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The synthesis and spectroscopic properties of novel, photochromic indolinobenzospiropyran-based homopolymers prepared via ring-opening metathesis polymerization

Sam-Rok Keum*, Su-Mi Ahn, Se-Jung Roh, So-Young Ma

Department of Advanced Material Chemistry, Korea University, Jochiwon 339-700, South Korea

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ABSTRACT

Three types of novel photochromic indolinobenzospiropyran-based homopolymers were prepared via the ring-opening metathesis polymerization of the strained bicyclic indolinobenzospiropyran derivative. The homopolymers were soluble in common organic solvents and displayed unusually high polydispersity as determined by gel permeation chromatographic analysis. UV–visible absorption spectroscopy analysis in solution revealed that the appealing photochromic behaviour exhibited by the respective monomers was retained.

1. Introduction

Photo- and thermochromic spiropyrans (SP) have recently received considerable attention owing to their potential application in many new technologies, such as data recording and storage, optical switching, displays and nonlinear optics [1,2]. Despite the potential applications of photochromic SP's, earlier studies mainly focused on evaluating the utility of monomeric SP systems in solution [3,4]. The photo- and thermochromic behaviour of monomeric spiropyrans is based on an equilibrium between the colorless "closed" spiropyran form and the colored "open" merocyanine (MC) form. Their photo- and thermochromic behaviour is normally based on UV irradiation promoting the opening of the spiro ring form to produce the colored MC species and photo and/or thermal relaxation regenerating the SP as in Fig. 1.

In the context of the practical applications, such as films, sheets, fibres, etc., polymeric rather than photochromic materials are preferred. Although various photochromic polymers that comprise spiropyran or other photochromic derivatives have been reported, such polymeric photochromic systems comprise polymer matrices that are either doped or side-chain-modified with photochromes to display photochromic behaviour [5–8]. Therefore, the concentration of photochromic component is low in the polymer and so the photochromic processes are weak. The use of homopolymers increases the concentration of the photochromic component in the polymer, which is desirable for many photochromic processes.

Ring-opening metathesis polymerization (ROMP) is a well-known polymerization method in which strained cyclic olefins (e.g. norbornene, 7-oxonorbornene) are polymerized in the presence of a metathesis catalyst [9]. In this work, the second generation catalyst, benzylidene [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(tricyclohexylphosphine)ruthenium, was used as the Grubbs' catalyst [10,11]. As one phosphine ligand is replaced by N-heterocyclic carbene (NHC) and ruthenium is coordinated to the two carbene groups, the second generation catalyst becomes highly active and oxygen/water sensitive. Therefore this catalyst needs to be handled under a nitrogen or argon, with a big caution (see MSDAS data provided by Aldrich). The ROMP technique has become very popular owing to the mild reaction conditions employed and their compatibility with a wide range of functional groups [12]. Additionally, as the polymer chain length can readily

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* Corresponding author. Tel.: +82 41 860 1332; fax: +82 41 865 5396.
E-mail address: keum@korea.ac.kr (S.-R. Keum).

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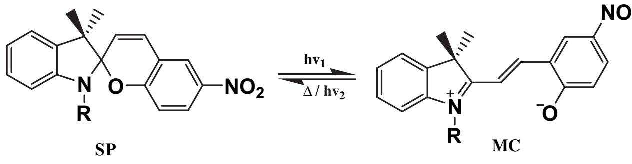

Fig. 1. Photo- and thermochromic behaviour of monomeric spiropyrans.

be adjusted to vary the catalyst:substrate stoichiometry, this makes the ROMP method an attractive choice to complement the photochromic versatility of the spiropyran photochrome.

In this paper, the novel photochromic spiropyran homopolymers, **P1**–**P3**, were prepared via the ROMP of the strained bicyclic olefinated indolinobenzospiropyrans derivatives (Fig. 2).

2. Experimental

All reagents used were purchased from Aldrich. 1,3-bis-(2,4,6-trimethylphenyl-2-imidazolidin ylidene)dichloro(phenylmethylene)–(hexylphosphine)ruthenium was purchased from Aldrich and was stored and weighed under a nitrogen atmosphere. Dichloroethane used for the ROMP reaction was degassed using the Freeze–Pump–Thaw method [12] THF distilled over sodium chloride was distilled over calcium hydride before use. All other solvents were used as received. Column chromatography was performed using the silica gel 60 (230–400 mesh) from Merck.

Melting points were determined using a Fischer–Jones melting point apparatus and were uncorrected. The ^{1}H nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AMX-300 spectrometer in DMSO-d_6. The IR spectra were taken with an Analet Instrument FT-IR (MAP-60) spectrometer using KBr pellets. The UV–vis absorption spectra were recorded using a Varian Cary 1E UV–Vis spectrophotometer. Photoirradiation was accomplished using a mercury lamp (Ushio, 1×10^{-3} m^2 kg s^{-3}) as the excitation light source. The GPC analyses (calibrated by polystyrene) were performed on the THF solutions of the polymers using a Waters 515 HPLC pump and a 2410 refractive index or a 486 tunable absorbance detector at a flow rate of 1.0 mL/min through a 7.8 × 300 mm column at 30 °C.

2.1. Synthesis of exo-N-(p-hydroxyphenyl)-3,6-epoxy-4-cyclohexene-1,2-dicarboximide **2**

A mixture of 7-oxa-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride **1** (caution: avoid contact with water/moisture and oxidants; 2.0 g, 12 mmol) and *p*-aminophenol (1.31 g, 12 mmol) were heated at reflux for 10 min in glacial acetic acid (3 mL), according to the known method [12]. The reaction mixture was cooled to room temperature and the precipitate filtered, washed with water and dried *in vacuo* to obtain compound **2** as a white solid with a yield of 68% (2.10 g, 8.16 mmol). Mp = 171.9 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.02 (s, 2H), δ 5.21(s, 2H), δ 6.58 (s, 2H), δ 6.83 (d, *J* = 8.75 Hz, 2H), δ 6.95 (d, *J* = 8.75 Hz, 2H), δ 9.71 (s, OH, 1H); ^{13}C NMR (75.49 MHz, DMSO-d_6) δ 175.9 (C), 157.3 (C), 136.5 (CH), 127.9 (C), 123.2 (CH), 115.4 (C), 80.7 (CH), 47.2 (CH); IR (acetone, cm^{-1}): 3328 (m, ν_{OH}), 3101 (w, $\nu_{=C-H}$), 2924 (w, ν_{amine}), 1772 (m, ν_{imide}), 1693 (s, ν_{CO}), 1610 (m, $\nu_{aromatic}$), 1448 (m, $\nu_{aromatic}$); MS (EI): (*m*/*z*) 257 [M]$^+$, 189 [M–C_4H_4O]$^+$.

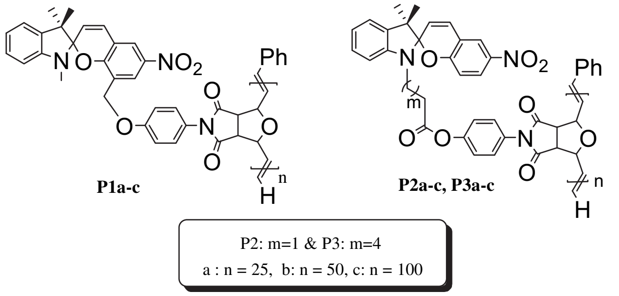

Fig. 2. General structure of the polymer prepared via ROMP of the strained bicyclic olefinated indolinobenzospiropyran derivatives. a–c denote the polymers prepared with three different catalyst-to-substrate stoichiometries (*n* = 25, 50 & 100, respectively).

2.2. Synthesis of 3-chloromethyl-5-nitrosalicylaldehyde **4**

5-Nitrosalicylaldehyde(2.00 g, 12.0 mmol) was dissolved in dry chloromethyl methyl ether (20 mL), to which sublimed aluminum trichloride (caution: reacts violently with water; prolonged storage may lead to pressure build-up; incompatible with alcohols and many other materials; 8.01 g, 60.0 mmol) was added under a nitrogen atmosphere, according to the reported method [13]. The reaction mixture was stirred for an hour at room temperature and then refluxed for 2.5 h after which time, ice-cooled water was added and the resulting off-white residue was recrystallized from hot hexane solution (500 mL), yielding colorless needles of compound **4** with a 66% yield (1.86 g, 8.63 mmol). Mp = 95 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.7 (s, CH_2Cl, 2H), δ 8.5 (s, aromatic, 2H), δ 10.0 (s, CHO, 1H), δ 12.1 (s, OH, 1H); IR (acetone, cm^{-1}): 3080 (w, ν_{OH}), 2871 (w, ν_{C-H}), 1663 (s, ν_{CHO}), 1625 (m, $\nu_{aromatic}$), 1532 (m, ν_{asNO}), 1440 (m, $\nu_{aromatic}$), 1346 (s, ν_{sNO}).

2.3. Synthesis of 1-(2-carboxyethyl)-2,3,3-trimetyl-3H-indolium bromide 6 and 1-(2-carboxypentyl)-2,3,3-trimetyl-3H-indolium bromide **7**

A mixture of 2,3,3-trimethyl-3*H*-indole (3 g, 18.84 mmol) **5** and 3-bromo-propionic acid (3.6 g, 23.53 mmol) or 6-bromohexanoic acid (4.6 g, 23.58 mmol) was heated to 80 °C for 12 h, according to the known method [14]. During this time, the highly viscous product came out of the solution; upon cooling, the reaction mixture was extracted with 200 mL of Et_2O three times to remove unreacted starting material. The remaining crystalline solid was dissolved in 10 mL of water and extracted three times each with 50 mL of Et_2O and 25 mL of CH_2Cl_2. The aqueous layer was separated and concentrated under vacuum (1.0 mmHg, 24 h) until it was dry. The resulting solid was crystallized from CH_2Cl_2 (20 mL) to compound **6** or **7** in the form of a pale pink solid.

6: Yield 66%; Mp = 81.3 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.53 (s, 6H), δ 2.71 (t, *J* = 7.2 Hz, 2H), δ 2.87 (s, 3H), δ 4.66 (t, *J* = 7.6 Hz, 2H), δ 7.59–7.62 (m, 2H), δ 7.83 (d, *J* = 9.3 Hz, 1H), δ 7.99 (d, *J* = 9.3 Hz, 1H); ^{13}C NMR (75.49 MHz, DMSO-d_6): δ 196.5 (C), 177.3 (C), 148.0 (C), 141.7 (C), 128.5 (CH), 126.2 (CH), 126.0 (CH), 125.7 (CH), 47.1 (CH2), 31.6 (CH2), 22.0 (CH3), 14.0 (CH3); IR (acetone, cm^{-1}): 3398 (w, ν_{OH}), 2972 (m, ν_{C-H}), 1724 (s, ν_{COOH}); Anal. Calcd. for $C_{14}H_{18}NO_2$; C, 72.39; H, 7.81; N, 6.03; O, 13.77, Found; C, 72.18; H, 7.79; N, 6.21; O, 13.82.

7: Yield 48%; Mp = 81.3 °C; δ 1.6 (s, 6H), δ 1.51–1,85 (m, 6H), δ 2.24 (t, *J* = 7.2 Hz, 2H), δ 2.87 (s, 3H), δ 4.45 (t, *J* = 7.6 Hz, 2H), δ 7.26–7.64 (m, 2H), δ7.78 (d, *J* = 9.3 Hz, 1H), δ 7.87 (d, *J* = 9.3 Hz, 1H); ^{13}C NMR (75.49 MHz, DMSO-d_6): δ 196.5 (C), 174.2 (C), 141.8 (C), 141.0 (C), 129.3 (CH), 128.9 (CH), 123.5 (CH), 115.4 (CH), 54.1 (C), 47.4 (CH2), 33.3 (CH2), 26.9 (CH2), 25.4 (CH2), 24.0 (CH2), 22.0 (CH3), 14.0 (CH3); IR (acetone, cm^{-1}): 3398 (w, ν_{OH}), 2972 (m, ν_{C-H}), 1724 (s, ν_{COOH}); Anal. Calcd. for $C_{17}H_{24}NO_2$; C, 74.42; H, 8.82; N, 5.10; O, 11.66, Found; C, 74.52; H, 8.90; N, 5.24; O, 11.34.

2.4. *Synthesis of 1,3,3-trimethyl-6-nitrospiro-[(2H)-1-benzopyran-2,2-indoline] derivatives* ***SP1–SP3***

The indolinobenzospiropyran derivatives **SP1–SP3** were prepared by the reaction of 1,3,3-trimethyl-2-methyleneindoline (FB) in acetone and an acetone solution of 3-chloromethyl-5-nitrosalicylaldehyde, using a 1:1 mol ratio, employing a method adapted from the known method [4].

A representative example of this method is the following: 1,3,3-Trimethyl-2-methyleneindoline (400 mg, 2.31 mmol) in acetone (20 mL) was added to the acetone solution (60 mL) of 3-chloromethyl-5-nitrosalicylaldehyde (500 mg, 2.32 mmol). The reaction mixture was heated at 40 °C for 12 h in the dark. After evaporation of the solvent, the resulting red wax was purified using silicagel column chromatography in the dark with a mixture of ethylacetate/hexane (1/60). The resulting yellow solid was recrystallized from a mixture of CH_2Cl_2/hexane (1/10) to form pure products.

SP1: yellow cubes; 38% yield; Mp = 137.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (s, 3H), δ 1.32 (s, 3H), δ 2.75 (s, 3H), δ 4.35 (d, *J* = 7.5 Hz, 2H), δ 5.88 (d, *J* = 10.2 Hz, 1H), δ 6.56 (d, *J* = 7.8 Hz, 1H), δ 6.78 (d, *J* = 10.2 Hz, 1H), δ 6.89 (t, *J* = 7.5 Hz, 1H), δ 6.96 (d, *J* = 7.8 Hz, 1H), δ 7.19 (t, *J* = 7.8 Hz, 1H), δ 8.00 (s, 1H), δ 8.14 (s, 1H); ^{13}C NMR (75.49 MHz, DMSO-d_6): δ 160.1 (C), 147.8 (C), 140.2 (C), 136.2 (C), 127.9, (CH), 127.0 (CH), 126.8 (CH), 126.0 (CH), 124.3 (C), 122.8 (CH), 121.8 (CH), 119.9 (CH), 118.8 (C), 115.2 (CH), 52.4 (C), 40.8 (CH_2), 29.0 (CH3), 26.0 (CH3), 20.1 (CH3); IR (acetone, cm^{-1}): 3052 (w, $\nu_{=\mathrm{C-H}}$), 2970 (w, $\nu_{\mathrm{C-H}}$), 2869 (w, ν_{amine}), 1609 (m, ν_{aromatic}), 1520 (m, $\nu_{as\mathrm{NO}}$), 1448 (m, ν_{aromatic}), 1335 (s, ν_{sNO}); *m/z* (ESI): 335.1 (100% $[M-Cl]^+$); Anal. Calcd. for $C_{20}H_{19}ClN_2O_3$; C, 64.78; H, 5.16; Cl, 9.56; N, 7.55; O, 12.94, Found; C, 64.34; H, 5.37; Cl, 10.21; N, 7.76; O, 12.32.

SP2: green solid; yield 56%; Mp = 211.4 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.18 (s, 3H), δ 1.32 (s, 3H), δ 2.40–2.63 (m, N–1–CH_2, 2H), δ 3.31–3.54 (m, 2H), δ 6.00 (d, *J* = 10.2 Hz, 1H), δ 6.66 (d, *J* = 7.8 Hz, 1H), δ 6.78 (d, *J* = 10.2 Hz, 1H), δ 6.80 (t, *J* = 7.5 Hz, 1H), δ 6.96 (d, *J* = 7.8 Hz, 1H), δ 7.11 (d, *J* = 7.5 Hz, 1H), δ 7.19 (d, *J* = 7.8 Hz, 1H), δ 8.04 (d, *J* = 7.8 Hz, 1H), δ 8.21 (s, 1H); ^{13}C NMR (75.49 MHz, DMSO-d_6): δ 159.9 (C), 147.8 (C), 140.9 (C), 136.2 (C), 127.9, (CH), 127.0 (CH), 126.0 (CH), 122.8 (CH), 121.8 (CH), 121.7 (CH), 119.9 (CH), 118.8 (CH), 115.6 (CH), 115.2 (CH), 106.5 (CH), 52.4 (C), 38.0 (CH_2), 36.4 (CH_2), 26.0 (CH3), 20.1 (CH3),; IR (acetone, cm^{-1}): 2969 (w, $\nu_{\mathrm{C-H}}$), 2869 (w, ν_{amine}), 1707 (s, ν_{COOH}), 1606 (w, ν_{aromatic}), 1508 (m, $\nu_{as\mathrm{NO}}$), 1440(m, ν_{aromatic}), 1328 (s, ν_{sNO}); Anal. Calcd. for $C_{21}H_{20}N_2O_5$; C, 66.31; H, 5.30; N, 7.36; O, 21.03, Found; C, 66.50; H, 5.19; N, 7.41; O, 20.90.

SP3: pink solid; yield 49.74% (1.9 g, 4.5 mmol). Mp = 211.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07 (s, 3H), δ 1.18 (s, 3H), δ 1.52–1.65 (m, 6H), δ 2.40–2.63 (m, N1–CH_2, 2H), δ 3.31–3.54 (m, 2H), δ 6.00 (d, *J* = 10.2 Hz, 1H), δ 6.66 (d, *J* = 7.8 Hz, 1H), δ 6.80 (t, *J* = 7.8 Hz, 1H), δ 6.86 (d, *J* = 10.2 Hz, 1H), δ 6.96 (d, *J* = 7.8 Hz, 1H), δ 7.11 (d, *J* = 7.5 Hz, 1H), δ 7.19 (t, *J* = 7.8 Hz, 1H), δ 8.04 (d, *J* = 7.8 Hz, 1H), δ 8.21 (s, 1H); ^{13}C NMR (75.49 MHz, DMSO-d_6): δ 159.8 (C), 147.8 (C), 140.9 (C), 136.2 (C), 127.9, (CH), 127.0 (CH), 126.0 (CH), 122.8 (CH), 121.8 (CH), 121.7 (CH), 119.9 (CH), 118.8 (CH), 115.6 (CH), 115.2 (CH), 106.5 (CH), 52.4 (C), 43.7 (CH_2), 36.1 (CH_2), 28.4 (CH_2), 26.8 (CH_2), 26.0 (CH3), 24.5 (CH_2), 20.1 (CH3); IR (acetone, cm^{-1}): 2969 (w, $\nu_{\mathrm{C-H}}$), 2869 (w, ν_{amine}), 1707 (s, ν_{COOH}), 1606 (w, ν_{aromatic}), 1508 (m, $\nu_{as\mathrm{NO}}$), 14,401(m, ν_{aromatic}), 1328 (s, ν_{sNO}); Anal. Calcd. for $C_{24}H_{26}N_2O_5$; C, 68.23; H, 6.20; N, 6.63; O, 18.94, Found; C, 68.31; H, 6.32; N, 6.56; O, 18.81.

2.5. *Synthesis of the strained bicyclic olefinated SP-monomer* ***SPM1***

A mixture of *exo*-N-(*p*-hydroxyphenyl)-3,6-epoxy-4-cyclohexene-1,2-dicarboximide (347 mg, 1.35 mmol) **2** and potassium carbonate (93 mg, 0.673 mmol) were heated under reflux for 1 h in acetonitrile (80 mL), and then 8-chloromethyl-1,3,3-trimethyl-6-nitrospiro-[(2*H*)-1-benzopyran-2,2-indoline] **SP1** (500 mg, 1.35 mmol) was added. The reaction mixture was heated at 70 °C for 24 h in the dark. After evaporation of the solvent, the resulting red wax was purified using silicagel column chromatography in the dark with a mixture of ethylacetate/hexane (2/1). The product was recrystallized from a mixture of dichloromethane/hexane (1/10) to form the violet colored material **SPM1** with a yield of 17% (140 mg, 0.236 mmol). Mp = 147.4 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.21 (s, 3H), δ 1.30 (s, 3H), δ 2.71 (s, N–Me, 3H), δ 2.72 (s, 2H), δ 4.81 (s, 2H), δ 5.38 (s, 2H), δ 5.91 (d, *J* = 10.2 Hz, 1H), δ 6.58 (s, *J* = 7.8 Hz, 2H), δ 6.66 (s, *J* = 7.8 Hz, 1H), δ 6.80 (d, *J* = 7.5 Hz, 1H), δ 6.86 (t, *J* = 10.2 Hz, 1H), δ 6.96 (d, *J* = 7.8 Hz, 1H), δ 7.05 (d, *J* = 8.75 Hz, 1H), δ 7.10 (d, *J* = 8.75 Hz, 2H), δ 7.16 (t, *J* = 7.8 Hz, 1H), δ 8.00 (s, 1H), δ 8.23 (s, 1H); ^{13}C NMR (75.49 MHz, DMSO-d_6): δ 176.1 (C), 160.1 (C), 156.2 (C), 147.6 (C), 141.0 (C), 137.5 (CH), 136.3 (C), 128.9 (C), 128.1 (C), 127.9, (CH), 126.9 (CH), 126.8 (CH), 125.9 (CH), 123.3 (C), 122.7 (CH), 121.8 (CH), 118.8 (CH), 118.9 (C), 115.4 (CH), 115.1 (CH), 106.6 (C), 80.9 (CH), 60.4 (CH_2), 52.4 (C), 47.3 (CH), 29.2 (CH3), 26.0 (CH3), 20.1 (CH3); IR (acetone, cm^{-1}): 3078 (w, $\nu_{=\mathrm{C-H}}$), 2958 (w, $\nu_{\mathrm{C-H}}$), 2855 (w, ν_{amine}), 1776 (w, ν_{imide}), 1707 (s, ν_{CO}), 1608 (m, ν_{aromatic}), 1511 (s, $\nu_{as\mathrm{NO}}$), 1450 (m, ν_{aromatic}), 1335 (s, ν_{sNO}); Anal. Calcd. for $C_{34}H_{29}N_3O_7$; C, 69.03; H, 4.94; N, 7.10; O, 18.93, Found; C, 68.94; H, 5.04; N, 6.97; O, 19.05.

2.6. *Synthesis of the strained bicyclic olefinated SP-monomers* ***SPM2–SPM3***

The strained bicyclic olefinated SP-monomers **SPM2** and **SPM3** were prepared from the reaction of *exo*-N-(*p*-hydroxyphenyl)-3,6-epoxy-4-cyclohexene-1,2-dicarboximide **2** with **SP2** or **SP3** in the presence of DCC and DMAP in THF, according to the reported method [15].

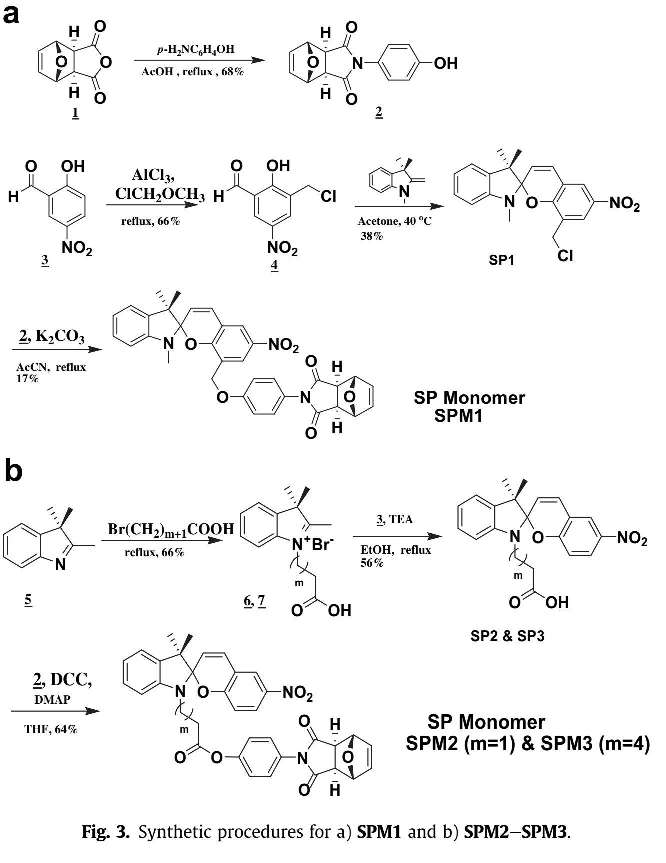

Fig. 3. Synthetic procedures for a) **SPM1** and b) **SPM2–SPM3**.

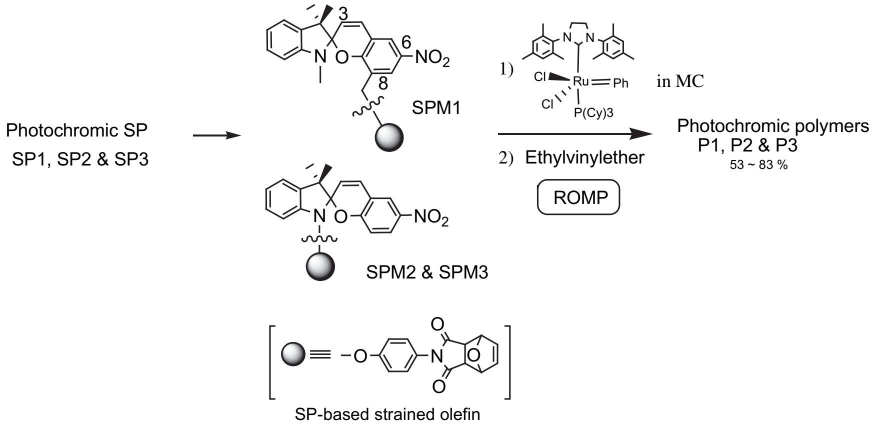

Fig. 4. Synthetic procedures for polymers **P1**–**P3** via the ROMP.

A representative example of this method is the following: **SP2** (0.87 g, 2.29 mmol) and **2** (0.59 g, 2.29 mmol) were placed in a 250-mL round-bottomed flask. After the solution was dissolved in dry THF (30 mL) and cooled to 0 °C, a solution of DCC (0.57 g, 2.76 mmol) and DMAP (0.12 g, 0.98 mmol) in THF (10 mL) was added dropwise over the course of 1 h. The mixture was stirred at 0 °C for an additional 2 h and then gradually warmed to 25 °C over the course of 24 h. During the warming period, a dicyclohexyl urea (DCU) precipitate formed, which was filtered and washed with THF (3 × 50 mL). After the filtrate was evaporated, the resulting red wax was purified using silicagel column chromatography in the dark with a mixture of ethylacetate/dichloromethane/hexane (1/5/1). The solution was recrystallized from a mixture of dichloromethane/hexane (1/10) to form the products.

SPM2: green colored; yield 64%; Mp = 124.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16 (s, 3H), δ 1.27 (s, 3H), δ 2.72 (s, 2H), δ 2.76–3.02 (m, N–CH_2, 2H), δ 3.55–3.81 (m, 2H), δ 5.38 (s, 2H), δ 5.90 (d, J = 10.2 Hz, 1H), δ 6.58 (s, 2H), δ 6.67 (d, J = 7.8 Hz, 1H), δ 6.80 (t, J = 7.8 Hz, 1H), δ 6.86 (d, J = 10.2 Hz, 1H), δ 6.96 (d, J = 7.8 Hz, 1H), δ 7.05 (d, J = 8.75 Hz, 2H), δ 7.10 (d, J = 8.75 Hz, 2H), δ 7.11 (d, J = 7.5 Hz, 1H), δ 7.19 (t, J = 7.8 Hz, 1H), δ 8.04 (d, J = 7.8 Hz, 1H), δ 8.21 (s, 1H); ^{13}C NMR (75.49 MHz, DMSO-d_6): δ 176.2 (C), 175.3 (C), 159.9 (C), 156.2 (C), 148.0 (C), 140.9 (C), 138.5 (CH), 136.3 (C), 128.9, (CH), 127.9 (CH), 127.0 (CH), 126.0 (CH), 123.3 (CH), 122.8 (CH), 121.8 (CH), 121.7 (CH), 119.8 (CH), 118.8 (CH), 115.6 (CH), 115.4 (CH), 115.2 (CH), 106.4 (CH), 80.8 (CH), 52.4 (C), 47.5 (CH), 38.0 (CH_2), 36.4 (CH_2), 26.0 (CH3), 20.1 (CH3); IR (acetone, cm^{-1}): 3071 (w, $\nu_{=C-H}$), 2967 (w, ν_{C-H}), 2869 (w, ν_{amine}), 1757 (m, ν_{imide}), 1711 (s, ν_{CO}), 1610 (w, $\nu_{aromatic}$), 1508 (m, ν_{asNO}), 1481(m, $\nu_{aromatic}$), 1337 (m, ν_{sNO}); Anal. Calcd. for $C_{35}H_{29}N_3O_8$; C, 67.84; H, 4.72; N, 6.78; O, 20.66, Found; 67.68; H, 4.63; N, 6.48; O, 21.21.

SPM3: green colored; yield 44%; Mp = 124.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16 (s, 3H), δ 1.27 (s, 3H), δ 1.52–1.65 (m, 6H), δ 2.76–3.02 (m, N–CH_2, 2H), δ 3.01 (s, 2H), δ 3.55–3.81 (m, 2H), δ 5.38 (s, 2H), δ 5.90 (d, J = 10.2 Hz, 1H), δ 6.58 (s, 2H), δ 6.67 (d, J = 7.8 Hz, 1H), δ 6.80 (t, J = 7.8 Hz, 1H), 6.86 (d, J = 10.2 Hz, 1H), δ 6.96 (d, J = 7.8 Hz, 1H), δ 7.05 (d, J = 8.75 Hz, 2H), δ 7.10 (d, J = 8.75 Hz, 2H), δ 7.11 (d, J = 7.5 Hz, 1H), δ 7.19 (t, J = 7.8 Hz, 1H), δ 8.04 (d, J = 7.8 Hz, 1H), δ 8.21 (s, 1H); ^{13}C NMR (75.49 MHz, DMSO-d_6): δ 175.4 (C), 175.1 (C), 159.9 (C), 156.2 (C), 147.8 (C), 140.8 (C), 138.5 (CH), 136.3 (C), 129.1 (C), 128.1 (CH), 127.0 (CH), 126.1 (CH), 123.0 (CH), 122.9 (CH), 121.8 (CH), 121.7 (CH), 119.9 (CH), 118.9 (CH), 115.6 (CH), 115.3 (CH), 115.2 (CH), 106.5 (CH), 80.7 (CH), 52.3 (C), 47.6 (CH), 43.9 (CH_2), 36.2 (CH_2), 29.2 (CH_2), 26.8 (CH_2), 24.4 (CH_2), 26.0 (CH3), 20.1 (CH3); IR (acetone, cm^{-1}): 3071 (w, $\nu_{=C-H}$), 2967 (w, ν_{C-H}), 2869 (w, ν_{amine}), 1757 (m, ν_{imide}), 1711 (s, ν_{CO}), 1610 (w, $\nu_{aromatic}$), 1508 (m, ν_{asNO}), 1481(m, $\nu_{aromatic}$), 1337 (m, ν_{sNO}); Anal. Calcd. for $C_{38}H_{35}N_3O_8$; C, 68.97; H, 5.33; N, 6.35; O, 19.34, Found; C, 69.05; H, 5.46; N, 6.47; O, 19.02.

Table 1
Polymerization yields and polymer characterization.

Monomer (equivalents)[a]	% yield	M_w	M_n	PDI (M_w/M_n)
P1a (25)	78	10,089	27,261	2.74
P1b (50)	83	14,131	51,890	3.67
P1c (100)	82	30,971	1,21,266	3.92
P2a (25)	74	24,121	68,817	2.85
P2b (50)	76	69,224	1,91,827	2.77
P2c (100)	79	1,52,961	4,28,589	2.80
P3a (25)	53	12,654	21,902	1.73
P3b (50)	57	12,926	28,205	2.18
P3c (100)	64	15,785	32,309	2.04

[a] Relative to the molar equivalents of catalyst used.

2.7. Synthesis of spiropyran-based homopolymer *P1–P3*

In a typical procedure, a solution of the monomer **SPM1–3** in rigorously inert CH_2Cl_2 was poured into a CH_2Cl_2 solution of (1,3-bis-(2,4,6-trimethylphenyl)-2-imimidazolidinylidene)dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium (0.01, 0.02 and 0.04 equivalents for a, b & c, respectively) in a Schlenk tube [10,12]. The final monomer concentrations were all 5 mM. Excess ethyl vinyl ether was added after stirring at room temperature for 14 h and then the solutions were stirred while exposed to the atmosphere for 30 min. The polymers were precipitated by pouring the reaction solutions into cold ether and collecting the precipitates using vacuum filtration.

Table 2
UV–visible spectroscopic data for spiropyrans **SP1–3** and their corresponding monomers **SPM1–SPM3** and polymers **P1–P3**.

Compounds	λ_{max}/nm ($\varepsilon \times 10^{-4}$ L mol^{-1} cm^{-1})		Color of the MC form
	SP form	MC form	
SP1	261 (0.449)	549 (0.307)	Reddish
SPM1	261 (0.155)	545 (0.412)	Reddish
P1c	267 (1.594)	554 (0.468)	Reddish
SP2	266 (0.114)	548 (0.448)	Purple
SPM2	264 (0.127)	551 (0.224)	Purple
P2c	276 (3.796)	572 (0.296)	Purple
SP3	265 (0.229)	543 (0.171)	Purple
SPM3	265 (0.842)	544 (0.656)	Purple
P3c	271 (2.973)	570 (0.488)	Purple

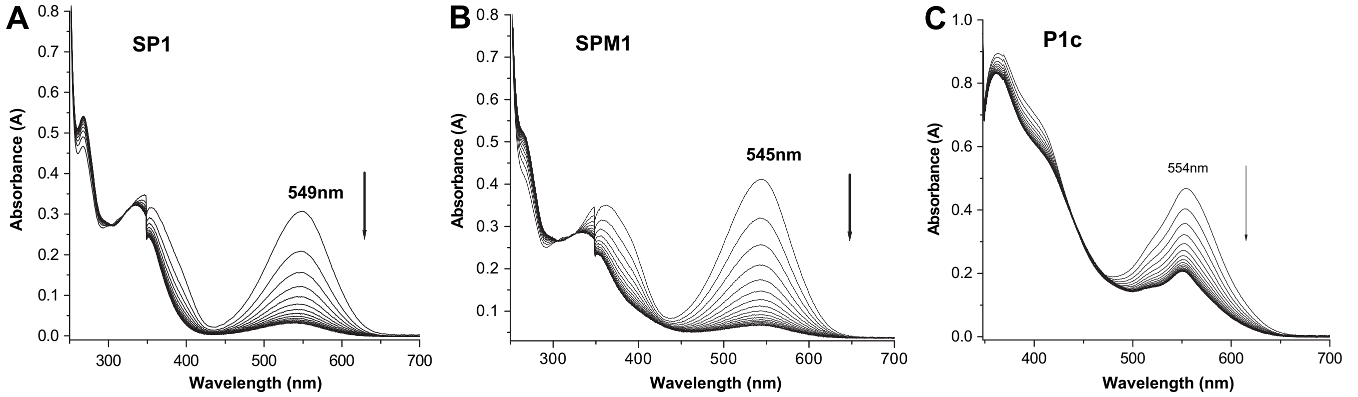

Fig. 5. UV–vis spectroscopic behaviors of **SP1** (A), monomer **SPM1** (B) in EtOH (3.03×10^{-5} M) and polymer **P1c** (C) in DMF (1.07×10^{-5} M) in every 3 min after UV light irradiation.

P1a–c: Yields: 78% for **P1a**, 83% for **P1b**, and 82% for **P1c**, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (br s), δ 7.93 (br s), δ 7.02 (m), δ 6.78 (m), δ 6.47 (br s), δ 6.11 (br s), δ 5.86 (br s), δ 4.74(m), δ 3.42 (br s), δ 2.7 (br s), δ 1.59 (br s), δ 1.25 (br s).

P2a–c: Yields: 74% for **P2a**, 76% for **P2b**, and 79% for **P2c**, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (br s), δ 7.20 (m), δ 7.07 (m), δ 7.03 (m), δ 6.87 (br s), δ 6.64 (br s), δ 6.07 (br s), δ 5.84(br s), δ 3.69 (m), δ 3.58 (m), δ 3.42 (br s), δ 2.79 (m), δ 1.25 (br s), δ 1.12 (br s).

P3a–c: Yields: 53% for **P3a**, 57% for **P3b**, and 64% for **P3c**, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (br s), δ 7.10 (m), δ 7.07 (m), δ 6.84 (br s), δ 6.69 (br s), δ 6.56 (br s), δ 6.10 (br s), δ 5.84(br s), δ 5.18 (m), δ 4.63(m), δ 3.74 (m), δ 3.45 (br s), δ 3.15 (br s), δ 2.49 (m), δ 1.69 (br s), δ 1.59 (br s), δ 1.40 (m), δ 1.25 (br s), δ 1.14 (br s).

3. Results and discussion

The second generation Grubbs' catalyst, benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium, was used in this work. Unlike the first generation catalyst, one phosphine ligand was replaced with *N*-heterocyclic carbene (NHC), and ruthenium was coordinated to the two NHC groups. This catalyst was very highly active and oxygen/water sensitive and therefore, had to be handled under a nitrogen or argon atmosphere.

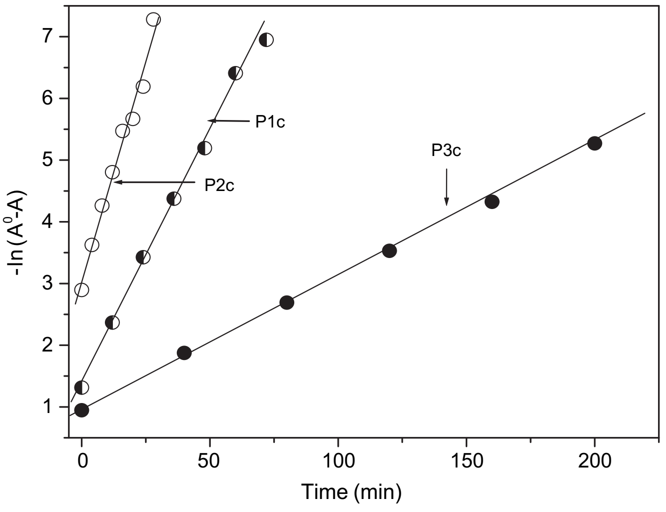

Fig. 6. The first-order kinetic treatment for the thermal isomerization of polymers **P1–P3** by plotting −ln(A° − A) against time, where A and A° denotes the absorbance at time *t* and infinite time.

The polymerization of the three monomers **SPM1–SPM3**, which were obtained from the corresponding precursors **SP1–SP3**, relied on the presence of the strained bicyclic olefins **5** in order to facilitate the ROMP process and generate the polymers **P1–P3**. Polymer **P1** was connected to a strained olefin fragment with an alkyl ether group on the 8-position of the spiropyran moiety, whereas polymers **P2** and **P3** were both connected on the ring nitrogen of the indole group with a carboxylic linkage. Polymers **P2** and **P3** differed only in the length of the N-alkyl chain of the indole group, which led to a difference in the distance between the polymer backbone and the photochromic pendant.

3.1. Synthesis of the strained bicyclic olefinated spiropyrans (monomers)

Fig. 3a and b shows the detailed processes for the synthesis of the strained bicyclic olefinated spiropyrans (monomers) of **SPM1** and **SPM2**, respectively. These monomers were then polymerized using the ROMP technique.

The strained bicyclic olefin, 7-oxanorbornene **2**, was readily prepared with a good yield using a known procedure, [12] through the condensation of 7-oxa-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride **1** with *p*-aminophenol. Chloromethylated spiropyran **SP1** was prepared from the reaction of 1,3,3-trimethyl-2-methyleneindoline (Fischer base) and 3-chloromethyl-5-nitrosalicylaldehyde **4**, which was obtained from the reaction of 5-nitrosalicylaldehyde **3** with chloromethyl methyl ether, according to a known method [13].

The N-carboxy alkylated spiropyran-based monomers **SPM2** ($m = 1$) and **SPM3** ($m = 4$) were then obtained from the reaction of the carboxyethylated indolium compounds **6** & **7**, respectively, with compound **3** in the presence of TEA. The carboxyethylated indolium compounds **6** & **7** were prepared through the reaction of 2,3,3-trimethyl-3*H*-indole **5** with 3-bromo-propionic acid and 6-bromohaxanonic acid, respectively, according to a previously reported method [16].

3.2. Synthesis and characterization of polymers *P1–3*

Monomers **M1–M3** were subjected to the ROMP conditions in Fig. 4.

A CH_2Cl_2 solution of commercially available (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium (Grubbs' 2nd catalyst) is cannulated into a vigorously stirred CH_2Cl_2 solution of the appropriate monomer under anhydrous conditions in a typical polymerization procedure [10,11]. The resulting homogeneous solution was stirred for 14 h at room temperature, and then the polymerization was

Table 3
Ring-formation rates of the open chain merocyanine forms of SP-monomers **SPM1**–**SPM3** and their corresponding polymers **P1**–**P3**.

Compounds	$k_{obs} \times 10^{-2}$ (s^{-1})	$t_{1/2}$ (min)	N	r	Wavelengths followed (nm)	Solvent
SPM1	2.87	24.1	9	0.999	545	EtOH
SPM2	7.41	9.35	8	0.999	551	
SPM3	3.41	20.3	10	0.999	544	
P1c	7.96	8.71	7	0.997	554	DMF
P2c	14.4	4.81	8	0.992	572	
P3c	2.22	31.2	7	0.998	570	

terminated by quenching the reaction mixtures with excess ethyl vinyl ether. The homopolymers were conveniently isolated in their pure forms by precipitating them from the cold ether and then washing them with the same solvent to remove the catalyst and any unreacted monomer.

The chain length of the polymers could be tailored by varying the relative molar ratios between the monomer **SPM1** and the ROMP catalyst used. Three different polymers **P1a**–**c** were prepared from the same monomer **SPM1**.

When 1, 2, and 4 mol% of the Grubbs' catalyst were used in the ROMP reaction, the 100-mer (**P1c**), the 50-mer (**P1b**), and the 25-mer (**P1a**) were isolated, respectively. In Table 1, the gel permeation chromatography (GPC) revealed that the relative ratio of the number-average molecular weights, M_n, for **P1c**:**P1b**:**P1a** was approximately 4:2:1, as expected from the stoichiometries (100:50:25) used in the polymerization process. The prepared polymers **P1** and **P2** showed similar tendencies, while the M_n values of 32,300, 28,200 and 21,900 were relatively constant the **P3** polymers **P3c**, **P3b,** and **P3a**, respectively.

The ^{1}H NMR spectra of all of the polymers **P1**–**3** showed broadened peaks compared to those of the monomers and the absence of the peak for the vinyl proton of the strained olefin. The GPC analysis of the polymers showed extremely high polydispersity indices (PDI, M_w/M_n) in **P1**, **P2** & **P3**, in Table 1.

3.3. UV–Vis absorption spectroscopy

Table 2 summarizes the UV–vis spectroscopic properties of the DMF solution of the novel polymers **P1**–**3** along with those for the EtOH solutions of spiropyrans **SP1**–**3** and the monomeric molecules **SPM1**–**3**, for comparison.

Photoinduced SP = MC isomerization was observed for all of the compounds studied at 335 nm with a short-wavelength UV lamp. All of the polymers showed typical absorbances for the colored-open forms of the spiropyran photochrome at 550–570 nm. Spectral changes were monitored in the UV–visible region after UV light irradiation in Fig. 5.

After previous irradiation of UV light for a standard period, interception produced a gradual decrease in the absorbances corresponding to the open form of the spiropyran photochrome at 543–572 nm. The decrease in these absorbances was accompanied by the increase in the absorbances for the colorless closed form of the photochrome centered at 330–350 nm.

The absorption spectra for spiropyran, monomers and the polymers (**P1 & P3**) in both the open and closed forms were similar, which illustrated that the intimacy of the photochromes covalently linked to the polymer backbone did not affect either the ground-state or the excited-state properties of the photochrome. Whereas **P2** showed comparatively small absorbance, namely the opened MC form of **P2** are less stable in DMF solution than others. This may means that the distance between the polymer backbone and the photochromic pendant are not long enough and hence its movement can be somewhat restrained, which makes it more difficult to be converted into the open form.

The rate of reversion to the colorless spiro ring (MC → SP) was measured after UV irradiation in EtOH and DMF for the monomer **SPM1** and the polymers **P1**–**3**, respectively, by following the disappearance of the absorption band in the 540–570 nm region. The decay rate of the photo-induced colored transients obeyed good first-order kinetics for all substrates examined in this work. The first-order kinetic treatments for the thermal isomerization of polymers **P1**–**P3** are shown in Fig. 6, by plotting $-\ln(A^\circ - A)$ against time, where A and A° denotes the absorbance at time t and infinite time.

The rate constants, k_{obs}, of the ring-formation of opened merocyanine forms are $2.87–7.41 \times 10^{-2}\ s^{-1}$ and $2.22–14.4 \times 10^{-2}\ s^{-1}$, for the monomer **SPM1**–**3** and the polymers **P1**–**3**, respectively. These are summarized in Table 3.

4. Conclusion

Novel photochromic indolinobenzospiropyran-based homopolymers were prepared through the ring-opening metathesis polymerization of the strained bicyclic indolinobenzospiropyran derivatives. When 1, 2, and 4 mol% of the Grubbs' catalyst were used in the ROMP reaction, the 100-mer (**c**), the 50-mer (**b**), and the 25-mer (**a**) were isolated, respectively. The gel permeation chromatography (GPC) analysis revealed that the relative ratio of the number-average molecular weights for **c**:**b**:**a** was approximately 4:2:1 for **P1** and **P2** but not for **P3**. All of the prepared homopolymers were soluble in common organic solvents, had high polydispersity indices (PDI, M_w/M_n) in **P1**, **P2** and **P3** and retained their photochromic properties in the polymeric systems. The PDI values obtained are unusually high for ROMP without any clear reasons. **P1** and **P3** showed excellent photochromic behaviors, while **P2** ($m = 1$) had a much weaker photochromic character, in the UV–vis spectroscopy. The UV–vis absorption spectroscopic behaviors of the polymers revealed that they retained the appealing photochromism of their corresponding monomers, as an example for **SP1**, **SPM1** & **P1** in Fig. 5.

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