Vapochromic features of new luminogens based on julolidine-containing styrene copolymers

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Abstract

We report on vapochromic films suitable for detecting volatile organic compounds (VOCs), based on new polystyrene copolymers containing julolidine fluorescent molecular rotors (JCAEM). Poly(styrene-co-hydroxyethylmethacrylate) copolymers functionalyzed by cyanovinyl-julolidine moieties of different compositions were prepared (P(STY-co-JCAEM)(m), with m = 0.06-0.61). The sensing performances of the spin-coated copolymer films demonstrated significant vapochromism when exposed to VOCs characterized by high vapour pressure and favourable interaction with the polymer matrix such as Et_2O and CH_2Cl_2. It is worth mentioning that the fluorescence decrease rate was 2 to 3 times faster than that of previously investigated julolidine-based fluorescent molecular rotors dispersed in PS films. This phenomenon was attributed to the better control of JCAEM moieties distribution in the polymer matrix conferred by the covalent approach, combined with a minimal film thickness of 4 microns. These factors, in concert, strongly accelerate the deactivation pathways of the JCAEM units in the presence of well interacting VOCs. Overall, the present results support the use of julolidine-enriched styrene copolymers as effective chromogenic materials suitable for the fast detection of VOCs.

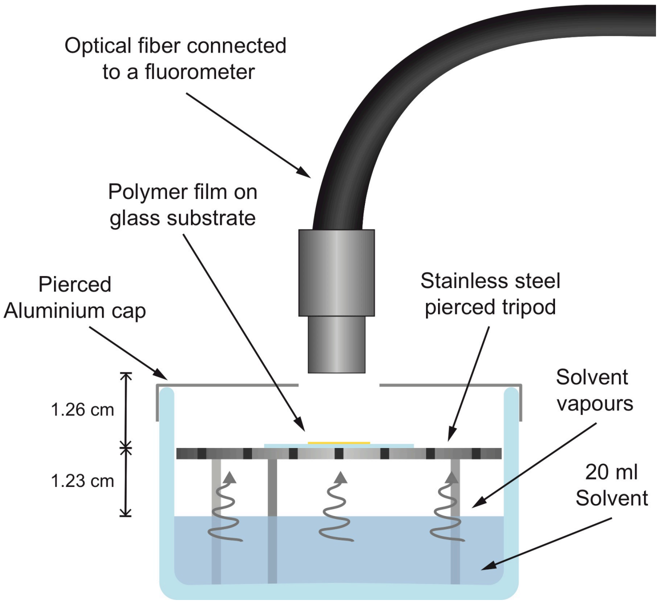
1. Introduction

Recently, the introduction of luminescent aggregachromic dyes into polymer films has been effectively used for the preparation of materials showing both typical polymer properties and optical response to visible light.[1-3] The basic principle of these chromogenic materials relies on colour changes in absorption or in emission associated with the structural modifications of the molecular assemblies of dyes dispersed in the polymer phase. The development of chromogenic materials is placed alongside the development of fluorophores with Aggregation-Induced Emission (AIE) features, which are rapidly expanding in literature.[4-6] The AIE phenomenon is based on the fact that chromophore aggregation plays a constructive, rather than destructive, role in the light emitting process. AIE fluorophores are non-emissive when molecularly dissolved in good solvents, but become highly luminescent when aggregated in poor solvents or in the solid state thanks to a mechanism of restriction of intra-molecular rotation (RIR).[5, 7] Such a behaviour enables the AIE to find potential high-tech applications as chemosensors, bioprobes, solid-state emitters with different emission ranges.[4, 8] Notably, AIE systems with donor–acceptor structure are also called Fluorescent Molecular Rotors (FMRs). In FMRs, the AIE effect is often ascribed to a non-emissive twisted intramolecular charge transfer (TICT) state which occurs in solution, while in aggregates or in viscous media, transition from LE to TICT is inhibited.[5] Those molecules have become rather popular in the last 5–10 years thanks to their easy applicability as non-mechanical viscosity sensors, tools for protein characterization, and local microviscosity imaging.[9-12] The application of FMRs in solution has been widespread since several years, and examples of their use in combination with polymer matrices have been efficiently reported for the detection of volatile organic compounds (VOCs).[12-14] VOCs are continuously released into the environment by different sources like industrial processes, transportation, agriculture, etc. and some of them have adverse effects on human health.

For example, julolidine-based FMRs were found to exhibit viscosity-dependent emission properties when dispersed at low loadings (< 0.1 wt.%) in polystyrene (PS) films.[15] The exposure of FMR/PS films to a saturated atmosphere of well-interacting VOCs (e.g., chloroform and toluene) caused polymer matrix plasticization thus yielding a significant drop of FMR fluorescence due to the favoured relaxation from the non-emissive TICT excited state.

Fluorophore dispersion into polymers is certainly a sustainable procedure and largely applied to proprietary polymers.[3] Nevertheless, efforts must be taken into account to prevent dye segregation and to confer the fastest response under VOCs exposure. This last issue is fundamental for the development of plastic sensors to VOCs.

Accordingly, it is expected that the introduction of julolidine-based FMR structure into the typical PS backbone may bring the polymer substantial selectivity and sensitivity when it is used for the detection of VOCs. Thereby, poly(styrene-co-hydroxyethylmethacrylate) copolymers functionalized by cyanovinyl-julolidine moieties of different compositions were designed and synthesized (P(STY-co-JCAEM)(m), with cyanovinyl-julolidine units content m = 0.06-0.61). Copolymer films were obtained by spin-coating on glass plate surfaces, and their sensing performances to VOCs were investigated with a homemade apparatus (Scheme 1).



Scheme 1. Experimental set-up adopted for the determination of the vapochromic response of spin-casted P(STY-co-JCAEM)(m) films

2. Experimental part

2.1 Materials and methods

Julolidine, sodium acetate anhydrous and pyperidine, were purchased from Aldrich and used as received. Phosphorous oxychloride (Aldrich), was purified by distillation at reduced pressure. Cyanoacetic acid (Aldrich) was recrystallized from a mixture of toluene/acetone 2:3 v/v. Azobisisobutyronitrile (AIBN) was recrystallized from acetone. N,N'-dicyclohexylcarbodiimide (DCC) (Aldrich) was dried by dissolution in a saturated solution of Na_2SO_4 in Ethyl Acetate. The solution was stored for 16 h then filtered and the anhydrous product was recovered evaporating the solvent under reduced pressure and further dried under high vacuum for several hours. N,N-dimethylformamide (DMF), dichloromethane and tetrahydrofuran (THF) (Aldrich) were refluxed over CaH_2 for 2 h and distilled under nitrogen. 2-Hydroxyethyl methacrylate (Fluka) was refluxed over CaH_2 for 2 h in presence of butylated hydroxytoluene (BHT) (Aldrich) as polymerization inhibitor, and distilled under reduced pressure. Spectroscopy grade solvents (Carlo Erba or Aldrich) were utilized without further purification.

2.2 Synthesis of 9-formyljulolidine (FJUL)

The synthesis of 9-formyljulolidine was carried out modifying a reported procedure.[16, 17] In brief, phosphorous oxychloride (0.7 mL, 7.65 mmol) was added dropwise to N,N-dimethylformamide (2 mL, 25.85 mmol) at 0 °C. A solution of julolidine (1.328 g, 7.76 mmol) in DMF (2.2 mL, 28.44 mmol) was then added and the mixture was stirred at 90 °C for 4.5 h. The solution was allowed to cool at r.t. and neutralized to pH 6-8 by the addition of a saturated sodium acetate solution (~30 mL). After stirring overnight at r.t., a greenish-yellow solid precipitate was recovered via filtration, washed with water (30 mL) and dried under high vacuum. The crude product was purified through column chromatography on silica gel (230-400 mesh) using ethyl acetate/$CHCl_3$ (70/30 v/v) as eluent mixture (67% yield).

FT-IR (KBr, cm^{-1}): 2758, 1651, 1594, 1527, 1321.

^{1}H NMR ($CDCl_3$): δ (ppm) = 9.6 (s, 1H, CHO), 7.3 (s, 2H, aromatic), 3.3 (t, 4H, NCH_2), 2.7 (t, 4H, $NCH_2CH_2C\underline{H}_2$), 1.9 (m, 4H, $NCH_2C\underline{H}_2$).

^{13}C NMR ($CDCl_3$): δ (ppm) = 191.3 (CHO), 149.1 (=C-N aromatic), 128.5 to 122.0 (aromatic), 49.3 (NCH_2), 28.1 to 20.4 ($NCH_2\underline{C}H_2\underline{C}H_2$).

EI-MS *m/z* (%): 201 (100, M^+).

The spectral characteristics of this compound are in agreement with those previously reported.[15]

2.3. Synthesis of 2-(2-cyanoacetoxy)ethyl methacrylate (CAEM)

A solution of DCC (2.58 g, 12.48 mmol) in anhydrous dichloromethane (12.5 mL) was added dropwise to a solution of cyanoacetic acid (1.08 g, 12.65 mmol) and 2-hydroxyethyl methacrylate (1.52 mL, 12.53 mmol) in anhydrous dichloromethane (25 mL). The mixture was kept under nitrogen and stirred at r.t. for 24 h. Then, 20 mL of dichloromethane were added and the mixture stored overnight at -20 °C to promote the precipitation of the DCU formed during the reaction. The solid was filtered off using a 22 μm PVDF membrane filter Durapore (Sigma) and washed with cold dichloromethane. The filtrate was concentrated at reduced pressure and stored again at -20° C for several hours to allow the precipitation of any further DCU. Filtration was repeated 2 more times in the same way. The filtrate was eventually dried at reduced pressure (mechanical vacuum). The colourless oily product was then purified through column chromatography on silica gel (230-400 mesh) using $CHCl_3$/Ethyl acetate (80/20 v/v) as eluent mixture (77% yield). All the operations were performed covering the glassware with aluminium foil in order to avoid the undesired polymerization of the product.

FT-IR (KBr, cm^{-1}): 2957, 2264, 1722, 1637, 1372, 1321, 1165

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.12 (s, 1H, $\underline{H}CH$= -cis), 5.61 (t, 1H, $HC\underline{H}$= -trans), 4.46 (m, 2H, $H_2C=C(-CH_3)-C(=O)-O-C\underline{H}_2-$), 4.38 (m, 2H, $NC-CH_2-C(=O)-O-C\underline{H}_2$), 3.50 (s, 1H, $NC-C\underline{H}_2-$), 1.94 (s, 3H, $-C\underline{H}_3$).

^{13}C-NMR (CDCl$_3$): δ (ppm) = 166.97 (O-$\underline{\mathrm{C}}$(=O)-C=C(-CH$_3$)), 162.81 (O-$\underline{\mathrm{C}}$(=O)-C-CN), 135.64 (C(=O)-$\underline{\mathrm{C}}$(-CH$_3$)=CH$_2$), 126.32 (H$_2\underline{\mathrm{C}}$=C(-CH$_3$)-), 112.67 (N$\underline{\mathrm{C}}$-C), 34.34 (H$_2$C=C(-CH$_3$)-C(=O)-O$\underline{\mathrm{C}}$H$_2$), 61.65 (NC-C-C(=O)-O-$\underline{\mathrm{C}}$H$_2$), 24.54 (NC-$\underline{\mathrm{C}}$H$_2$), 18.12 (H$_3\underline{\mathrm{C}}$-C(=CH$_2$)-).

EI-MS *m/z* (%): 112 (91), 69 (100), 41 (50).

2.4 Synthesis of 2-(methacryloxy)ethyl-2-cyano-3-julolidin-acrilate (JCAEM) (Scheme 2)

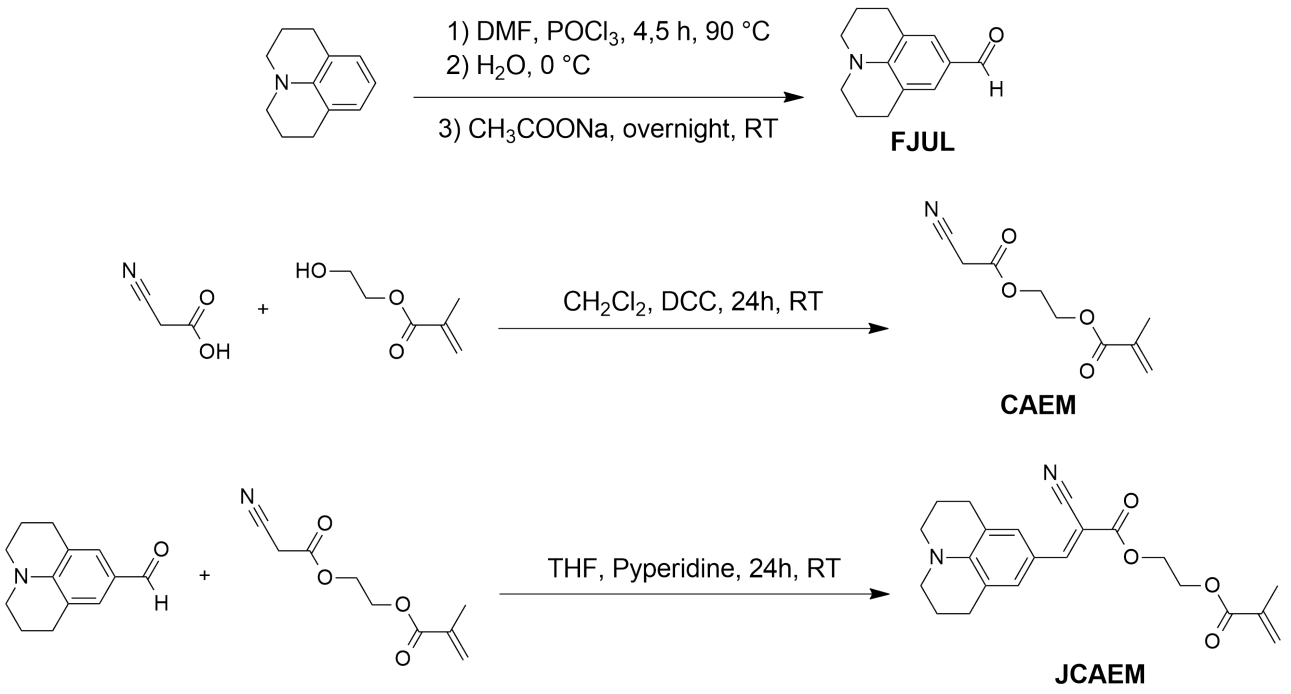
Pyperidine (0.24 mL, 2.45 mmol) was added to a solution of FJUL (0.4660 g, 2.32 mmol) and CAEM (0.45 mL, 2.51 mmol) in anhydrous THF (12.5 mL). The mixture was kept under stirring at r.t. for 24 h. The solvent was then removed under reduced pressure. The crude product was purified by recrystallization from dichloromethane/*n*-hexane mixture. Yellow-orange needle-like crystals were recovered and washed several times with *n*-Hexane and dried under mechanical vacuum (72% yield). Also in these steps, operations were performed covering the glassware with aluminium foil.

FT-IR (KBr, cm^{-1}): 2957, 2207, 1721, 1706, 1618, 1588, 1566, 1368, 1324, 1232, 1171, 1121, 1101.

^{1}H-NMR (CDCl$_3$): δ (ppm) = 7.94 (s, 1H, Ar-CH=C(-CN)-), 7.52 (s, 2H, aromatic), 6.17 (s, 1H, HCH= -cis), 5.60 (s, 1H, HCH= -trans), 4.51 (m, 2H, H$_2$C=C(-CH$_3$)-C(=O)-O-C$\underline{\mathrm{H}}_2$-), 4.44 (m, 2H, -C=C(-CN)-C(=O)-O-CH$_{\underline{2}}$-), 3.34 (t, 4H, -N-CH$_2$), 2.75 (t, 4H -N-CH$_2$-CH$_2$-C$\underline{\mathrm{H}}_2$), 1.96 (m, 7H -N-CH$_2$-C$\underline{\mathrm{H}}_2$-, -CH$_3$).

^{13}C-NMR (CDCl$_3$): δ (ppm) = 167.17 (O-$\underline{\mathrm{C}}$(=O)-C=C(-CH$_3$)), 164.64 (O-$\underline{\mathrm{C}}$(=O)-C(-CN)=), 154.70 (Ar-$\underline{\mathrm{C}}$H=C(-CN)-), 147.86 (-N-$\underline{\mathrm{C}}$(-C-)=C-), 135.92 (H$_3$C-$\underline{\mathrm{C}}$(=CH$_2$)-), 131.83 (-C(-CN)=C-$\underline{\mathrm{C}}$(-C)=C-), 126.17 (H$_2\underline{\mathrm{C}}$=C(-CH$_3$)-), 120.81 (-C(=C)-$\underline{\mathrm{C}}$H=C(-C)-CH=), 118.38 (-CH$_2$-$\underline{\mathrm{C}}$(=C-)-CH(=C)), 117.81 (N$\underline{\mathrm{C}}$-C(=CH-)-), 90.92 (NC-$\underline{\mathrm{C}}$(=CH-)-C(=O)-), 63.01 (H$_2$C-C(-CH$_3$)-C(=O)-O-$\underline{\mathrm{C}}$H$_2$), 62.29 (H$_2$C-C(-CH$_3$)-C(=O)-O-CH$_2$-$\underline{\mathrm{C}}$H$_2$), 50.18 (-N(-CH$_2$)-), 27.53 (-N(-CH$_2$-CH$_2$-$\underline{\mathrm{C}}$H$_2$-)-), 21.07 (-N(-CH$_2$-$\underline{\mathrm{C}}$H$_2$-CH$_2$-)-), 18.26 (H$_3\underline{\mathrm{C}}$-C(=CH$_2$)-).

EI-MS *m/z* (%): 381 (100, M$^+$).



Scheme 2. Reaction pathway for the synthesis of the JCAEM monomer

2.5. Synthesis of random copolymers P(STY-co-JCAEM)(m)

Free radical copolymerization of styrene with various amounts of JCAEM led to copolymers P(STY-co-JCAEM)(m), where “m” indicate the molar content of JCAEM in the copolymer composition (Scheme 3). We describe in detail the typical preparation for the P(STY-co-JCAEM)(0.12).

A solution of JCAEM (0.0050 g, 0.013 mmol), Styrene (1.10 mL, 9.602 mmol) and AIBN (0.0100 g, 0.061 mmol) in anhydrous toluene (10 ml) was introduced into a dry reaction tube with a Rotaflow PTFE tap under nitrogen. After three freeze-pump-thaw cycles, the tube was sealed under vacuum through the PTFE screw at the top and the polymerization was let to proceed at 60 °C for 7 days. After cooling to r.t., the polymer was then recovered by precipitation into methanol. The polymer was centrifuged and the supernatants collected and then dried at reduced pressure. The polymer was finally purified by repeated precipitations from dichloromethane solutions into methanol. Yield 68%; $M_n = 13\ 700$ g mol^{-1} (by GPC).

FT-IR (KBr, cm^{-1}): 3100-3000, 2924, 2849, 2213, 1601, 1493, 1452, 1028, 757, 697, 540.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.08 (broad, 3H, aromatic), 6.60 (broad, 2H, aromatic), 1.86 (broad, 1H, $-CH_2-C\underline{H}(-C_6H_5)-$), 1.45 (broad, 2H, $-C\underline{H}_2-CH(-Ph)-$) typical of polystyrene and 3.31 (broad, $-N-C\underline{H}_2$), 2.72 (broad, $-N-CH_2-CH_2-C\underline{H}_2$) characteristic of JCAEM.

^{13}C-NMR ($CDCl_3$): δ (ppm) = 145.23 (broad, $-CH_2-CH-\underline{C}(=CH)-CH-$), 127.99 and 126.65 (broad, aromatic) 43,93 (broad, $-\underline{C}H_2-CH-Ph$), 40.45 (broad, $-CH2-\underline{C}H-Ph$) typical of polystyrene and 167.24 ($O-\underline{C}(=O)-C=C(-CH_3)$), 163.61 ($O-\underline{C}(=O)-C(-CN)=$), 50.19 ($-N(-\underline{C}H_2)-$), 27.60 ($-N(-CH_2-CH_2-\underline{C}H_2-)-$), 21.13 ($-N(-CH_2-\underline{C}H_2-CH_2-)-$) characteristic of JCAEM.

UV-Vis ($CHCl_3$, $c = 5\cdot10^{-5}$ M JCAEM): λ_{max} (nm) = 453

Reaction pathway for the preparation of random copolymers P(STY-co-JCAEM)(m)

2.6. Preparation of P(STY-co-JCAEM)(m) films

Thin polymer films (4 μm) of P(STY-co-JCAEM)(m) were obtained by spin-coating on glass substrate. A 2.4x2.4 mm glass cover slip was cleaned and then placed on the vacuum chuck hold-down of a WS-400B-6NPP-LITE (Laurell Technologies Corp.) spin-coater. A viscous solution of the copolymer (5 mg) in $CHCl_3$ (40 μL) was placed in the centre of the glass, and the coating was performed at a 750 rpm for 22 sec., with an acceleration index of 004 (~448 rpm·s^{-1}). The obtained films were allowed to slowly dry at r.t. for 24 h before any measurement. Film thickness was measured with a dial indicator Borletti CM1S with ruby movement bearing.

2.6. Characterization of materials

FT-IR spectra were recorded through a Perkin-Elmer Spectrum GX FT-IR at room temperature, on pellets made from grinding mixtures of anhydrous KBr with ~1% w/w of the solid product, and pressing the mixture. EI-MS spectra were recorded at 70 eV by GLC-MS, performed on an Agilent 6890N gas-chromatograph interfaced with Agilent 5973N mass detector. NMR spectra were recorded with a Bruker Advance DRX 400 at room temperature at 400 MHz (^{1}H) and 100 MHz (^{13}C) and were referred to the residual protons of deuterated solvents.

Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight dispersion (M_w/M_n) of polymer samples with respect to polystyrene standards. GPC measurements were performed in $CHCl_3$ as solvent on a four-channel pump Jasco PU-2089 Plus chromatograph, equipped with a Jasco RI 2031 Plus refractometer and a multichannel Jasco UV-2077 Plus UV-Vis detector set at 252 and 360 nm. The flow rate was 1 mL·min^{-1} at a temperature of 30 °C held through a Jasco CO 2063 Plus Column Thermostat. A series composed by two Polymer Laboratories columns PLgel™ MIXED D and a PLgel™ precolumn packed with polystyrene-divinylbenzene was used to perform the analysis (linearity range 100 Da-400 kDa).

Thermogravimetric (TG) analyses were carried out by means of a Mettler Toledo TGA/SDTA 851 apparatus. Samples were heated from 25 to 700 °C at 10 °C·min^{-1} under a nitrogen flow. DSC thermograms were recorded under nitrogen atmosphere by a Mettler Toledo DSC 922e Module Stare apparatus equipped with a liquid nitrogen cooling system. Samples were heated from 25 to 180 °C at 10 °C·min^{-1}, then cooled to 0 °C at the same speed. The heating was repeated in the same conditions after 3 min of annealing at 0 °C.

Absorption spectra were recorded at room temperature on a Perkin-Elmer Lambda 650 spectrometer. Fluorescence spectra were measured at room temperature on a Horiba Jobin-Yvon Fluorolog®-3 spectrofluorometer equipped with a 450 W xenon arc lamp, double-grating excitation and single-grating emission monochromators.

The fluorescence quantum yield (Φ) in methanol/glycerol mixtures was determined at room temperature relative to fluorescein ($\Phi_S = 0.79$ in 0.1 N NaOH) according to the relation:

$$\Phi = \Phi_{ST} \frac{\int_0^\infty I(\nu)\, d\nu}{\int_0^\infty I_{ST}(\nu)\, d\nu} \frac{(1-10^{-A_{ST}})}{(1-10^{-A})} \frac{n^2}{n_{ST}^2} \qquad \text{(eq.1)}$$

where the subscripts ST are referred to standard, the integrals $\int_0^\infty I(\nu)\,d\nu$ and $\int_0^\infty I_{ST}(\nu)\,d\nu$ are the areas under the emission curves of the investigated compound and standard (range 450-675 nm), A and A_{ST} are the absorbances of the investigated compound and standard at the excitation wavelength (430 nm), n and n_{ST} are the refractive index of the solvents, i.e. 1.332 for methanol, 1.474 for glycerol. The refractive index of MeOH/Glycerol mixtures was predicted by the Arago-Biot additive rule:[18]

$$n_{mix} = \phi_1 n_1 + \phi_2 n_2 \qquad \text{(eq. 2)}$$

In the same way, the viscosity of MeOH/Glycerol mixtures was predicted by the Grunberg-Nissan simplified additive rule:[19]

$$\eta_{mix} = \phi_1 \eta_1 + \phi_2 \eta_2 \qquad \text{(eq. 3)}$$

where the subscripts 1 and 2 are referred to solvent 1 and 2 respectively, ϕ_i are the volume fraction, n_i are the refractive index and η_i are the viscosity of pure substances.

The chemical composition of copolymers was evaluated by UV–Vis spectroscopy by means of a calibration curve obtained form $5\cdot10^{-7}$–$1\cdot10^{-5}$ $CHCl_3$ solutions of JCAEM.

Emission spectra (λ_{exc} 430 nm) of polymer films were recorded on the same spectrofluorometer in the dark by using a F-3000 Fibre Optic Mount apparatus coupled with optical fibre bundles. Light generated from the excitation spectrometer is directly focused on the sample using optical fibre bundles. Emission from the sample is then directed back through the bundle into the collection port of the sample compartment. The emission response of the films was tested by exposing the sample held by a steel tripod in a 50 mL beaker closed by a pierced aluminium foil lid (scheme 1), to 20 mL of various organic solvents of different vapour pressure and PS-solvent Flory–Huggins interaction parameter χ (Table 1), at 25 °C and atmospheric pressure.

Table 1. Vapour pressure of different solvents at 25 °C,[20] PS-solvent Flory–Huggins interaction parameter χ,[21] for utilized solvents

solvent	**vapour pressure (kPa)**	χ
cyclohexane	13	1.49−1.14
toluene	2.9	0.42−0.31
THF	21.6	0.16−0.70
$CHCl_3$	21.3	0.52−0.17
CH_2Cl_2	58.2	0.78−0.71
Et_2O	71.7	0.17−0.05
acetone	30.8	0.81−0.94
MeOH	16.9	2.44
CH_3CN	11.9	2.02−0.93

3. Results and discussion

3.1 Synthesis

The synthesis of the hydroxyethylmethacrylate monomer functionalized by a cyanovinyl-julolidine moiety (JCAEM, Scheme 2) and its incorporation into styrene polymers by conventional radical polymerization have never been described before. The chemical structure of JCAEM was in fact designed in such a way that cyanovinyl-julolidine should act as a viscosity-sensitive FMR unit in glassy polystyrene (PS) environment. Unlike recently published julolidine-based fluorophores dispersed in PS,[15] the covalent bonding of the FMR unit with the macromolecular backbone should confer a more sensitive and reproducible response towards multiple cycle of VOCs exposure.

In detail, commercially available julolidine was formylated with phosphorus oxychloride and dimethylformamide to afford 9-formyljulolidine (FJUL). The cyanoacetoxy-ethyl methacrylate ester (CAEM) was obtained via dicyclohexyl carbodiimide-induced esterification of cyanoacetic acid with 2-hydroxyethyl methacrylate. Knoevenagel condensation of the CAEM ester with FJUL in the presence of piperidine produced the desired JCAEM monomer. The desired amount of JCAEM was then copolymerized with styrene *via* radical polymerization with AIBN for seven days to afford P(STY-co-JCAEM)(m) copolymers (Scheme 3). Copolymers composition, molecular weights and thermal behaviour were reported in table 2.

Table 2. Characteristics of the *P(STY-co-JCAEM)(m)* copolymers

Copolymer	m (% mol.)	M_n (g/mol)	M_w/M_n	Tg (°C)
P(STY-co-JCAEM)(0.06)	0.06	16,400	1.7	99
P(STY-co-JCAEM)(0.12)	0.12	13,700	1.8	100
P(STY-co-JCAEM)(0.25)	0.25	17,700	1.6	101
P(STY-co-JCAEM)(0.61)	0.61	14,200	1.5	102

Four distinct copolymers were prepared and containing progressive amounts of JCAEM, i.e. from 0.06 to 0.61 mol%, as determined by ^{1}H NMR and UV-Vis experiments, i.e. assuming the julolidine-based FMR to have the same molar extinction coefficient as the corresponding low molecular weight dyes (JCAEM).

The polymerization feed was tuned so that the resulting fluorophore concentrations could be comparable with those of PS films containing dispersed julolidine based fluorophores already reported in literature by our group.[15] It is worth noting that no evident effect of JCAEM comonomer on the copolymers molecular weight and thermal properties is present. The copolymers showed a glass transition temperature close to 100 °C, while they started degrading above 410 °C.

3.2 Optical properties in solution

JCAEM methanol solution showed absorption maximum around 460 nm ($\varepsilon = 57{,}450\ M^{-1}\ cm^{-1}$), with emission maximum between 470 and 500 nm. Quantum yield was negligible (Table 3), due to the formation of a TICT excited state, which rapidly decayed in a non-radiative way through internal rotation.[22, 23]

Table 3. Optical features of $5\cdot10^{-6}$ M JCAEM solutions

Solvent	**Absorption max (nm)**	**Emission max (nm)**	$\boldsymbol{\Phi_f}^{(a)}$
methanol	453	492	$3.2\cdot10^{-4}$
methanol/glycerol 10:90 v/v	465	502	$7.9\cdot10^{-3}$

$^{(a)}$Fluorescence quantum yield (Φ_f) determined at room temperature relative to fluorescein ($\Phi^s{}_f$ = 0.79 in 0.1 N NaOH). $\lambda_{exc.} = 430$ nm

JCAEM exhibited an evident solvatochromism and a significant viscosity-dependent fluorescence when glycerol was added to methanol solutions (Figure 1 and Table 3). JCAEM experienced a strong increase in quantum yield (about 25 times higher) when dissolved in viscous environments like glycerol solutions (viscosity $\eta = 945$ mPa·s at 20 °C for glycerol, as compared to 1.2 mPa·s for methanol). According to the literature,[24] in viscous media the molecular internal rotation is hindered, thus favouring a radiative decay of the LE state and an increase in quantum yield. Conversely, the absorption and emission wavelength appeared less sensitive to polarity variations (dielectric constant $\varepsilon = 45.2$ for glycerol, as compared to 32.7 for methanol) and the red-shift in glycerol was limited to 10 nm. JCAEM FMR can be therefore utilized as viscosity probe even in environments where polarity changes are expected.

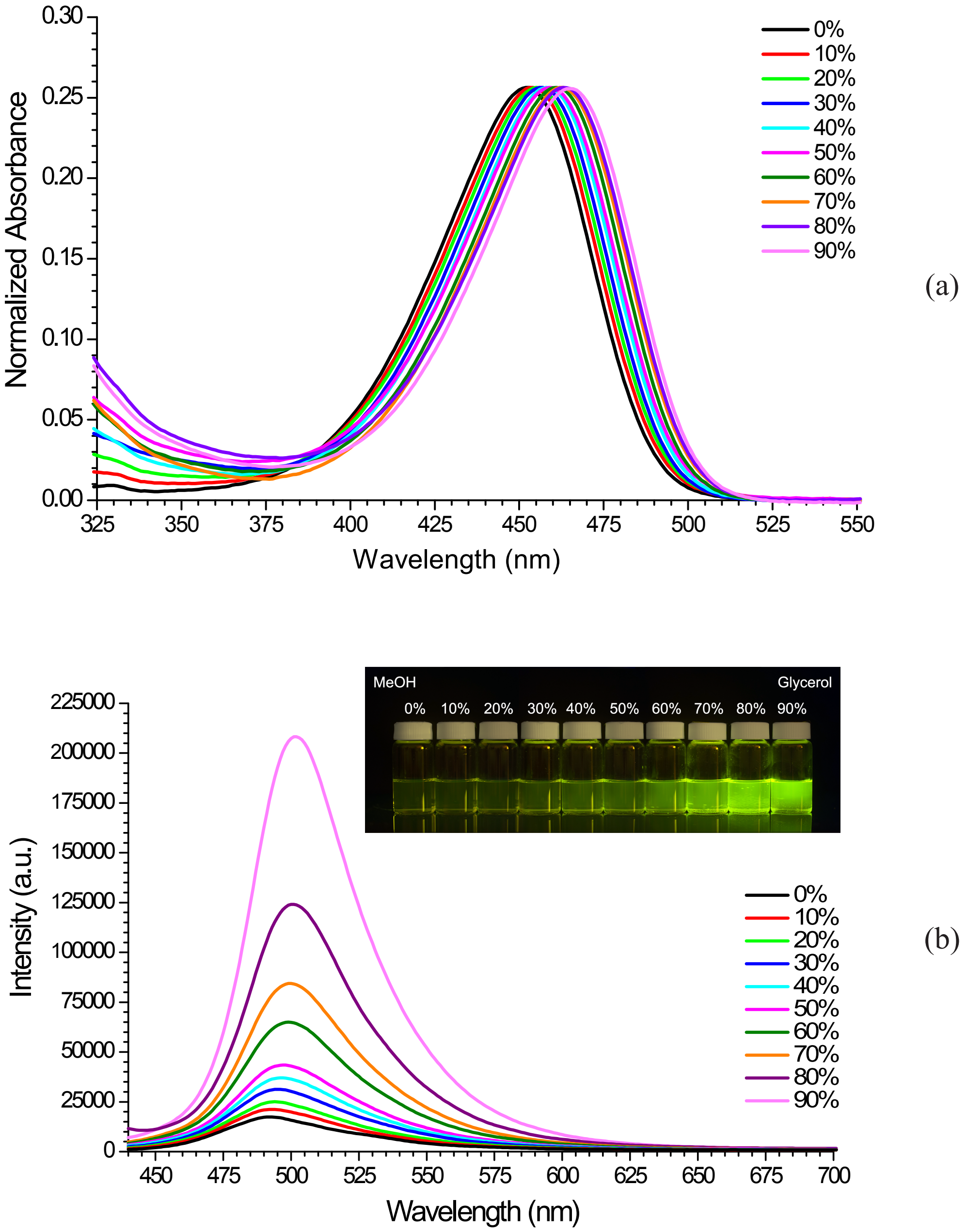


Figure 1. Absorption (a) and fluorescence (b, $\lambda_{exc.}$ = 430 nm) of $5\cdot10^{-6}$ M JCAEM solutions in methanol/glycerol mixtures with different glycerol volume contents. In the inset picture, JCAEM solutions were excited with a Dark Reader 46B transilluminator (~ 450 nm)

Notably, JCAEM followed a Förster-Hoffmann behaviour according to equation 3 (Figure S1, supplementary information), which relates the (double logarithmic) quantum yield with viscosity:

$$\log \Phi_f = C + x\cdot\log \eta \qquad \text{(eq. 3)}$$

where C and x are constants. η was calculated by using equation 2 (see Experimental part).

The x parameter, i.e. the viscosity sensitivity of the FMR, was found to be between 0.46, in agreement with the highest values reported for similar systems in literature.[25]

The effect of the JCAEM covalent incorporation in the PS backbone is clearly visible in figure 2. We selected two chloroform solutions (the shift from methanol to chloroform was required due to the insolubility of the copolymer in the former solvent) containing JCAEM and P(STY-co-JCAEM)(0.06), respectively, with the same concentration of JCAEM chromophores as confirmed by UV-vis absorptions.

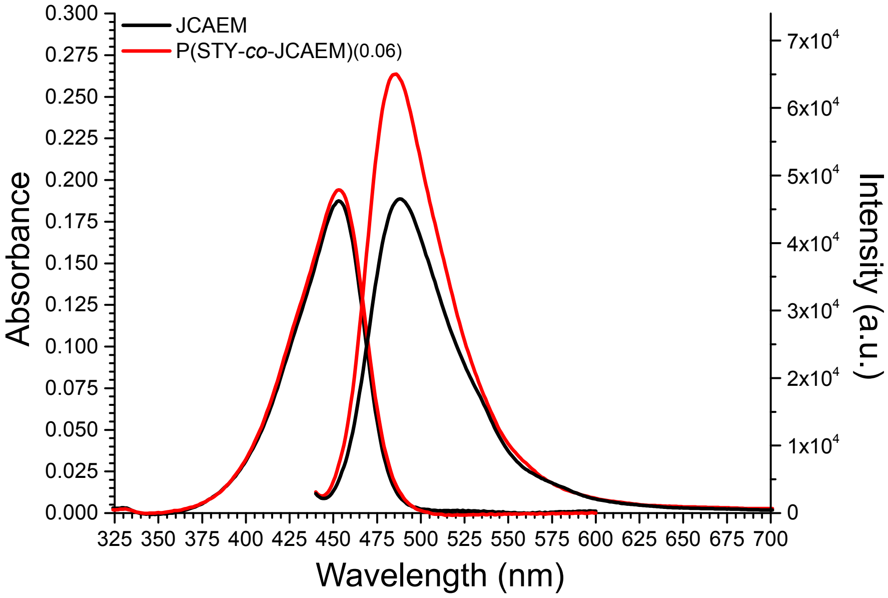


Figure 2. Absorption and fluorescence ($\lambda_{exc.}$ = 430 nm) of $5\cdot10^{-6}$ M JCAEM and 0.038 wt.% P(STY-co-JCAEM)(0.06) chloroform solutions

While both solutions showed the same absorption intensity, the fluorescence of the dissolved P(STY-co-JCAEM)(0.06) resulted more intense, possibly due to the increased viscosity of the chloroform solution caused by the dissolved polymer. Conversely, the introduction of the JCAEM in the PS backbone did not alter the position of the absorption and emission maxima peaks.

3.3 Vapochromic behaviour of P(STY-co-JCAEM)(m) film

Thin polymer films (4 μm) of P(STY-co-JCAEM)(m) were obtained by spin-coating on 2.4x2.4 mm cleaned glass cover slides. All the films appeared quite homogeneous with absorption features similar to those collected in solution ($\lambda_{max.}$ = 450 nm). P(STY-co-JCAEM)(m) are amorphous copolymers with a glass transition temperature of about 100 °C. Thus, JCAEM were connected to a network in which the intramolecular rotations of their julolidine fluorophores were in fact completely arrested. This would strongly favour the emission of light from their locally excited (LE) states.

Consistent with these findings, the fluorescence spectrum of P(STY-co-JCAEM)(0.06) film (Figure 3) showed about 15–20 nm blue-shifted emission intensities similar to those collected from methanol/glycerol 10:90 v/v solutions. This blue shift is ascribed to the lower dielectric constant of the polymer matrix ($\varepsilon \sim 2.6$) as compared to that of solvent mixtures. The very similar emission spectral shape can be ascribed to the covalent incorporation of the julolidine-based fluorophore, which ensured an effective and homogeneous distribution of the FMRs moieties within the polymer.

One of the peculiarities of FMRs is their emission variation in response to changes in viscosity or sterical constraints. It is reported that interactions between a polymer and vapours of a suitable solvent are able to induce an evident relaxation of macromolecular chains (localized plasticization). This phenomenon is followed by a greater mobility with an increase in the free volume and a consequent decrease in the local microviscosity.[26] On this account, the fluorescence emission of FMRs dispersed in glassy amorphous polymer films was reported to be strongly affected by vapour exposure, even if a fast vapochromism during the early stages of exposure is still required.[12, 14, 15]

We therefore explored the effect of several VOCs on the emission behaviour of P(STY-co-JCAEM)(m) thin films by selecting different kinds of organic solvents. An illustration of the fluorescence emission dependence on exposure time to chloroform vapours is shown in figure 3. Notably, the P(STY-co-JCAEM)(0.06) films underwent a significant variation in emission intensity when exposed to a saturated atmosphere of chloroform (Figure 3).

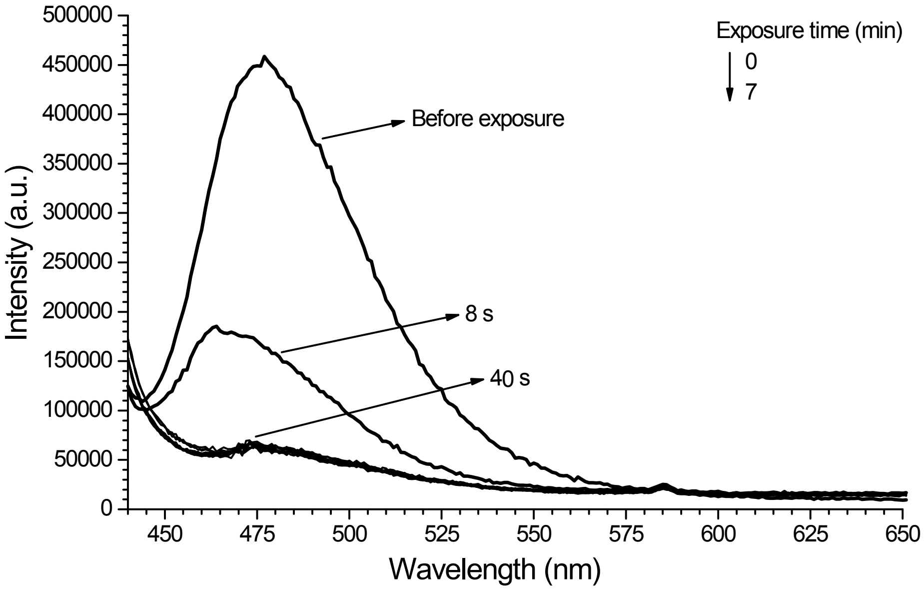


Figure 3. Progressive changes in the fluorescence emission of P(STY-co-JCAEM)(0.06) film as a function of the exposure to chloroform vapours. The spectra were collected for 7 min with a time interval of 40 s after the first scan.

The emission intensity dropped by more than 50% after less than 10 seconds of exposure. This extremely sensitive solvent dependence was ascribed to the sensitivity of the FMRs and resides in the reorganization energy of the excited transition state (from LE to TICT states) with increasing solvent uptake. PS matrix is in the glassy state with an associated large fraction of free volume in the form of channels and holes of molecular dimensions. Considering that chloroform vapours fill these empty spaces, diffusion and swelling of the polymer start from the outer surface layers inwards. In turn, an overall decrease of the local microviscosity evolves, thus triggering fluorescence dropping. After a few minutes, the system reached an equilibrium since the film across its whole thickness is involved in solvent permeation. Hereafter, all FMR moieties were connected in a polymer environment with homogeneous microviscosity and their emission did not change any longer for prolonged exposure times.

A more evident and accurate vapochromic response is observed by monitoring the fluorescence variation as a function of VOCs exposure time (Figure 4). All P(STY-co-JCAEM)(m) thin films were monitored and exhibited a similar behaviour upon exposure to chloroform vapours. It is worth noting that the fluorescence variation appeared faster and more pronounced for those films containing the lowest JCAEM content (i.e., P(STY-co-JCAEM)(0.06) and P(STY-co-JCAEM)(0.12)) and reached a plateau after about 60 s (Figure 4). This result is not surprising since polymers containing low amounts of emitting species are expected to provide the largest emission variations during the early stages of VOCs exposure.

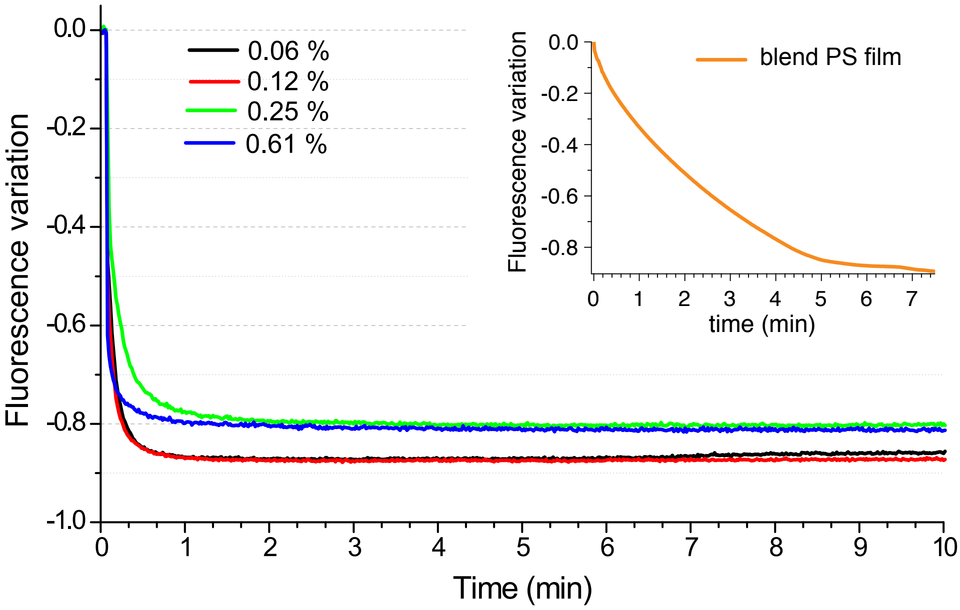


Figure 4. Variation of the fluorescence maximum intensity with exposure time to chloroform vapours for all P(STY-co-JCAEM)(m) films and (inset) for the most sensitive julolidine-based FMR dispersed in PS[15]

In contrast to P(STY-co-JCAEM)(m) films, julolidine-based FMRs dispersed in PS films displayed a lesser reduction in fluorescence emission and a levelling off to a constant value only after 400 s (6-7 min) of chloroform exposure.[15] This noteworthy result is attributed to a combination of effects: a) the first resides on the covalent incorporation of the FMR moieties, whose homogeneous distribution within the polymer backbone implies the presence of isolated FMR units in the chain, thus enabling a prompt and simultaneous response of all portions of the film; the second involves the spin-coating procedure that allowed P(STY-co-JCAEM)(m) films to have thickness of only 4 μm, i.e. about one order of magnitude less than that of blend PS films. It was actually reported that, the lower the thickness, the faster is the vapochromic response.[14] Blend PS films containing dispersed julolidine-based FMR with thickness lower than 20-30 μm were not obtained due to poor film homogeneity.

P(STY-co-JCAEM)(0.06) films were then exposed to solvents with different vapour pressures and Flory–Huggins interaction parameter χ (Table 1, experimental part). It is worth noting that χ is small in the case of effective solvent/polymer interactions.

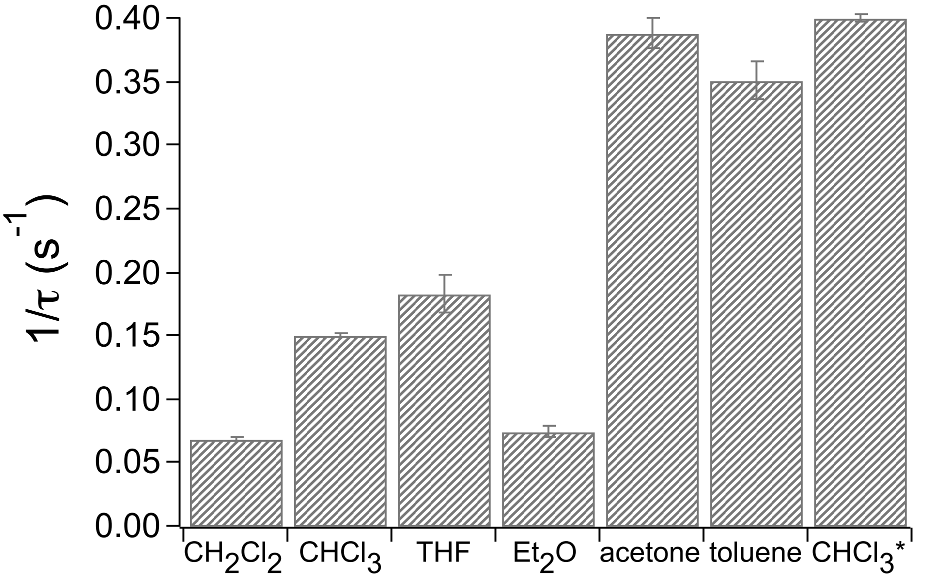


Figure 4. Fluorescence decreasing constant rates (1/*τ*, obtained from the monoexponential fits of data reported in Figure S2) for the different highly interacting VOCs with the (STY-co-JCAEM)(0.06) films. In the graph, the constant rate recorded for $CHCl_3$ exposure ($CHCl_3$*) was also reported for the most sensitive julolidine-based FMR dispersed in PS[15]

The fluorescence variation of P(STY-co-JCAEM)(0.06) films appeared similar when highly interacting solvents were utilized as probing VOCs (Figure S2). Notably, Et_2O and CH_2Cl_2 showed the fastest decreasing rate (Figure 5, as expressed by 1/*τ*, obtained from the monoexponential fits of data reported in Figure S2) thanks to the favourable combination of χ and vapour pressure, whereas the associated time constants differ significantly for acetone (χ = 0.81−0.94) and toluene (χ = 0.42−0.31). While the slower decreasing rate can be possibly attributed for acetone to its higher χ value (i.e. χ = 0.81−0.94 for acetone against 0.17−0.05 for Et_2O), the lower vapour pressure of toluene (i.e., 2.9 kPa for toluene against 71.7 kPa for Et_2O, at 25 °C) can delay solvent adsorption by the film during the initial stages of exposure. Moreover, P(STY-co-JCAEM)(0.06) films appeared quite responsive also to THF (χ = 0.16−0.70), and chloroform (χ = 0.52−0.17), whereas the emission was barely affected by cyclohexane (χ = 1.49−1.14), methanol (χ = 2.44), and acetonitrile (χ = 2.02−0.93) vapours (Figure S2). This behaviour can arise from a combination of effects: the lower vapour pressure of those classes of solvents (i.e., 12.7 kPa for methanol at 25 °C), which can delay solvent adsorption by the film, and their limited affinity with the polymer matrix. This feeble interaction hampers solvents uptake by the polymer, thus making the fluorescence variation of the films negligible. Notably, solvents with χ values lower than 1−2 well interact with the polymer matrix, thus providing the vapour sensing behaviour. Notably, P(STY-co-JCAEM)(0.06) films confirmed their faster response (~ 2-3 times) towards $CHCl_3$ vapours with respect to julolidine-based FMRs dispersed in PS films.

P(STY-co-JCAEM)(0.06) films were then exposed to $CHCl_3$/MeOH mixtures in order to determine whether the system could be sensitive and selective to mixed vapours of varied composition (Figure 5). MeOH was selected as co-solvent being inactive in the fluorescence variation even for prolonged exposure time. It is worth noting that exposing the films to solvent mixtures containing progressively lower chloroform content (expressed as vol.%), the fluorescence variation became smaller in extent, according to the decreasing amount of chloroform in the corresponding vapour composition.

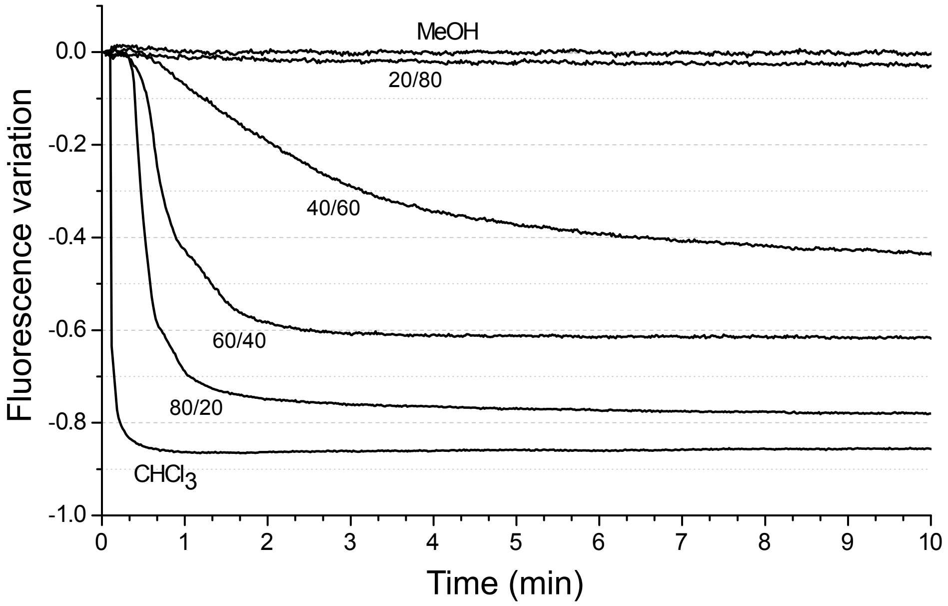


Figure 5. Variation of the fluorescence maximum (λ = 476 nm) with exposure time to vapours of chloroform/methanol mixtures (v/v) for P(STY-co-JCAEM)(0.06) films

Moreover, the curve recorded with solution containing more than 60 vol.% of methanol showed a continuous descending response without levelling off, thereby suggesting incompleteness of the phenomenon within the collection time of 10 min. Notably, P(STY-co-JCAEM)(0.06) films' sensitivity limit of 20 vol.% chloroform in the solution corresponds to about 40−45 vol.% in the vapour phase.[27] Interestingly, the value of the fluorescence variation collected at the end of the analysis showed an almost linear decreasing trend with the chloroform mole fraction in the gas phase (Figure 6).

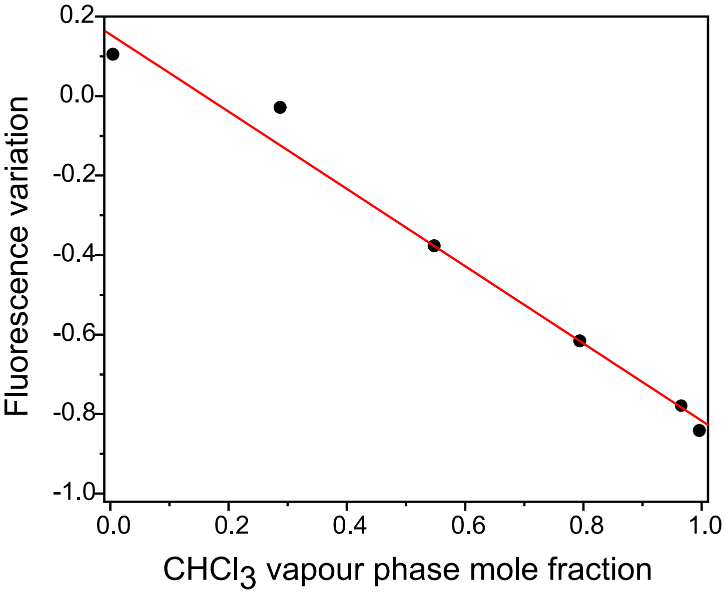


Figure 6. Fluorescence variation of P(STY-co-JCAEM)(0.06) films as a function of the chloroform mole fraction in the gas phase as calculated from the Wilson equation applied to $CHCl_3$/MeOH mixtures of known composition at 25 °C[27] and linear correlation (red curve) with a R-squared value of 0.98.

This result indicates that the composition of the vapour phase might be easily and effectively determined by means of luminescent experiments.

Another advantages of the proposed vapochromic systems is that the experimental setup did not affect sample size within the time interval investigated (< 20 min). Solvent then gradually desorbed at room temperature and pressure from the film when removed from the apparatus, allowing complete recovery of the film emission within 24 hours. This indicates the complete reversibility and reusability of the investigated vapochromic system.

4. Conclusions

We have demonstrated that julolidine-based FMR (JCAEM), characterized by sensitivity toward solvent viscosity, once copolymerized with styrene, confers significant vapochromic features to the resulting polymer films. Poly(styrene-co-hydroxyethylmethacrylate) copolymers functionalyzed by cyanovinyl-julolidine moieties of different compositions (P(STY-co-JCAEM)(m), with m = 0.06-0.61) exhibited viscosity-dependent emission properties when exposed to saturated atmospheres of volatile and well interacting VOCs. These films showed a pronounced decrease in their emission due to solvent-induced changes in the local viscosity of the medium, and their response appeared faster and more pronounced for copolymers with the lowest JCAEM content, as expected. On the contrary, the films emission remained unaffected when barely interacting VOCs were tested such as methanol, acetonitrile and cyclohexane. It is worth noting that the observed vapochromic response of (P(STY-co-JCAEM)(m) resulted much faster than that of julolidine-based FMR dispersed in PS films.[15] This behaviour can be ascribed to the role of the covalent approach in providing more reactive FMR moieties being uniformly distributed in polymer films with reduced thickness.

All these findings consistently support the effective preparation and use of julolidine-enriched styrene copolymers as a new class of powerful vapochromic plastic materials.

Acknowledgements

This work was supported by MIUR-PRIN (2010XLLNM3). The authors are grateful to Dr. M. Lessi for assistance with EI-MS measurements.

References

1. A. Seeboth, D. Loetzsch, R. Ruhmann and O. Muehling, *Chem. Rev.*, 2014, **114**, 3037-3068.
2. G. Prampolini, F. Bellina, M. Biczysko, C. Cappelli, L. Carta, M. Lessi, A. Pucci, G. Ruggeri and V. Barone, *Chemistry--A European Journal*, 2013, **19**, 1996-2004.
3. F. Ciardelli, G. Ruggeri and A. Pucci, *Chemical Society Reviews*, 2013, **42**, 857-870.
4. J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam and B. Z. Tang, *Chem. Rev.*, 2015, **115**, 11718-11940.
5. J. Mei, Y. Hong, J. W. Y. Lam, A. Qin, Y. Tang and B. Z. Tang, *Adv. Mater.*, 2014, **26**, 5429-5479.
6. R. Hu, N. L. C. Leung and B. Z. Tang, *Chemical Society Reviews*, 2014, **43**, 4494-4562.
7. Y. Hong, W. Y. Lam Jacky and B. Z. Tang, *Chem Soc Rev*, 2011, **40**, 5361-5388.
8. R. T. K. Kwok, C. W. T. Leung, J. W. Y. Lam and B. Z. Tang, *Chemical Society Reviews*, 2015, **44**, 4228-4238.
9. E. Y. Choi, S. Y. Nam, C. E. Song, K.-j. Kong, C. Lee, I. H. Jung and S. C. Yoon, *RSC Advances*, 2015, **5**, 107540-107546.
10. M. A. Haidekker, T. P. Brady, D. Lichlyter and E. A. Theodorakis, *Bioorganic Chemistry*, 2005, **33**, 415-425.
11. M. A. Haidekker, T. Ling, M. Anglo, H. Y. Stevens, J. A. Frangos and E. A. Theodorakis, *Chemistry & Biology*, 2001, **8**, 123-131.
12. P. Minei, M. Koenig, A. Battisti, M. Ahmad, V. Barone, T. Torres, D. M. Guldi, G. Brancato, G. Bottari and A. Pucci, *Journal of Materials Chemistry C: Materials for Optical and Electronic Devices*, 2014, **2**, 9224-9232.
13. P. Minei and A. Pucci, *Polymer International*, 2016, **65**, 609-620.
14. P. Minei, M. Ahmad, V. Barone, G. Brancato, E. Passaglia, G. Bottari and A. Pucci, *Polymers for Advanced Technologies*, 2016, **27**, 429-435.
15. G. Martini, E. Martinelli, G. Ruggeri, G. Galli and A. Pucci, *Dyes and Pigments*, 2015, **113**, 47-54.
16. G. Cai, N. Bozhkova, J. Odingo, N. Berova and K. Nakanishi, *Journal of the American Chemical Society*, 1993, **115**, 7192-7198.
17. J. M. Kauffman, S. J. Imbesi and M. A. Aziz, *Organic Preparations and Procedures International*, 2001, **33**, 603-613.
18. J. C. R. Reis, I. M. S. Lampreia, Â. F. S. Santos, M. L. C. J. Moita and G. Douhéret, *ChemPhysChem*, 2010, **11**, 3722-3733.
19. D. W. Green and R. H. Perry, *Perry's Chemical Engineers' Handbook*, McGraw-Hill, New York, 8th edn., 2007.
20. D. R. Lide, *CRC Handbook of Chemistry and Physics, 86th Edition*, CRC Press LLC, Boca Raton, FL, USA, 2004.
21. J. E. Mark, *Physical properties of polymers handbook*, Springer Science + Business Media, LLC, New York, 2nd edn., 2007.
22. M. A. Haidekker and E. A. Theodorakis, *Org. Biomol. Chem.*, 2007, **5**, 1669-1678.
23. F. Zhou, J. Shao, Y. Yang, J. Zhao, H. Guo, X. Li, S. Ji and Z. Zhang, *European Journal of Organic Chemistry*, 2011, **2011**, 4773-4787, S4773/4771-S4773/4770.
24. B. Valeur and M. N. Berberan-Santos, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim (Germany), 2012.
25. J. Sutharsan, D. Lichlyter, N. E. Wright, M. Dakanali, M. A. Haidekker and E. A. Theodorakis, *Tetrahedron*, 2010, **66**, 2582-2588.
26. B. A. Miller-Chou and J. L. Koenig, *Progress in Polymer Science*, 2003, **28**, 1223-1270.
27. M. Martin, M. Cocero and F. Mato, *J Solution Chem*, 1991, **20**, 87-95.