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Synthesis and switching properties of photochromic carbazole–spironaphthoxazine copolymer

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Abstract

A photochromic switching copolymer was synthesized by typical radical copolymerization of 2-(9H-carbazol-9-yl) ethyl methacrylate, a vinyl monomer having a spironaphthoxazine residue. It reversibly changed the fluorescent intensity by alternative irradiation with ultraviolet and visible light probably due to the photoinduced electron transfer (PET) between carbazoles and the open form of spirooxazine (SPO) moiety. By the observation of photoresponsive viscosity and conductivity changes, it was confirmed that the copolymer could exhibit excellent viscosity and conductivity switching behaviors.

Keywords: Synthesis; Photochromic; Spironaphthoxazine; Carbazole; Copolymer

1. Introduction

Organic photochromic materials attract much attention because of their numerous potential applications for optical devices, such as ultra-high-density optical information storage, variable-transmission filters, and photoregulated molecular switches [1–4]. In particular, photochromic polymers might meet the requirements in many probably practical applications because of their excellent photoresponsive behavior in the solids or crystals [5–8]. Multifunctional photoresponsible polymers including photoswitchable luminescence polymers are the most promising polymers because bistable photoswitching of fluorescence emission is considered to be a promising signaling mode, not only because the fluorescence signals can be readily and sensitively recognized, but also because the small number of photons required for their excitation induce few side effects to spoil the digitalized signals [9,10]. Among various types of photochromic compounds, spirooxazines (SPO) [11,12] are well-known photochromic compounds that have been attracting much interest from the viewpoint of fundamental elucidation of photochemical reactions and potential applications in optical memories. Photochromism in spirooxazine compounds generally involves the UV-induced dissociation of the spiro C–O bond, from the oxazine ring to form a planar structure. However, photocontrollable fluorescent changes of spirooxazine are very scarce [13]. Especially, the multiswitchable fluorescent photochromic spirooxazine polymers are almost no report. We have reported a series of interesting photochromic spirooxazine polymers [14–18]. This work describes the synthesis and switching properties of copolymer containing carbazole (Cz) and SPO moieties in the pendant groups (PMMA-Cz-SPO) as shown in Scheme 1, with a photoregulation luminescence change, photoresponsive viscosity, and conductivity changes by alternative irradiation with ultraviolet and visible light.

2. Experimental

2.1. Materials and methods

Most chemicals were purchased from Aldrich Chemical Co. and TCI. Solvents were purified by normal procedures and handled under moisture-free atmosphere. The other materials were commercial products and were used without further purification. Compound 2 was prepared using previously described procedures [19,20].

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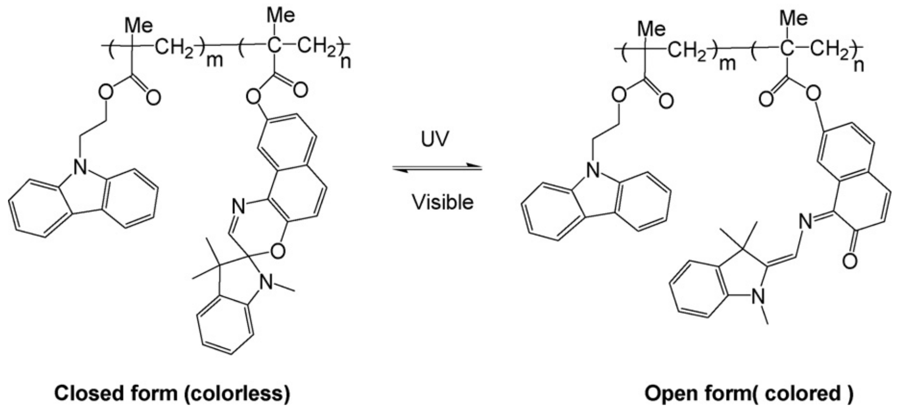


Scheme 1. Photoswitchable process of PMMA-Cz-SPO copolymer by alternative irradiation with UV and visible light.

2.2. Instruments and spectral measurements

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. Fluorescence spectra were measured on a Shimadzu RF- 5301PC fluorescence spectrophotometer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using electron energy of 70 eV and the direct probe EI method. ^1H NMR spectra were recorded using a Varian Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. The weight-average molecular weights (Mn) and polydispersity (Mw/Mn) of the polymer was measured on a PL-GPC model 210 chromatograph at 25 °C using THF as the eluent and standard polystyrene as the reference. The polymer film is spin-cast from 0.1 wt.% toluene solution approximately 10–25 nm thick for UV–vis and fluorescence measurements. For the measurement of photoinduced ionic conductivity, the device comprised with two ITO glasses (3 × 3 cm) separated by a 0.1 mm thickness spacer of photoinduced electron transfer (PET) film was prepared and placed so as to face each other on the inside of the cell, and the edges of the cell were sealed with insulating epoxide resin. Prior to the final sealing, the space between the electrodes was filled with 0.1% PMMA-Cz-SPO copolymer in THF solution and 1 mmol of tetra-*n*-butylammonium perchlorate, $[CH_3(CH_2)_3]_4NClO_4$, as electrolyte. A high-pressure mercury lamp (Ushio, SP3-250D) was used as the UV radiation source and was calibrated with a monochromator at 366 nm.

2.3. Synthesis of 2-(9H-carbazol-9-yl) ethyl methacrylate monomer 4

2-(9H-carbazol-9-yl) ethanol **1** (4.1 g, 19 mmol) in 30 ml of anhydrous dichloromethane solution containing 3 ml of pyridine was cooled to 0 °C in a water–ice bath for 30 min. To this was added dropwise and under vigorous stirring (2.40 ml, 24 mmol) of methacryloyl chloride **3** in 10 ml of anhydrous dichloromethane and left to react overnight under N_2 atmosphere. After filtration, the reaction mixture was diluted with dichloromethane and was washed with water (2 × 30 ml), 5% $NaHCO_3$ (2 × 30 ml), and then dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica) using chloroform as an eluent, followed by further recrystallization from ethanol. Yield 3.9 g, 73%. m.p. 76.8 °C.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.1 (d, J = 7.52 Hz, 2H), 7.46 (m, 4H), 7.24 (m, 2H), 5.93 (s, 1H), 5.49 (s, 1H), 4.63 (t, 2H, N–CH_2), 4.53 (t, 2H, O–CH_2), 1.80 (s, 3H, CH_3). MS: m/z = 279.

2.4. Synthesis of spirooxazine–methyacryloyl monomer **5**

9′-Hydroxy-1,3,3-trimethylspiro[indoline2,3′-[3H]naphtha[2,1-b] [1,4] oxazine] **2** (2.5 g, 7.62 mmol) was added to 50 ml of anhydrous dichloromethane in a 100 ml round bottomed flask. Triethylamine (1.20 g, 11 mmol), was added and the reaction was stirred for half an hour. Then methacryloyl chloride **3** (1.0 g, 8.8 mmol), was dissolved in 10 ml anhydrous dichloromethane and added dropwise to the reaction under N_2 atmosphere, cooled to 0 °C. The reaction was stirred at 0 °C for a further hour, and then at room temperature for 24 h. The product was washed with 100 ml 0.5 M NaOH, 100 ml water, 100 ml 0.5 M HCl, 100 ml water, 100 ml brine and dried with $MgSO_4$. The final solution was rotary evaporated to produce crude compound. This crude product was then recrystallized using methanol. Yield 2.54 g, 85%. m.p. 143 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.26 (s, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.70 (s, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.16 (m, 1H), 7.08 (d, J = 7.52 Hz 1H), 7.00 (d, 1H), 6.90 (m, 1H), 6.58 (d, 1H), 6.41 (s, 1H), 5.79 (s, 2H), 2.76 (s, 3H), 2.10 (s, 3H), 1.56 (s, 3H, CH_3), 1.34 (s, 3H, CH_3). FAB–MS, m/z = 412.

2.5. Synthesis of carbazole–spironaphthoxazine copolymer (PMMA-Cz-SPO)

The 2-(9H-carbazol-9-yl) ethyl methacrylate monomer **4** (55.8 mg, 2 mmol), spirooxazine–methyacryloyl monomer **5** (82.4 mg, 2 mmol), and AIBN (16.4 mg, 1 mmol) were dissolved in anhydrous THF (20 ml). After this mixture was shaken for 5 min at ambient temperature, and the reaction mixture was degassed by subjecting it to freeze–thaw cycle three times. After being heated for six days at 65 °C, the resultant mixture was poured into ether and precipitated with ether four times. The resulting copolymer was dried in vacuum to give satisfactory yields as blue powder. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.28(br), 7.90 (br), 6.85–7.30 (br), 6.4 (br), 4.3 (br), 3.64 (m), 2.51 (br), 1.6–1.22 (m). GPC: Mn: 5437, Mw: 8161, MP: 5841, Mw/Mn: 1.50.

3. Results and discussion

3.1. Synthesis

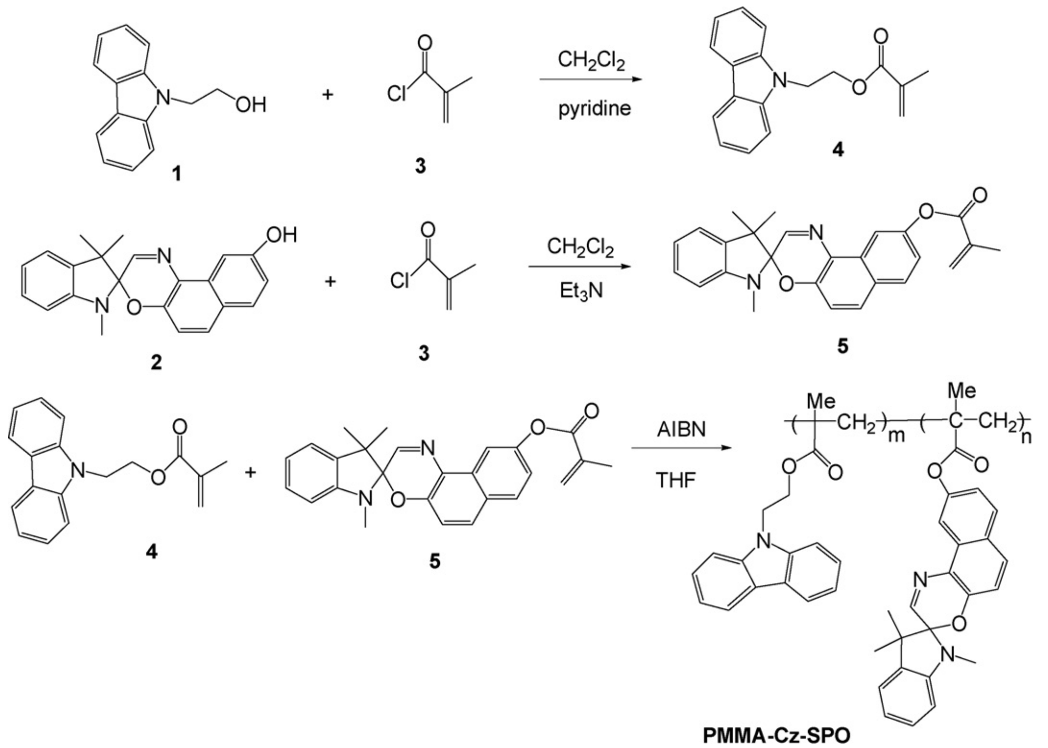
The basic strategy employed for the synthesis of photochromic PMMA-Cz-SPO copolymer was based on the radical polymerization reaction as shown in Scheme 2. In this copolymer, the pendant Cz group in the ethyl acrylate spacer units serves as the electron-donor and hole-transporting moiety [21], the SPO derivative serves as the electron-acceptor and electron-transporting moiety [22]. The key intermediate monomers 2-(9H-carbazol-9-yl) ethyl methacrylate **4** and spirooxazine–methyacryloyl monomer **5** were prepared by 2-(9H-carbazol-9-yl) ethanol **1** and 1,3,3-trimethyl-6′-hydroxyspiro-[2H]-indol-2,30-[3H]-naphtha[2,1-b] [1,4] oxazine **2** reacting with methacryloyl chloride **3**, respectively. Finally compound **4** and compound **5** were copolymerized in the presence of AIBN as radical initiator in THF solutions. The PMMA-Cz-SPO copolymer was dissolved in THF and precipitated with ether four times. The resulting copolymer was dried in vacuum to give satisfactory yields as blue powder. The chemical structures of the intermediate **4** and **5** are characterized by ^{1}H NMR, MS; the polydispersity index of PMMA-Cz-SPO copolymers was determined by gel permeation chromatography (GPC) against the polystyrene standards and the data of GPC analysis and ^{1}H NMR.

3.2. UV–vis absorption spectral changes of spirooxazine–methyacryloyl monomer 5

The photochromic reaction is caused by the reversible spiro-heterolytic cleavage of the C_{sp3}–O bond under UV irradiation, yielding the colored form that can return to the colorless form by ring closure under visible light irradiation or in the dark. UV–vis absorption spectral changes of spirooxazine–methyacryloyl monomer **5** in THF solution (2.0×10^{-4} mol L^{-1}) upon irradiation with UV light are depicted in Fig. 1. The original spectral pattern is reversibly recovered within 7 s. The new band is ascribable to the generation of the open merocyanine form from the closed spiro form. Spectra measured after UV irradiating are at any time proportional to each other in the visible region, indicating that only one species is formed. This allowed the absorption to be monitored at λ_{max} (600 nm) as a function of time to obtain thermal color fading rate (k). The kinetic equation approach to the open merocyanine to closed spiro form via first-order reaction [Eq. (1)]:

$$\ln\left(\frac{\mathrm{At} - A\infty}{\mathrm{Ai}}\right) = kt \qquad (1)$$

In the present case, where Ai is the absorbance at 600 nm, and At is the absorbance at 600 nm at any time t after UV irradiation. A_∞ and k refer to absorbance at 605 nm after 1 h and first-order color



Scheme 2. Synthetic routes of PMMA-Cz-SPO copolymer.

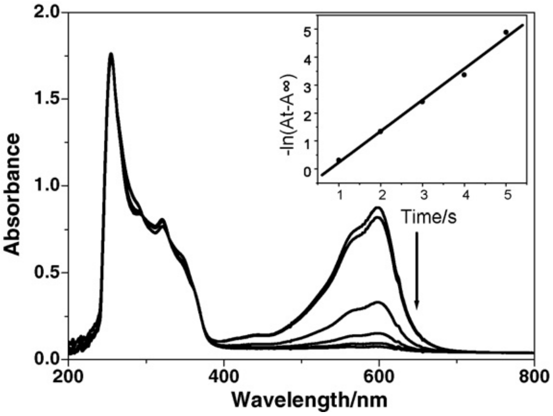


Fig. 1. UV–vis absorption spectral changes of spirooxazine–methyacryloyl monomer **5** in THF solution ($2.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) upon irradiation with UV light. The inset figure shows the first-order decolouration kinetic plot of photoisomerization reaction of spirooxazine–methyacryloyl monomer **5** in THF solution ($2.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$).

changing rate constant, respectively. In the thermal color changing process, the kinetic analysis predicts the logarithm of the difference between A_∞ and At at time t to be linear with time, the slope giving the discoloration rate constant, k. First-order plots according to Eq. (1) for spiroxazine monomer 5 is shown in Fig. 1 inset. The color changing rate constant $\mathrm{k} = 11.2 \times 10^{-2}\,\mathrm{s^{-1}}$ was obtained from the slope.

3.3. Photochromism of carbazole–spironaphthoxazine copolymer (PMMA-Cz-SPO)

The discolored absorption spectra of PMMA-Cz-SPO copolymer in THF solution are shown in Fig. 2. Upon irradiation at UV light, the PMMA-Cz-SPO copolymer exhibited excellent photochromism, with a growth in intensity of the band at about 600 nm, corresponding to the generation of the open form. The open form generated was thermally unstable and readily underwent thermal bleaching, to the closed form. The rate of discoloration of this copolymer in solution obeyed first-order kinetics and agreed well with that of spirooxazine–methyacryloyl monomer **5**. The slope giving the discoloration rate constant, k. First-order plots according to Eq. (1) for PMMA-Cz-SPO is shown in Fig. 2 inset. The color changing rate constant $\mathrm{k} = 5.26 \times 10^{-2}\,\mathrm{s^{-1}}$ was obtained from the slope.

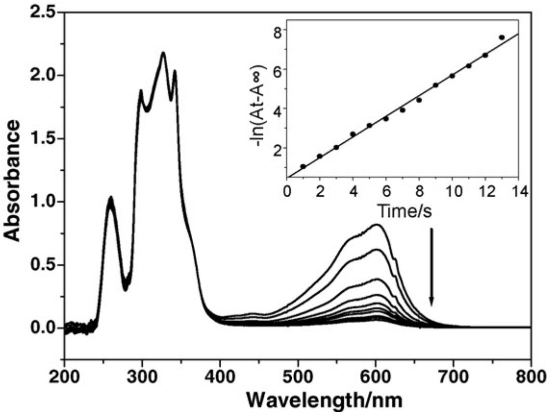


Fig. 2. UV–vis absorption spectral changes of PMMA-Cz-SPO copolymer in THF solution ($2.5 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) upon irradiation with UV light. The inset figure shows the first-order decolouration kinetic plot of photoisomerization reaction of PMMA-Cz-SPIO copolymer in THF solution ($2.5 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$).

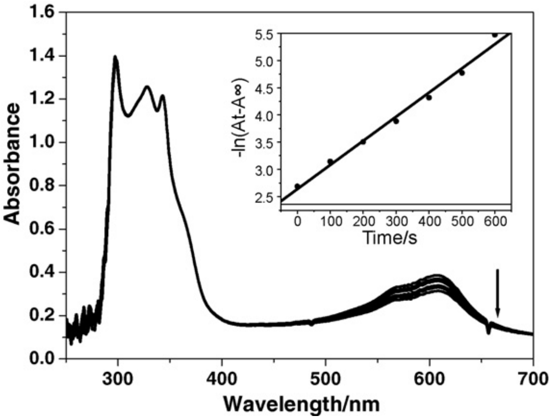


Fig. 3. UV–vis absorption spectral change of PMMA-Cz-SPO copolymer in film upon irradiation with visible light. The inset figure shows the first-order decolouration kinetic plot of photoisomerization reaction of PMMA-Cz-SPO copolymer in film.

The PMMA-Cz-SPO copolymer was soluble in toluene and can be cast into transparent, uniform thin films from solutions by spin-coating onto the glass substrate. The discoloured absorption spectra of film are shown in Fig. 3. The absorbance of PMMA-Cz-SPO copolymer film at its $\lambda_{\max}$ was recorded immediately after 50 s irradiation with UV light. The absorption band appeared with a $\lambda_{\max}$ at 605 nm, which demonstrated that it exhibited excellent photochromic properties. The decoloration process of PMMA-Cz-SPO in film was similar to the discoloration in solution. First-order plots according to Eq. (1) for the copolymer is shown in inserted figure of Fig. 3. The color changing rate constant $\mathrm{k} = 4.0 \times 10^{-3}\,\mathrm{s^{-1}}$ was obtained from the slope. The thermal discoloration of this copolymers film was markedly slower than that of in solution, indicating that steric effects play an essential role in film [14,15].

3.4. Fluorescent switching of carbazole–spironaphthoxazine copolymer

The carbazole is an interesting fluorescent chromophore for incorporation on to polymer owing to its higher thermal stability, solubility, extended glassy state, and moderately high oxidation potential [23,24]. In addition, it is well-known that the carbazole containing oligomers and conjugated polymers are good hole-transport materials [25,26]. Fig. 4 shows the fluorescence spectra change of PMMA-Cz-SPO in film with excitation wavelength at 342 nm. The fluorescence intensity change was regulated by the photochromic reaction. Before irradiation with UV light, it showed a broad emission in the range of 400–550 nm with λ_{em} round 450 nm. Upon irradiation with UV light, the fluorescent intensity of PMMA-Cz-SPO gradually decreased and almost wholly quenched, The possible explanation for the fluorescence

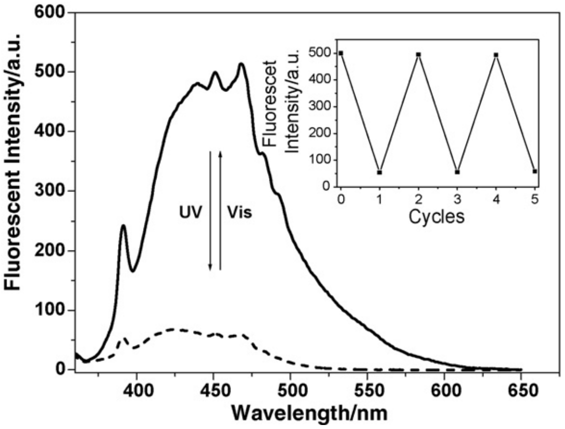


Fig. 4. Fluorescence emission spectra changes of PMMA-Cz-SPO copolymer in film upon irradiation with UV light (excited at 342 nm) at room temperature. The inset figure shows fluorescence monitoring of cycles on and off (by alternate irradiation with UV and visible light) photoconversion of PMMA-Cz-SPO copolymer in film.

quench are due to an increase in PET between the carbazole units and the spirooxazine isomers in PMMA-Cz-SPO film [27]. After irradiation with visible light, the original emission spectra are regenerated. Irradiation of photo-stationary of PMMA-Cz-SPO film with visible light led to a complete recovery of the initial fluorescence signal. From what can be seen Fig. 4 inset, the fluorescence intensity reversibly changed at 450 nm (excitation: 342 nm) by alternate irradiation with UV and visible light and this cycle could be repeated more than 10 times, which is an excellent photochromic fluorescence switch.

3.5. *Photocontrolled viscosity switching of carbazole–spironaphthoxazine copolymer*

A viscosity change by photoirradiation of spiropyran system was observed for the first time for poly (methylmethacrylate) with spiropyran pendant groups by Irie et al. [28]. A change in dipole moment due to isomerization from photochromic spirooxazine to the merocyanine form would be expected to alter intramolecular interaction of polymer chain when the spirooxazines are incorporated into the polymer pendant groups or backbone groups. Fig. 5 shows the viscosity changes of carbazole–spironaphthoxazine copolymer in THF before and after UV irradiation. The viscosity during UV irradiation returns to the initial value in less than 5 min at −5 °C after the light is removed. In THF the relative viscosity after UV irradiation is 15% higher than the viscosity before UV irradiation. The recovery cycles of the viscosity can be repeated many times without any noticeable fatigue. The viscosity changes are due to intramolecular dipole-induced dipole interaction in between merocyanines and carbazole groups.

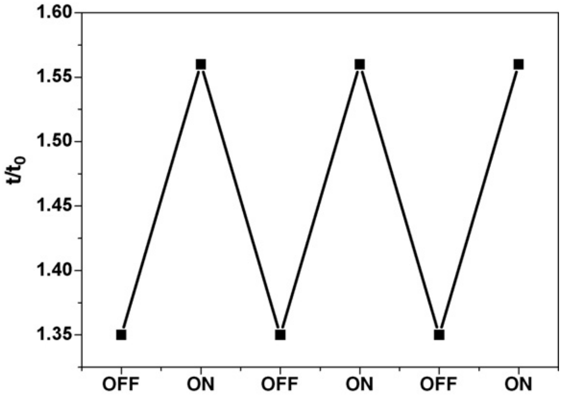


Fig. 5. Changes of the viscosity of PMMA-Cz-SPO copolymer in a THF solution upon irradiation with UV light at −5 °C concentration of polymer is 2% *w/v*.

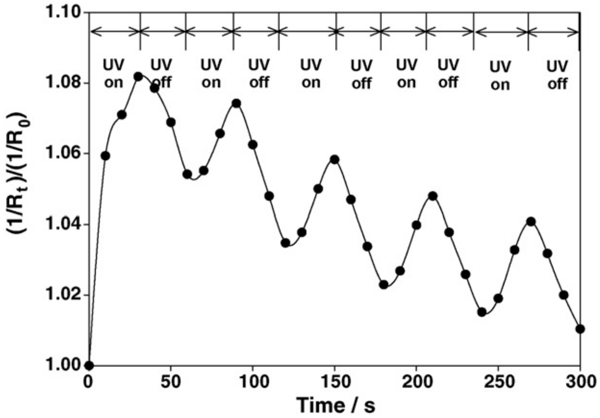


Fig. 6. Photoinduced conductivity changes of PMMA-Cz-SPO copolymer at room temperature.

3.6. *Photocontrolled conductivity switching of carbazole–spironaphthoxazine copolymer*

The carbazole compounds are excellent electron-donor and hole-transporting materials. The photoinduced conductivity response was described in Fig. 6, which shows a cycling experiment in which the maximum absorption of PMMA-Cz-SPO solution is monitored upon alternate irradiation with UV and visible light. The photoinduced conductivity response was analyzed at room temperature. The photoinduced conductivity can be estimated from the expression $(1/R_t)/(1/R_0)$ where R_0 and R_t are the resistance before and after UV irradiation. The conductivity increased upon UV irradiation, which brought about the generation of zwitterions form interaction with carbazoles, and subsequently decreased in dark or irradiation with visible light, which in turn brought about the generation of closed spiro form. Sufficient reversibility was found in this copolymer and this response was completely synchronized with that in the absorbance changes.

4. Conclusions

A usefulness of fluorescent photochromic copolymer containing carbazole and spironaphthoxazine moiety has been synthesized and it showed an attracting photoregulation luminescence properties. The luminescence of carbazole chromophore is effectively regulated by toggling between the two isomers of the spirooxazine subunit in solid film, attributed to the change in PET between the carbazole and each form of the spirooxazine photochrome. Interestingly, the photocontrolled viscosity and conductivity changes were also observed by alternatively irradiation with UV and visible light, this photoregulated multiswitching behaviors could be potentially applied in all-photon mode molecular devices.

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