Reactive & Functional Polymers 70 (2010) 827–835

Contents lists available at ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Synthesis and characterization of side-chain oxazoline–methyl methacrylate copolymers bearing azo-dye

Valentin Victor Jerca [a,*], Florica Adriana Nicolescu [a], Adriana Baran [b], Dan Florin Anghel [b], Dan Sorin Vasilescu [c], Dumitru Mircea Vuluga [a]

[a] Centre for Organic Chemistry "Costin D. Nenitescu", Romanian Academy, 202B Spl. Independentei CP 35-108, Bucharest 060023, Romania
[b] "Ilie Murgulescu" Institute of Physical Chemistry, Colloid Department, 202 Spl. Independentei CP 12-194, Bucharest 060021, Romania
[c] University "POLITEHNICA" of Bucharest, Department of Polymer Science, 149 Calea Victoriei, Bucharest 010072, Romania

ARTICLE INFO

Article history:
Received 27 May 2010
Received in revised form 19 July 2010
Accepted 20 July 2010
Available online 25 July 2010

Keywords:
2-Isopropenyl-2-oxazoline
Azobenzene
Methyl methacrylate
Polymer analogous reaction
Ester–amide

ABSTRACT

We synthesized new polymeric structures by attaching a side-chain azo-moiety on poly(oxazoline) and poly(oxazoline-*co*-methyl methacrylate)s. For the polymer analogous transformation, we took advantage of the highly effective ring-opening addition of carboxyl group to the oxazoline cycle. The comonomers feed ratio allowed us to control the composition of the products while the kinetic treatment, employing an integral method, revealed a statistical copolymerization tendency of 2-isopropenyl-2-oxazoline with methyl methacrylate in acetonitrile at 70 °C. The elemental analysis and ^{1}H NMR spectroscopy provided almost identical composition data for both the substrates and the side-chain copolymers. The UV spectroscopy sustained the quantitative addition of 4-(4-hydroxy-3,5-dimethylphenylazo)benzoic acid to the oxazoline rings. Both the unmodified copolymers and the coloured ones exhibited good thermal stabilities, up to 371 °C and 302 °C, respectively. The glass transition temperatures ranged from 141.5 to 177.5 °C and from 153.8 to 200.9 °C for the substrates and for the modified copolymers, respectively. Preliminary investigations showed fluorescence activity for all copolymers bearing azo-moieties.

1. Introduction

Cyclic imino ethers, also known as 2-oxazolines generated a considerable amount of research since their discovery by Kagiya in 1960s [1–6]. The 2-oxazolines can be polymerized only by cationic ring-opening mechanism, leading to well-defined polymers of narrow average molecular weight distribution, through a living or quasi-living process. From the organic chemistry point of view the oxazoline ring can give hydrolysis, oxidation and addition reactions with organic acids, phenols, thiols or aniline [7,8]. Due to this variety of reactions, 2-oxazolines with dual functionality, which could undergo both radical and cationic polymerization, were early introduced by Kagiya with his original cyclic imino ether bearing an isopropenyl substituent attached in the 2-position of the oxazoline ring [9]. Depending on the reaction conditions, a variety of macromolecular architectures is available. For example, 2-vinyl-2-oxazoline can be polymerized by four mechanisms. The cationic ring-opening produces alkenyl substituted poly(ethyleneimine), while radical, anionic [9–12] or cationic polymerization [13,14] with retention of the oxazoline ring, give poly[1-(2-oxazoline-2-yl)alkene]s. The spontaneous polymerization during the process of N-alkylation of the 2-vinyl-2-oxazoline with a strong alkylating agent leads to poly[1-(3-alkyl-2-oxazolinium-2-yl)ethylene]s [15–19]. A series of reactive polymers were developed from these monomers, with aim to producing thermosets, adhesives, coatings, hydrogels and composites [8,20,21].

Polymers of 2-isopropenyl-2-oxazoline and its copolymers with methyl methacrylate or styrene, obtained through radical mechanism [9], were reported in the 1970s but their physical properties were not thoroughly investigated. Specific applications such as powder water-borne coatings and humidity sensors, rely on their ability to undergo polymer analogous reactions (cross-linking of oxazoline with dicarboxylic acids or ammonium salts) [22,23]. Compatibilization of immiscible polymers [24,25] and synthesis of glass-ionomer cements [26] emerged as another important area of application. Addition reactions of poly(2-isopropenyl-2-oxazoline) with carboxylic acids or thiols yielded poly(ester–amide)s and poly(thio-ester–amide)s, respectively [27,28]. These reactions provide highly effective modification, when working at elevated temperatures. These features underline the usefulness of the 2-isopropenyl-2-oxazoline (co)polymers in the synthesis of various polymeric structures if the modifying agent has a suitable acid group.

The design of molecular systems that change their physical and chemical properties in response to light is of interest because of a

---

[*] Corresponding author.
E-mail address: victor_jerca@yahoo.com (V.V. Jerca).

1381-5148/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.reactfunctpolym.2010.07.018

wide range of applications. Investigation of azobenzene derivatives as promising nonlinear optical materials relies on their advantages like easy preparation, increased solubility and high hyperpolarizability [29,30].

The numerous backbones used as scaffolds for azo-moieties, include methacrylates [31], maleimides [32], amide–imides [33], imides [34], thiophenes [35], urethanes [36], styrenes [37], and others [38,39]. A thorough survey of the literature background on polymers containing azobenzene derivatives reveal that the poly(oxazoline)s or related copolymers were never used as backbones for azo-moieties. The lack of data concerning the physical properties of such azo-polymers led us to investigate them.

However, it is known that azobenzene molecules do not fluoresce in solution with appreciable quantum yield due to their ability to undergo *trans–cis* isomerization [40]. Reports on tuning fluorescence properties of azobenzene derivatives mostly dealt with small organic molecules, rather than polymers. For instance, self-assembled membranes [41,42] built from azobenzene-containing amphiphiles, boron-substituted azobenzene [43,44] and ortho-metalated azobenzene complexes [45,46] were reported to exhibit fluorescence.

There are few papers in the literature dealing with azobenzene based polymers (main-chain or side-chain) exhibiting intense fluorescence at room temperature. Fluorescence emission from an azobenzene diblock copolymer-containing a hydrophilic quaternized poly(4-vinyl pyridine) and a hydrophobic liquid crystalline polymethacrylate bearing azobenzene side groups in solution was reported [47]. The micellization of the polymer in water induce the fluorescence emission at 450 nm upon excitation of azobenzene groups at 360 nm. Fluorescence in the 600 nm region was also noticed from some azobenzenes dendrimers due to the formation of J-aggregates [48].

One of the issues of successful use of azobenzene derivatives implies the availability of suitable matrix materials. It is believed that the structure of the chromophore can be tailored for this particular application, if suitable substituents are introduced into azobenzenes rings. Rau [49] proved that hydroxyazobenzene has fluorescence at room temperature, while Smitha and coworkers [50] recently reported that 4-(4-hydroxy-phenylazo)benzoic acid exhibits fluorescence activity. However, attempts to synthesize a fluorescent polymer starting from 4-(4-hydroxy-phenylazo)benzoic acid failed due to the synthetic approach.

The main objective of the current work is to obtain binary copolymers with controlled content of oxazoline units as scaffolds for tailored fluorescent dye, the 4-(4-hydroxy-3,5-dimethylphenylazo)benzoic acid, attached at the carboxyl function. Advanced physico-chemical characterization of the newly synthesized side-chain polymers as well as preliminary identification of the fluorescence activity are the subsidiary goals of the study.

2. Experimental

2.1. Materials

4-Aminobenzoic acid (ABN, Merck, 98%), 2,6-dimethyl phenol (DMP, Aldrich, 99.5%), tetrahydrofuran (THF, Merck, 99.5%) and diethyl ether (Merck, 99.5%), were used as such. Acetonitrile (Merck) was distilled from $CaCl_2$ prior to use. 2-Isopropenyl-2-oxazoline (IPRO, Aldrich), 2-ethyl-2-oxazoline (EtOZO, Aldrich), methyl methacrylate (MMA, Merck) and N,N-dimethylformamide (DMF, Merck) were purified by low pressure distillation. 2,2′-azobis(2-methylpropionitrile) (AIBN, Aldrich) was recrystallized from ethanol prior to use.

2.2. Physico-chemical characterization

2.2.1. General measurements

FT-IR spectra were recorded on a Bruker Vertex 70 spectrometer fitted with a Harrick MVP2 diamond ATR device. ^1H NMR spectra were recorded on a Varian Unity Inova 400 spectrometer in $CDCl_3$ and in DMSO-d$_6$, at 30 °C and at 60 °C, respectively. The number average molecular weights (Mn) have been evaluated by SEC with Agilent 1200 Series Refractive Index Detector, (G1310A)-ISO HPLC Pump; using dimethylformamide as eluent (flow rate 1 mL/min), against polystyrene standards (10^2–10^6 Da) at 23 °C. The thermal analysis (simultaneous TGA–DSC, MS hyphenated) was performed on a NETZSCH STA 449C Jupiter system, coupled to an Aeolos II MS detector. TGA–DSC were typically carried out, for all the samples, from ambient temperature up to 700 °C at a heating rate of 5 °C/min under helium gas flow. The elemental analysis was carried out on a Costech ECS 4010 CHNS analyzer. The UV–Vis spectra were recorded on a Varian Cary 100 Bio UV–Vis spectrophotometer. Steady-state fluorescence measurements were carried out on a Horiba-Jobin-Yvon Fluoromax 4P spectrofluorimeter. Excitation was set at 262 nm recording the emission in the 280–580 nm range, and at 380 nm monitoring the emission from 400 to 550 nm.

2.2.2. Theory section

The composition dependence of the copolymer T_g was analyzed using Fox (Eq. (1)) [51] and Gordon–Taylor (Eq. (2)) models [52].

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{1}$$

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \tag{2}$$

T_g is the glass transition temperature of copolymer, w_i and T_{gi} are the weight fractions and the T_g values of the homopolymers, respectively; the subscript 2 refers to the component with the higher T_g. The constant k takes account of the specific coefficients of expansion of the two homopolymers 1 and 2 in the melt (liquid or rubbery state) and in the glassy state as follows:

$$\frac{\Delta\alpha_2 \rho_1}{\Delta\alpha_1 \rho_2} \tag{3}$$

where ρ_i, is the density of the polymer i and $\Delta\alpha_i$ is the change in cubic expansion coefficient of the ith component at its glass transition temperature. In most cases k is used as an adjustable parameter.

2.3. Synthesis

2.3.1. Synthesis of 4-(4-hydroxy-3,5-dimethylphenylazo)benzoic acid (C_0) [53]

ABN (50.8 mmole) was mixed with 10 mL H_2O and $NaNO_2$ (51 mmole) to form a paste, which was subsequently poured into a mixture of crushed ice (15–20 g) and 18 mL HCl (36%). The reaction was carried out for 0.5 h in an ice bath. The diazonium solution was allowed to warm up to room temperature and then slowly added over the phenoxide solution prepared as follows: DMP (50.9 mmole) was dissolved in sodium hydroxide solution (100 mL warm water with NaOH (51 mmole) and Na_2CO_3 (51 mmole). The reaction was left to continue overnight. Then, the crude precipitate was filtered off and washed several times with saline water (saturated), and finally, dried under vacuum at 60 °C for 24 h. The obtained orange crystals, recrystallised from chloroform, have mp: 226–228 °C, yield: 80%; λ_{max} (DMSO): 370 nm. ^1H NMR (DMSO-d$_6$, 30 °C) δ (ppm): 8.02–8.20 (d, J = 8.4 Hz, 2 aromatic H ortho to COOH), 7.75–8 (d, J = 8.0 Hz, 2 aromatic H meta to COOH), 7.59 (s, 2 aromatic H meta to OH), 2.26 (s, 6H); ^{13}C NMR (DMSO-d_6, 30 °C) δ (ppm): 166.78, 157.66, 154.64, 144.98, 131.68, 130.50, 124.99, 123.73, 121.94, 16.62. Elem. Anal. Calcd. C, 66.66%, H, 5.22%, N, 10.36%; Found C, 66.65%, H, 5.22%, N, 10.38%. FT-IR (ATR) ν (cm^{-1}): 3384 br (OH), 1681 (C=O).

2.3.2. Synthesis of 2-isopropenyl-2-oxazoline–methyl methacrylate copolymers (P_x)

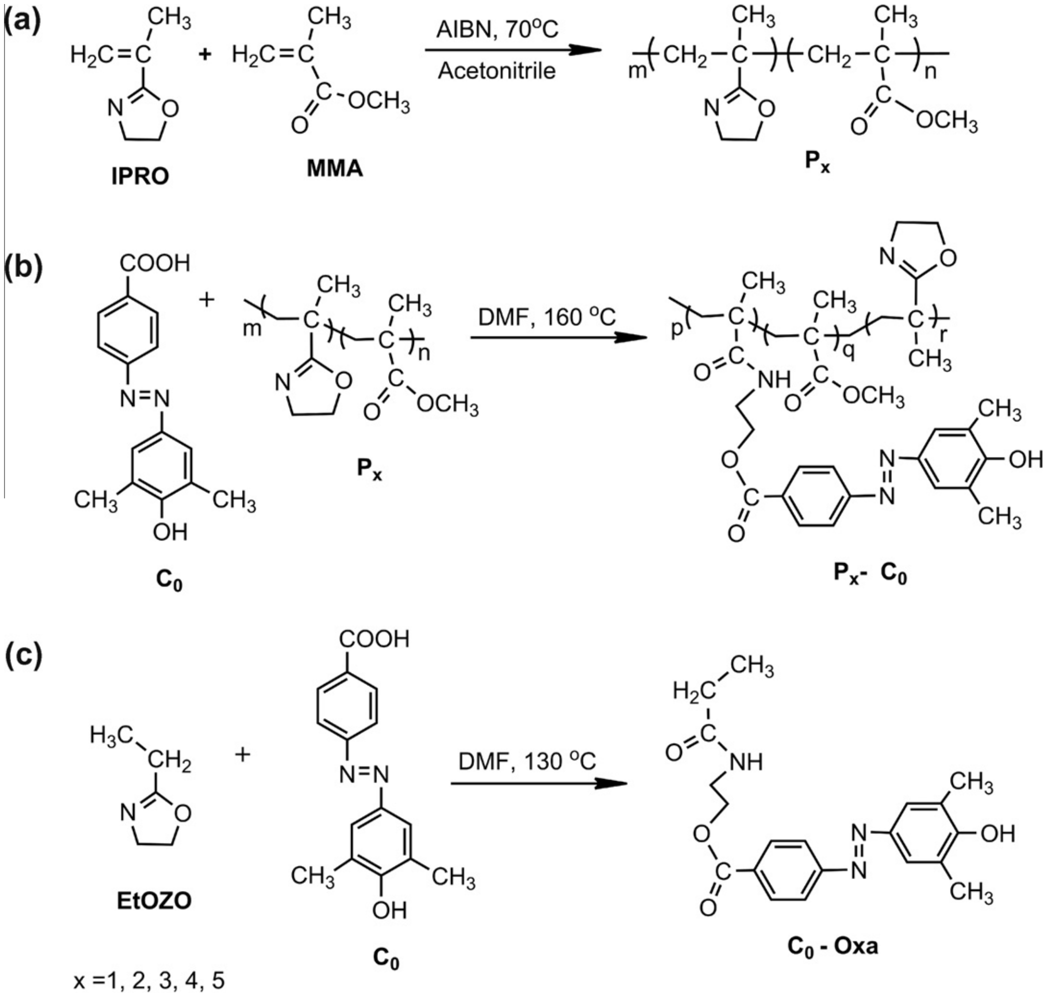
IPRO was copolymerized with MMA using the following molar feed ratios between comonomers: IPRO:MMA = 4:1, IPRO:MMA = 2.33:1, IPRO:MMA = 1:1, IPRO:MMA = 1:2.33 and IPRO:MMA = 1:4, respectively (see Scheme 1a).

A representative copolymerization was as follows: 4.5 mmole of IPRO and 4.5 mmole of MMA were taken in a vial. Then, AIBN (5×10^{-3} M) and 2 mL of freshly distilled acetonitrile were added to prepare the final solutions. The resulting mixture was well degassed and sealed off under argon cushion. The polymerizations were carried out at 70 °C for 24 h. After cooling at room temperature, the solutions were precipitated in diethyl ether. The copolymers were purified from unreacted monomers by reprecipitation from THF in diethyl ether. Subsequently, the products were dried under vacuum at 70 °C for 48 h. A homopolymer of IPRO (P_0) was synthesized under the same conditions and purified in the same manner as the MMA–IPRO copolymers. All copolymers were obtained with good purities and with the following yields: P_0 60%; P_1 65%; P_2 69%; P_3 71%; P_4 81%; P_5 83%. ^{1}H NMR for P_3 (DMSO-d_6, 30 °C) δ (ppm): 3.9–4.2 (2 aliphatic protons vicinal to oxygen atom in oxazoline ring), 3.6–3.85 (2 aliphatic protons vicinal to nitrogen atom in oxazoline ring), 3.37–3.6 (OCH_3 protons form MMA), 1.4–2 (methylene protons from the backbone both IPRO and MMA), 0.5–1.3 (methyl protons from the backbone both IPRO and MMA). When calculating the reactivity ratios, we used only samples having the conversions of the comonomers less than 20%.

2.3.3. Synthesis of azo-dye functionalized copolymers (P_x-C_0)

The modified copolymers were obtained by oxazoline ring-opening addition in the presence of C_0 (see Scheme 1b). In a typical run, 15 mL of dried DMF were added to 1.33 mmole of C_0 and 2.37 mmole of P_3 (IPRO units: 1.21 mmole) in a round bottom flask. The solution was heated at 160 °C and left under stirring for 10 h. The reaction mixture was precipitated in diethyl ether after cooling and the resulting coloured polymer was filtered and dried. The product was purified twice by reprecipitation from THF in diethyl ether and dried at 60 °C for 48 h under vacuum. The polymer analogous reaction for P_0 homopolymer was carried out under the same conditions, leading to the modified homopolymer P_0-C_0.

^{1}H NMR for P_3-C_0 (DMSO-d_6, 30 °C) δ (ppm): 7.96–8.34 (2 aromatic H ortho to COOH), 7.69–7.94 (2 aromatic H meta to COOH), 7.36–7.67 (2 aromatic H meta to OH), 4.18–4.5 (2 aliphatic protons vicinal to ester group), 2.7–3.7 (2 aliphatic protons vicinal to amide group overlap with OCH_3 protons form MMA), 2.1–2.36 (6H), 1.4–2



Scheme 1. Synthetic route for P_x, the related P_x-C_0s copolymers, and the C_0-Oxa structure.

(methylene protons from the backbone both IPRO and MMA), 0.5–1.3 (methyl protons from the backbone both IPRO and MMA).

2.3.4. Synthesis of 2-propionamidoethyl 4-(4-hydroxy-3,5-dimethylphenylazo) benzoate (C_0-Oxa)

1.85 mmole of C_0 was dissolved in 10 mL DMF, then 1.85 mmole of EtOZO was added under continuous stirring (see Scheme 1c). The mixture was heated at 130 °C and the reaction was allowed to continue for 10 h. After that, the solvent was removed under reduced pressure. A carrot-orange compound was obtained after recrystallization from benzene. Yield: 80%; mp: 138 °C, UV–Vis λ_{max} (DMSO): 380 nm; λ_{max} (THF): 373 nm; λ_{max} (Dioxane): 368 nm; λ_{max} (CH_2Cl_2): 364 nm. The molar extinction coefficient (ε = 23,552 L/mol cm) was calculated in DMSO, due to the fact that the final polymers (P_x-C_0) were investigated in the same solvent. ^{1}H NMR ($CDCl_3$, 30 °C) δ (ppm): 8.09–8.18 (d, J = 8.7 Hz, 2 aromatic H ortho to COOH), 7.82–7.9 (d, J = 8.8 Hz, 2 aromatic H meta to COOH), 7.64 (s, 2 aromatic H meta to OH), 4.39–4.51 (t, J = 5.3 Hz, 2 aliphatic protons vicinal to ester group), 3.6–3.77 (dd, J = 5.5 Hz, J = 10.8 Hz, 2 aliphatic protons vicinal to amide group), 1.96 (s, 6H), 1.7–1.98 (q, J = 7.6 Hz, 2H), 0.72–0.9 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 30 °C) δ (in ppm): 174.46, 166.47, 156.46, 155.79, 146.38, 130.76, 130.51, 124.31, 124.20, 122.42, 64.09, 39.08, 29.80, 16.24, 9.92. Elem. Anal. Calcd. C, 65.03%, H, 6.28%, N, 11.37%; Found C, 65.05%, H, 6.22%, N, 11.38%. FT-IR (ATR) ν (cm^{-1}): 3277 (br OH, NH), 1721 (C=O), 1620 (amide I), 1556 (amide II).

3. Results and discussion

The present study addresses a very interesting issue which is the synthesis of azo-dye fluorescent polymers. Firstly a fluorescent azobenzene dye with designed functions (hydroxyl for fluorescence properties and carboxyl for chemical linkage) was synthesized and its fluorescent properties were investigated. Secondly a synthetic strategy was developed in order to preserve this property onto polymeric structures.

The first step consisted in the preparation of several IPRO–MMA copolymers by radical copolymerization with controllable oxazoline content. The second step was based on the quantitative addition reactions of oxazoline (co)polymers with carboxylic acid. Thus, we were able to obtain structures with desired azobenzene content and tune up their fluorescent properties.

3.1. Solubility, kinetics and molecular weights

The P_x polymers showed excellent solubility in polar solvents, such as: $CHCl_3$, CH_2Cl_2, dichlorobenzene, dioxane, THF, acetone, DMF, dimethylsulfoxide, and even in alcohols. The solubility in alcohols and water increases with the IPRO content. The chemically modified structures (P_x-C_0s) became insoluble in chlorinated solvents, while P_{3-5}-C_0 remained partially soluble in THF. Dimethylsulfoxide and DMF proved to be the best solvents for all copolymers.

The P_x copolymer molar compositions were determined by two different methods, namely: elemental analysis and ^{1}H NMR spectroscopy (see Table 1). The compositions given by elemental analysis were calculated based on nitrogen content, while the compositions given by ^{1}H NMR spectroscopy were calculated based on the O—CH_2 protons integral at 3.9–4.2 ppm from the oxazoline ring against the methoxy protons integral at 3.37–3.6 ppm from MMA. The values provided by these two methods of characterization were almost identical, consequently we consider the copolymer compositions reliable ones.

The MMA–IPRO system was investigated for the first time by Kagya et al. in benzene in 1970 [9]. They reported only monomer reactivity ratios (at low conversions), calculated by differential methods such as Fineman–Ross (FR) or Kelen–Tüdös (KT), and the corresponding "Q–e values". No investigations regarding the physical properties were given. We used an integral method and software, namely the *OptPex2 program* provided by Hagiopol and his coworkers [54], to calculate reactivity ratios and the corresponding "Q–e" values. Using the molar compositions given by ^{1}H NMR, the reactivity ratios were calculated and the values are listed in Table 2 together with the "Q–e" values. The reactivity ratios obtained by us are slightly different from those reported by Kagya and coworkers, probably due to the better accuracy of the integral method. The r_1 and r_2 values are very close to one another, pointing out that both radicals are more reactive towards the other monomer (cross-propagation). The diagram of composition was plotted for MMA–IPRO system (see Fig. 1), to underline its particularities. In our case, the behaviour is not ideal; though we can notice an azeotrope point at exactly 0.5 M fraction. This type of diagram and the value of $r_1r_2 < 1$ reveals a statistic distribution of monomer units in the copolymers backbone.

High number average molecular weights (Mn) were attained by copolymerization and the values are given for all P_x copolymers in

Table 1
Physical features for P_x and the related P_x-C_0 copolymers.

Polymer code	IPRO feed fraction	[a]Cop. comp.	[b]Cop. comp.	Mn (Da)	PDI	T_g (°C)	[c]T_d (°C)
P_0	1	1	1	25,500	1.97	177.5	371.0
P_1	0.8	0.74	0.74	26,300	1.88	166.1	352.8
P_2	0.7	0.66	0.66	27,700	1.85	162.3	348.4
P_3	0.5	0.50	0.52	28,900	1.79	152.5	328.8
P_4	0.3	0.35	0.34	29,600	1.61	146	329.4
P_5	0.2	0.25	0.26	30,500	1.49	141.5	317.0
Polymer code	Yield (%)	[a]Cop. comp.	[d]Deg. (%)	[e]Deg. (%)	[f]Deg. (%)	T_g (°C)	[c]T_d (°C)
P_0-C_0	44	1	95	95	96	200.9	255.4
P_1-C_0	59	0.74	92	94	95	188	261.4
P_2-C_0	65	0.66	90	94	93	186.2	271.0
P_3-C_0	70	0.50	98	96	97	175.6	276.4
P_4-C_0	84	0.35	90	93	94	168.9	286.8
P_5-C_0	91	0.25	89	90	92	153.8	302.6

IPRO molar fraction in copolymer.
[a] Given by ^{1}H NMR.
[b] Given by elemental analysis.
[c] Temperature represents 10% weight loss in TGA measurements at heating rate of 5 °C/min degree of substitution at IPRO units.
[d] Given by ^{1}H NMR.
[e] Given by Elem. Anal.
[f] Given by UV–Vis.

Table 2
Reactivity ratios and "Q–e" values for MMA–IPRO system.

Polymer code	Conv (%)	IPRO feed fraction	[a]Cop. comp.	[b]r_1	r_2	Q_1	e_1
P_1	15.1	0.8	0.74	0.71	0.63	1.77	1.29
P_2	16.2	0.7	0.66				
P_3	14.9	0.5	0.50				
P_4	14	0.3	0.35				
P_5	16.5	0.2	0.25				

[a] Given by ^{1}H NMR.
[b] IPRO was considered as the first monomer.

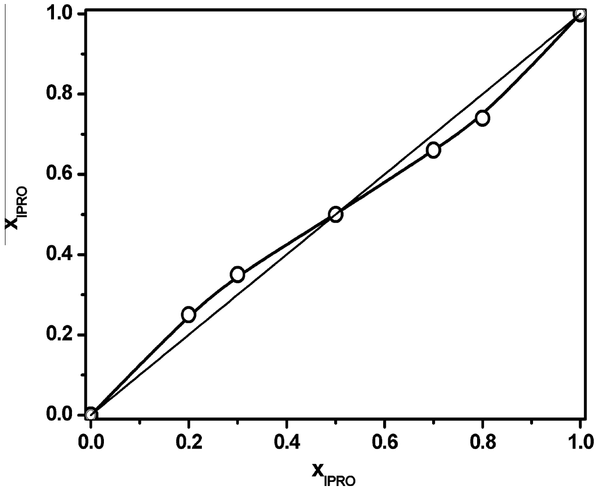


Fig. 1. The diagram of composition for P_x copolymers.

Table 1 together with their polydispersity indices (PDI). The theoretical values of Mw/Mn for polymers produced via radical combination and disproportionation are 1.5 and 2.0, respectively [55]. The polydispersity index of P_0 suggested that chain termination by disproportionation outweighs coupling, consistent with increased rigidity of the chains provided by the high IPRO contents. The values of Mw/Mn in copolymerization are also known to depend on chain termination in the same way as in homopolymerization [56]. The values of Mw/Mn for the copolymers suggested a tendency for chain termination by disproportionation at high IPRO feed and chains termination by combination at low IPRO feed ratios.

3.2. Thermal analysis

The copolymer T_g values ranged between 106–177.5 °C, and 106–200.9 °C for the P_x and P_x-C_0, respectively. Also, it can be noticed that the glass transition temperatures increased with the content of the oxazoline or C_0 units in copolymers (see Table 1). The variation of T_g with the composition of the copolymers is shown in Fig. 2. The glass transition temperatures of P_x copolymers increase rapidly and nonlinearly in the 0–0.3 range of weight fraction of IPRO units. In this interval, the polymer analogous reaction induces a steep increase of T_g. For molar fractions of IPRO units in copolymer higher than 0.3, the chemical modification regularly rises the T_g by 20 °C.

Fox (Eq. (1)) and Gordon–Taylor (Eq. (2)) equations were used to fit the experimental T_g data of the P_x and P_x-C_0 copolymers.

One may see that the experimental T_g values for both modified and unmodified copolymers do not agree with the theoretical values predicted by Fox equation (Fig. 2), which assumes that the T_g of a copolymer depends only on the relative amounts of each monomer and T_g of the respective pure homopolymers. Therefore, we used the Gordon–Taylor method which takes into account the densities and the change in expansivity at the glass transition of the homopolymers. Fig. 2 shows the best fit curve based on the Gordon–Taylor equation, where k is 0.48 for P_x and 0.36 for P_x-C_0 (k was taken as adjustable parameter). The reasonable prediction of the Gordon–Taylor equation for T_g composition curve of P_x and P_x-C_0 sustained the fact that the copolymers have a random distribution.

The thermal stability was investigated for all copolymers by TGA analysis. Again, in P_x series the thermal stability (T_d, temperature at 10% weight loss) was influenced by the molar content of IPRO units. The best T_d was attained by the P_0 homopolymer, due to a better stability of the oxazoline heterocycle towards the ester bonds from MMA units (see Table 1). The situation is quite reversed in the P_x-C_0 series; consequently, the thermal stability decreased with the increase of molar content of C_0 moieties. This reversed situation is directly linked to the thermal degradation of the azo-moiety (C_0). Previous studies were carried out by Smitha regarding the thermal degradation of this particular azo-dye [57]. The reported T_d of C_0 was in the range of 237 °C. According to our TGA–MS analysis, the first step of weight loss is attributed to

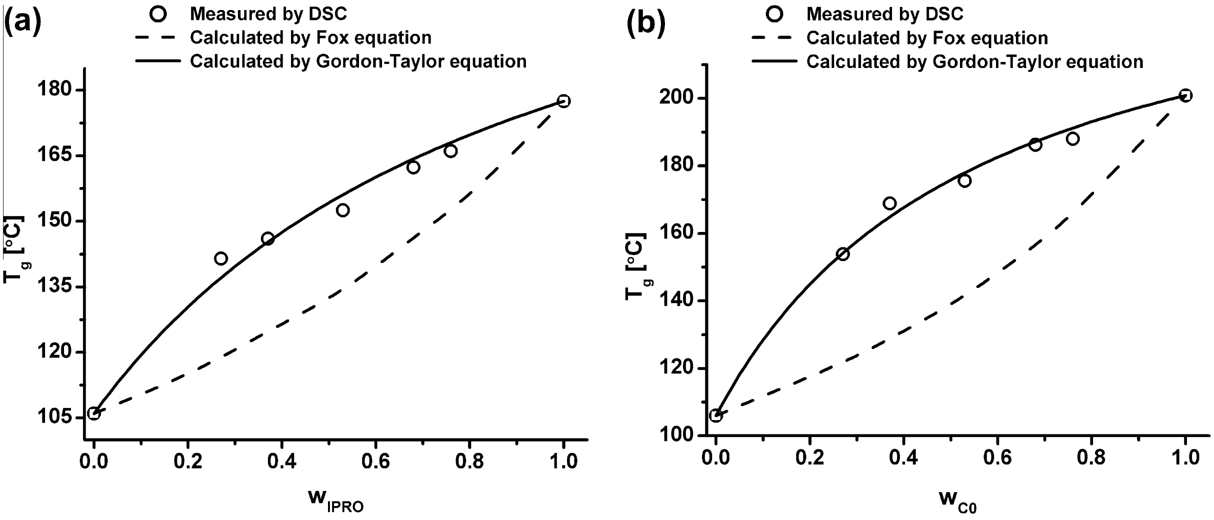


Fig. 2. The dependence of T_g-s as a function of weight fractions for P_x copolymers (a); the dependence of T_g-s as a function of weight fractions for P_x-C_0 copolymers (b).

several fragments that came out from the scission of N=N double bonds, which are known as most unstable. Mass fragments corresponding to nitrogen ($m/z = 28$) and aromatic ring ($m/z = 76$) could be detected in the first degradation step. Therefore, the more azo-moieties are present in the copolymers, the lower the thermal stability is. The elimination of CO_2 due to α-quaternary (both aromatic and aliphatic) ester linkages took place at higher temperature.

3.3. FT-IR characterization

The FT-IR spectra were recorded for all copolymers (P_xs and P_x-C_0s) and, homopolymers (P_0 and the related P_0-C_0). After the polymer analogous reaction took place, a significant spectral change was noticed in all P_x-C_0s. When the oxazoline ring opens, an *ester–amide* group is generated due to the linkage of C_0 onto the P_x backbone (see Scheme 1b). To underline this, the IR spectrum of P_0 is given in Fig. 3a together with that of the modified homopolymer (P_0-C_0). The P_0 spectrum showed characteristic absorptions of oxazoline ring at 1651 and 1118 cm^{-1} attributable to C=N and C—O stretching, while other ring skeletal vibrations can be found at 986 and 951 cm^{-1}. The sharp band at 1651 cm^{-1} from the former P_0 spectrum appeared as a broad band in the current P_0-C_0 spectrum due to the absorption of amide I ($\nu_{C=O}$) band. The amide II band (ν_{C-N}) can be found at 1520 cm^{-1} in the P_0-C_0 spectrum along with the characteristic ester bands ($\nu_{C=O}$, ν_{C-O-C} and ν_{C-O}) at 1710, 1265 and 1115 cm^{-1}, respectively. The band at 1596 cm^{-1} from the P_0-C_0 spectrum can be assigned to the substituted benzene rings vibrations from the azo-moiety. Also, the *trans* N=N absorption band from the azo-dye can be found at 1478 cm^{-1}.

The FT-IR spectra for the P_{1-5} and related P_x-C_0 copolymers are more complicated since the MMA units contribute to the abundance of esters groups. Nevertheless, the same ester–amide group is formed in the case P_x-C_0s too and its typical absorptions could be identified at 1712 ($\nu_{C=O}$), 1262 and 1115 (ν_{C-O-C} and ν_{C-O}), 1648 (amide I, $\nu_{C=O}$) and 1521 (amide II, ν_{C-N}), all in cm^{-1}. The P_x-C_0s spectra are given together in Fig. 3b to underline some of their particularities. One may notice that the intensity of the amide II peak increases with the molar ratio of IPRO in the P_x copolymers (see arrow). The same tendency has the peak at 1595 cm^{-1} from the azo-moiety of the benzene rings. We can conclude that the azo-dye content is proportional with the oxazoline units and increases in the following order: P_5-C_0 < P_4-C_0 < P_3-C_0 < P_2-C_0 < P_1-C_0. The amide I peak cannot be discussed as the former one since it may overlap with the peak from the residual oxazoline ring. The peak at 1712 cm^{-1} ($\nu_{C=O}$) is affected by errors since it results from overlapping of two different carbonyl stretching vibrations. This peak is useful for identifying newly formed ester group in IPRO homopolymer only.

3.4. ^{1}H NMR characterization

The related P_x-C_0s were also characterized by ^{1}H NMR spectroscopy. After the ring-opening, the distinctive signals of —CH_2—O— group at 4.12 ppm are shifted downfield at 4.37 ppm, while the signals from —CH_2—N= group that appear like a shoulder at 3.7 ppm in the P_4 spectrum are shifted upfield under the signal of methoxy groups (—OCH_3) at 3.5 ppm in the P_4-C_0 spectrum. Furthermore, the aromatic protons from the azo-moiety show up at 7.5 to 8.2 ppm in the P_4-C_0 spectrum due to the chemical linkage, while the o,o′-methyl signals can be found at 2.25 ppm. The backbone protons lie in the range of 0.5–2.0 ppm in both P_4 and P_4-C_0 spectra. The degree of chemical modification (Deg.%) was appreciated from the P_x-C_0s spectra based on the areas of aromatic signals relatively to those of the backbone. The values are summarized in Table 1. According to these values, an almost quantitative modification was obtained on P_x copolymers (regardless of their initial compositions). Typical examples of ^{1}H NMR spectra are given in Fig. 4 for P_4-C_0 in contrast with its initial copolymer P_4. These features were displayed by all P_x-C_0s.

3.5. UV–Vis characterization

To determine with accuracy the C_0 content in the modified copolymers we synthesized the C_0-Oxa structure. This saturated

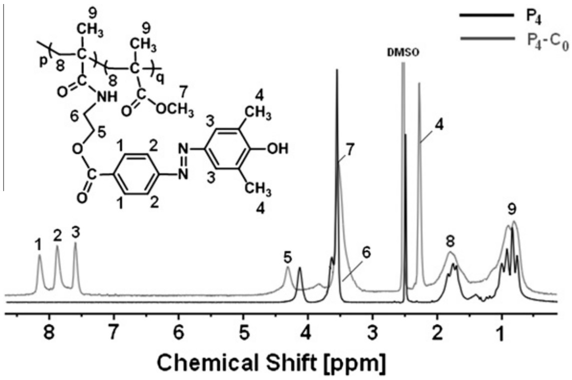


Fig. 4. The ^{1}H NMR spectra for P_4 and P_4-C_0 copolymers.

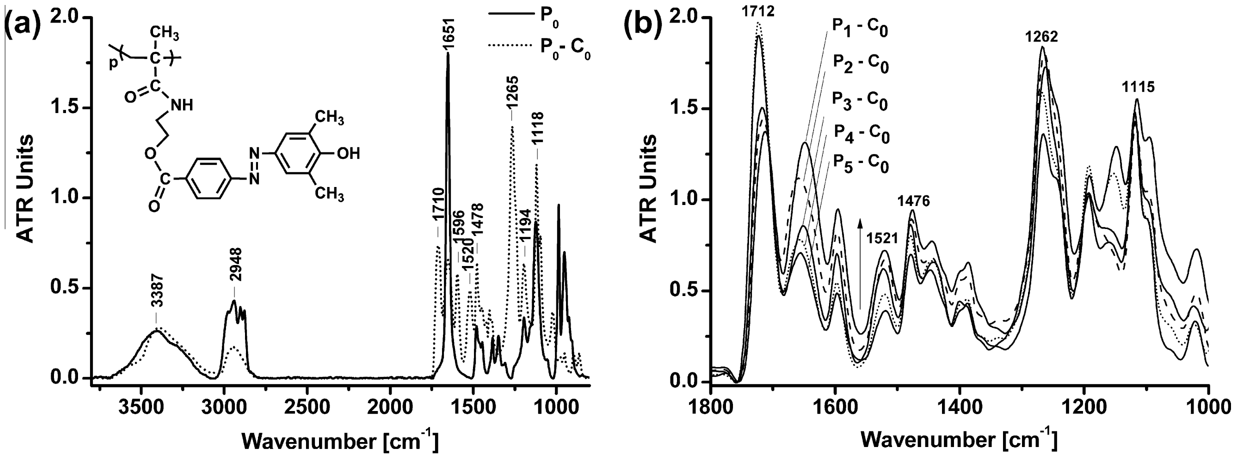


Fig. 3. The FT-IR spectra for P_0 and P_0-C_0 polymers (a), and for the P_x-C_0 copolymers (b).

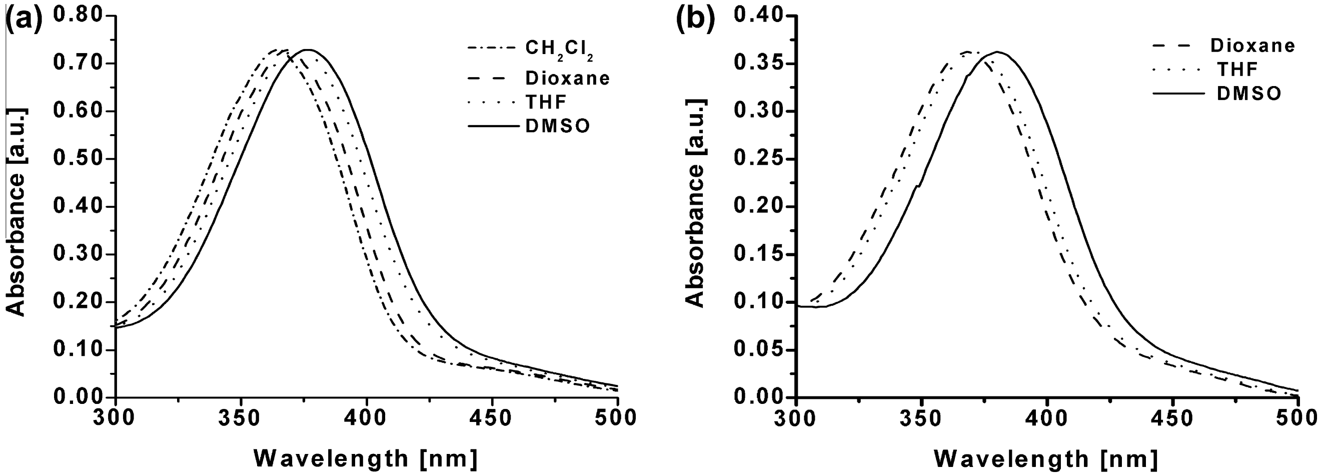


Fig. 5. The UV–Vis spectra for C_0-Oxa in different solvents at 3×10^{-5} M (a); the UV–Vis spectra for P_3-C_0 copolymers in different solvents at 3×10^{-5} M (b).

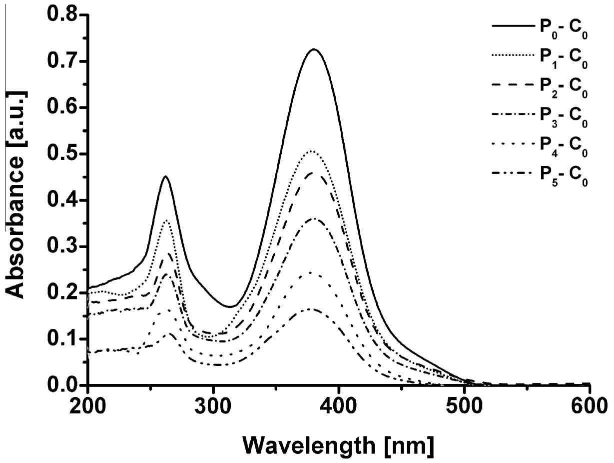


Fig. 6. The UV–Vis spectra for P_x-C_0 copolymers at 3×10^{-5} M in DMSO.

structure is similar with the units found in all P_x-C_0 (co)polymers after ring-opening. The UV–Vis spectra of C_0-Oxa in DMSO had an absorption maxima at $\lambda = 380$ nm which corresponds to a π–π^* first single electron transition, while the maximum at 262 nm can be attributed to the π–π^* transitions of the aromatic rings. The molar extinction coefficient, ε, was determined for the first absorption band (380 nm, red shifted towards C_0 $\lambda_{max} = 370$ nm) and used to calculate the degree of C_0 addition to IPRO rings for all polymers; the values are given together in Table 1. Solvatochromic effects of C_0-Oxa were also investigated. The extent of solvatochromic response is related to the molecular polarizability. The solvatochromic shifts in solvents of varying polarities like dioxane, THF, dichloromethane and DMSO are shown in Fig. 5a. The C_0-Oxa showed a positive solvatochromism with the maximum shift in DMSO suggesting higher polarizability in this solvent. Such behaviour is characteristic for charge-transfer transitions with an increase of dipole moment upon excitation. This behaviour was preserved upon modification of the P_x copolymers with C_0 (see Fig. 5b). P_3-C_0 was chosen for exemplification due to its similar solubility as the C_0-Oxa. The solvatochromic response is almost identical with the C_0-Oxa in dioxane, THF and DMSO. Dichlormethane became out of question due to the fact that all the modified copolymers, regardless their C_0 ratio, are insoluble. This proves that our synthesis strategy was a successful one in preserving intact the optical properties of the C_0-Oxa structure when it was embedded in oxazoline polymeric structures.

The absorption spectra of all P_x-C_0 polymers showed two intense bands at 262 and 380 nm in the UV spectral region (Fig. 6).

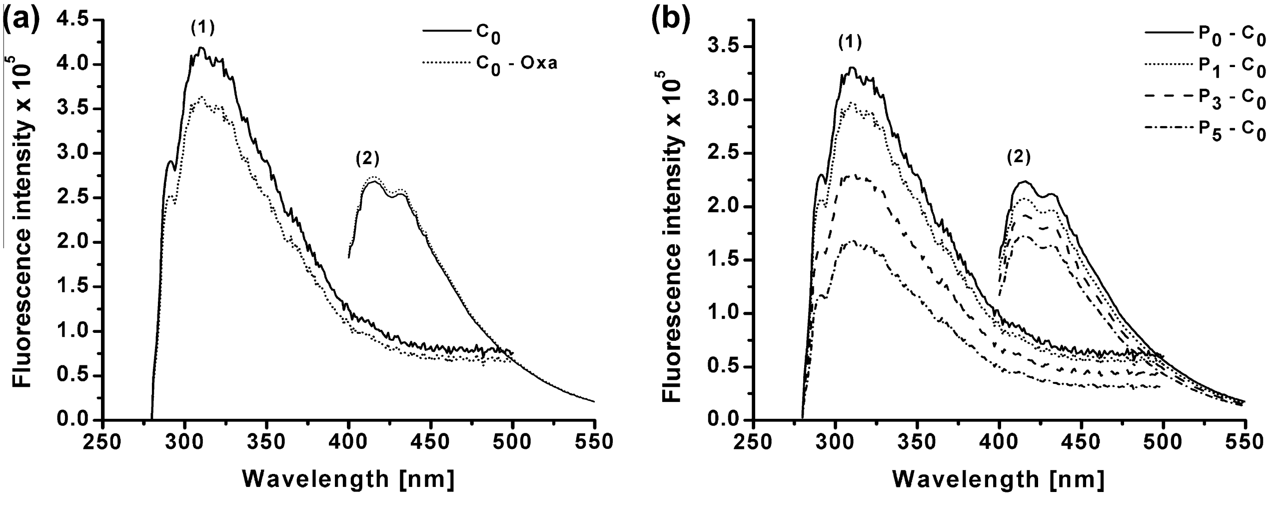


Fig. 7. Emission spectra for the C_0 and C_0-Oxa (a), and P_x-C_0 copolymers (b) at 3×10^{-5} M; $\lambda_{excitation} = 262$ nm (1) and $\lambda_{excitation} = 380$ nm (2).

We can notice that the absorbance decreases in intensity in the same order that the C_0 content decreases, when the molar concentration of modified copolymers is kept constant at 3×10^{-5} M.

3.6. Fluorescence characterization

The fluorescence of hydroxy azobenzene can be explained in terms of azo-hydrazone tautomerism [49]. Smitha and Asha [50] synthesized an azo-dye polymer with a similar structure starting from 4-(4-hydroxy-phenylazo)benzoic acid methyl ester. They mentioned that the fluorescence was lost upon coupling the azo-dye with methacryloyl chloride and subsequent polymerization. This fact sustained the idea that the emission properties are due to the hydrazone form. For that reason, we used a different synthetic strategy that preserved the hydroxyl group. At the same time, supplementary methyl groups were introduced in the 3′ and 5′ positions of the benzene rings, because they are known to shifting the tautomeric equilibrium towards the hydrazone species [58].

Solutions of C_0, C_0-Oxa and P_x-C_0 (3×10^{-5} M) in DMSO were excited at 262 nm corresponding to the π–π^* transition of the fluorophore. The C_0 had the highest fluorescence emission intensity, while the emission intensity of P_x-C_0 copolymers was slightly reduced as compared to C_0-Oxa (see Fig. 7). The emission intensity of the polymers is directly related to the content of azo-dye, and increases with the molar ratio of the chromophore. The emission spectra at the π–π^* transition of the azobenzene units ($\lambda_{\text{excitation}}$ = 380 nm) were recorded for all the above-mentioned solutions. The C_0 and C_0-Oxa had identical spectra (the profiles are given in Fig. 7a); suggesting that the newly formed ester–amide structure does not interfere with the emissive properties of C_0.

We ascribe the lower intensity of P_0-C_0 as compared to the C_0-Oxa to the azo-hydrazone tautomerism. The tautomerism in polymers is shifted toward the azo form due to the interactions between chains. The same dependence of fluorescence intensity on the molar ratio of azo-dye was noticed in all our polymers (Fig. 7b). However, we have to stress that here we reported only preliminary results; further investigations on this matter are now in progress and will be reported later.

4. Conclusions

The MMA–IPRO was the ideal system in our experiments due to an excellent control upon the IPRO units in copolymer. The azophores content in copolymers can be adjusted either from the reaction time of the analogous substitution or from feed molar ratio. Therefore, if a higher content of azo-dye is required then the P_0 homopolymer would be an excellent choice, while other different compositions can be provided by the P_x-C_0 copolymers. The ring-opening method can be easily used to design other side-chain polymers, without laborious work, keeping intact all features provided by the first step of polymerization. The polymer analogous reaction took place with a high degree of substitution, regardless of the P_x molar content in IPRO units. The molar compositions for P_x-C_0s were appreciated from three distinct methods of characterization, which were in a good agreement with one another. The modified polymers (P_x-C_0) exhibited higher glass transition temperatures compared to the P_x copolymers, while the thermal stability decreased due to the azobenzene moieties. Our original synthetic approach favours, at least partially, the retaining of the fluorescent activity in copolymers. These results suggest that a balanced choice of chemical substituents and embedding environment can be valuable for exploitation of the azo-hydrazone tautomerism of C_0 in fluorescence applications.

Acknowledgements

This work was partially achieved by means of PN2 CNMP Parteneriate 71-029 “Nabieco” and 31-056 “Biopolact” Projects (financed by the Romanian Ministry of Education & Research), and PN-II-ID-2008-2 “Macromolecular materials containing chromophores” Project (financed by Romanian National Council for Scientific Research in Higher Education).

References

[1] K. Aoi, M. Okada, Prog. Polym. Sci. 21 (1996) 151–208.
[2] R. Hoogenboom, Angew. Chem. Int. Ed. 48 (2009) 7978–7994.
[3] S. Kobayashi, H. Uyama, J. Polym. Sci. Part A: Polym. Chem. 40 (2002) 192–209.
[4] A. Levy, J. Polym. Sci. Part A: Polym. Chem. 6 (1968) 57–62.
[5] A. Levy, M. Litt, J. Polym. Sci. Part A: Polym. Chem. 6 (1968) 1883–1894.
[6] R. Hoogenboom, Macromol. Chem. Phys. 208 (2007) 18–25.
[7] J.A. Frump, Chem. Rev. 71 (1971) 483–505.
[8] B.M. Culbertson, Prog. Polym. Sci. 27 (2002) 579–626.
[9] T. Kagiya, T. Matsuda, M. Nakato, R. Hirata, J. Macromol. Sci. Chem. 6 (1972) 1631.
[10] J.M. Havard, M. Yoshida, D. Pasini, N. Vladimirov, J.M.J. Frechet, D.R. Medeiros, K. Patterson, S. Yamada, C.G. Willson, J.D. Byers, J. Polym. Sci. Part A: Polym. Chem. 37 (1999) 1225–1236.
[11] V.V. Jerca, A.F. Nicolescu, A.-M. Albu, D.M. Vuluga, Mol. Cryst. Liq. Cryst. 483 (2008) 78–88.
[12] Z. Ning, H. Stephan, S. Anita, L. Robert, J. Rainer, Macromolecules 42 (2009) 2215–2221.
[13] M. Masatoshi, L. Peter, K. Shin-ya, S. Takeo, Polym. Bull. 34 (1995) 249–256.
[14] D.A. Tomalia, B.P. Thill, M.J. Fazio, Polym. J. 12 (1980) 661–675.
[15] M. Miyamoto, Y. Sano, Y. Kimura, T. Saegusa, Macromolecules 18 (1985) 1641–1648.
[16] M. Miyamoto, Y. Sano, Y. Kimura, T. Saegusa, Makromol. Chem. 187 (1986) 1807–1817.
[17] M. Miyamoto, Y. Sano, T. Saegusa, Makromol. Chem. 187 (1986) 2747–2752.
[18] M. Miyamoto, Y. Sano, T. Saegusa, Polym. J. 19 (1987) 557–566.
[19] M. Miyamoto, Y. Sano, T. Saegusa, J. Macromol. Sci. A 25 (1988) 627–641.
[20] S. Nivedita, M. Amol, S. G, F. Sushmita, G. Hua, J. Appl. Polym. Sci. 117 (2010) 1718–1730.
[21] J.T. Yoona, W.H. Joa, M.S. Leeb, M.B. Koc, Polymer 42 (2001) 329–336.
[22] C.-W. Lee, H.-S. Park, M.-S. Gong, Sens. Actuators B 109 (2005) 256–263.
[23] D.L. Schmidt, R.F. Brady Jr., K. Lam, D.C. Schmidt, M.K. Chaudhury, Langmuir 20 (2004) 2830–2836.
[24] W.E. Baker, M. Saleem, Polymer 28 (1987) 2057–2062.
[25] H. Matthias, B. Matthias, L. Holger, G. Wolfram, M. Rolf, J. Polym. Sci. Part A: Polym. Chem. 36 (1998) 1821–1827.
[26] B.M. Culbertson, J. Dent. 34 (2006) 556–565.
[27] T. Nishikubo, A. Kameyama, H. Tokai, Polym. J. 28 (1996) 134–138.
[28] T. Kagiya, T. Matsuda, Polym. J. 3 (1972) 307–314.
[29] S.K. Yesodha, C.K.S. Pillai, N. Tsutsumi, Prog. Polym. Sci. 29 (2004) 45–74.
[30] Y. Zhao, T. Ikeda, Smart Light Responsive Materials-Azobenzene-Containing Polymers and Liquid Crystals, John Wiley & Sons, New Jersey, 2009.
[31] N.J. Li, J.M. Lu, X.W. Xia, Q.F. Xu, L.H. Wang, Polymer 50 (2009) 428–433.
[32] H.T. Pu, L. Liu, W.C. Jiang, X.W. Li, J.P. Chen, J. Appl. Polym. Sci. 108 (2008) 1378–1384.
[33] E. Schab-Balcerzak, B. Sapich, J. Stumpe, Polymer 46 (2005) 49–59.
[34] M. He, Y.M. Zhou, F. Dai, R. Liu, Y.P. Cui, T. Zhang, Polymer 50 (2009) 3924–3931.
[35] L.H. Gan, X.L. Xia, Y.C. Chan, X. Hu, X.Y. Zhao, Polym. Adv. Technol. 14 (2003) 260–265.
[36] Y. Sui, D. Wang, J. Yin, Z.K. Zhu, Z.G. Wang, Chem. Phys. Lett. 339 (2001) 186–190.
[37] A. Zerroukhi, A. Trouillet, D. Blanc, B. Boinon, A. Cachard, J.P. Montheard, J. Appl. Polym. Sci. 51 (1994) 1165–1173.
[38] X.B. Chen, J.J. Zhang, H.B. Zhang, Z.H. Jiang, G. Shi, Y.B. Li, Y.L. Song, Dyes Pigm. 77 (2008) 223–228.
[39] S. Suresh, R.J. Gulotty, S.E. Bales, M.N. Inbasekaran, M.A. Chartier, C. Cummins, D.W. Smith, Polymer 44 (2003) 5111–5117.
[40] H. Rau, Photoisomerization and photo-orientation of azobenzenes, in: Z. Sekkat, W. Knoll (Eds.), Photoreactive Organic Thin Films, Academic Press, Elsevier Science, 2002, pp. 3–38.
[41] M. Shimomura, T. Kunitake, J. Am. Chem. Soc. 109 (1987) 5175–5183.
[42] K. Tsuda, J. Am. Chem. Soc. 122 (2000) 3445–3452.
[43] J. Yoshino, N. Kano, T. Kawashima. Synthesis of the Most Intensely Fluorescent Azobenzene by Utilizing the b–n Interaction, 2007, pp. 559–561.
[44] J. Yoshino, N. Kano, T. Kawashima, Chem. Lett. 37 (2008) 960–961.
[45] M. Ghedini, D. Pucci, G. Calogero, F. Barigelletti, Chem. Phys. Lett. 267 (1997) 341–344.
[46] Y. Wakatsuki, H. Yamazaki, P.A. Grutsch, M. Santhanam, C. Kutal, J. Am. Chem. Soc. 107 (1985) 8153–8159.
[47] Q. Bo, Y. Zhao, Langmuir 23 (2007) 5746–5751.
[48] J. Nithyanandhan, N. Jayaraman, R. Davis, S. Das, Chem. Eur. J. 10 (2004) 689–698.

[49] H. Rau, Angew. Chem. Int. Ed. 12 (1973) 224–235.

[50] P. Smitha, S.K. Asha, J. Phys. Chem. B 111 (2007) 6364–6373.

[51] T.G. Fox, Bull. Am. Phys. Soc. 1 (1956) 123.

[52] M. Gordon, J.S. Taylor, J. Appl. Chem. 2 (1952) 493–500.

[53] F.A. Nicolescu, V.V. Jerca, C. Draghici, D.M. Vuluga, D.S. Vasilescu, Des. Monomers Polym. 12 (2009) 553–563.

[54] C. Hagiopol, Copolymerization-toward a Systematic Approach, Plenum Publisher, New York, 1999.

[55] S. Teramachi, A. Hasegara, M. Atasuka, A. Yamashita, N. Takemoto, Macromolecules 11 (1978) 1206–1210.

[56] H.W. Melville, B. Noble, W.F. Watson, J. Polym. Sci. 4 (1949) 629–637.

[57] P. Smitha, S.K. Asha, C.K.S. Pillai, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 4455–4468.

[58] J.-A. Farrera, I. Canal, P. Hidalgo-Fernandez, M.L. Perez-Garcia, O. Huertas, F.J. Luque, Chem. Eur. J. 14 (2008) 2277–2285.