copolymer **14**.

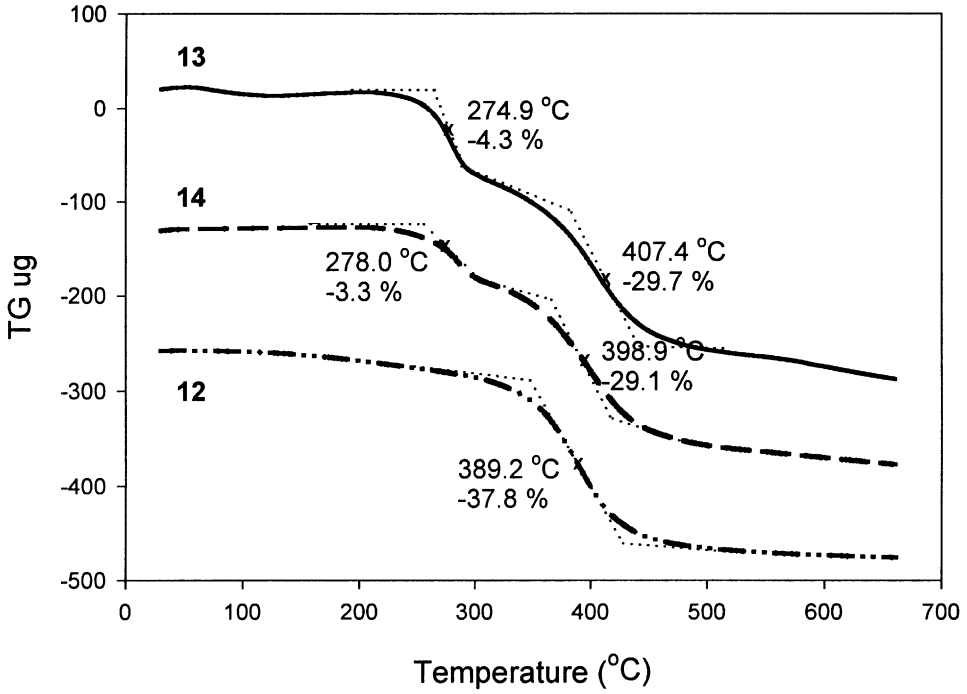


Fig. 2. TGA thermogram of polymer **12**, polymer **13** and copolymer **14**.

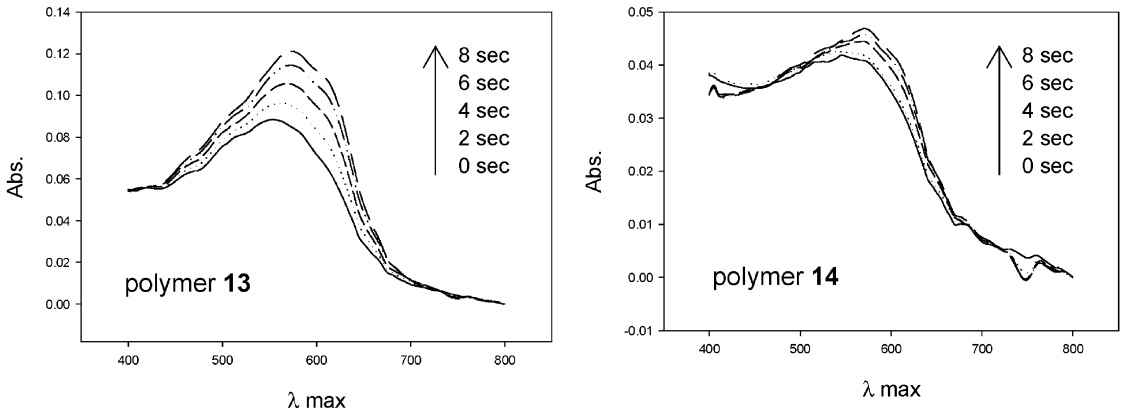


Fig. 3. Visible spectral changes of polymer **13** and polymer **14** upon UV irradiation.

gradually by UV irradiation which is ascribe to the generation of the open merocyanine form from the closed spiro form. When the sample of polymer **13** and **14** was left in the dark at room temperature of irradiation, the absorbance at 600 nm decreased slowly. Spectra measured after UV irradiation are proportional to each other in the visible region, indicating that only one species was formed. This allowed the absorption to be monitored at λ max (575 nm) as a function of time to obtain the thermal colour fading rate (k) of the transformation from the open merocyanine form to closed sipro form via a first-order reaction [Eq. (1)]:

$$A_t - A_\infty = A_i \cdot \exp(-kt) \quad (1)$$

Where A_i is the absorbance at 575 nm, A_t the absorbance at 575 nm at time t after UV irradiation. A_∞ and k refer to the absorbance at 575 nm after 50 s and first-order colour changing rate constant, respectively. In this thermal colour change process, the kinetic analysis predicts the logarithm of the difference between A_8 and A_t at time t to be linear with time, the slope giving the decolouration rate constant, k. First-order plots according to Eq. (1) for the polymer **13** and **14** are shown in Fig. 4.

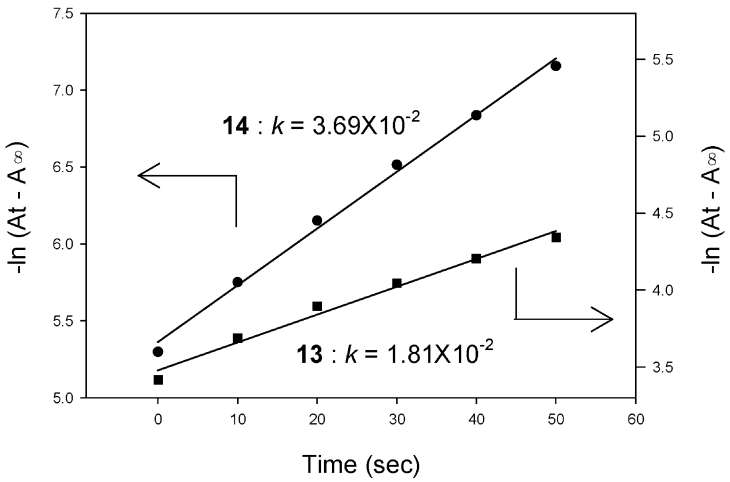
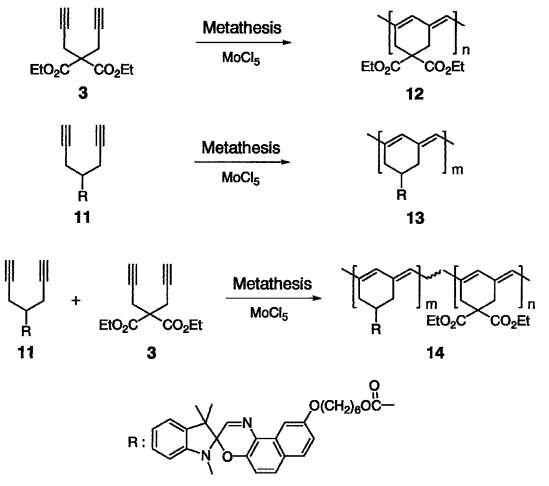


Fig. 4. Plot of $-\ln(A_t - A_\infty)$ as a function of time according to Eq. (1) for the decolouration of polymer **13** and **14**.



Scheme 2.

The first-order decolouration rate constant of polymer **13** in the thin solid film state was smaller than that of polymer **14** ($k = 1.81 \times 10^{-2}$ for polymer **13**, $k = 3.69\text{x}10^{-2}$ polymer **14**); which indicates that open-to-close occurs more readily in polymer **14** than in the polymer **13**.

This behavior can be tentatively interpreted as a result of two different environments surrounding the open form of spiroxazine moiety in the thin solid film.

The open form molecules in polymer **13** are surrounded mostly by similar open form molecule. On the other hand, the presence of monomer **3** unit in polymer **14** could result in more space or free volume in the thin solid film state as compared to the polymer **13**. In other words, the monomer **3** unit may have a matrix-like effect on the photoisomerization of spiroxazine moiety.

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