Highly effective low temperature route to pyrroloperimidines synthesis and their copolymerization with styrene and methyl methacrylate

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ABSTRACT

A novel highly effective low temperature route to synthesis of perinone type compounds, namely pyrroloperimidines, based on catalytic cyclization reaction of amic acids was developed. According to this route a series of perinones with polymerizable double carbon–carbon bond were synthesized and their free radical copolymerizations with styrene and methyl methacrylate were investigated. It was shown that incorporation of the perinones into polymer chains occurs by homolytic cleavage of the carbon–carbon π-bond, and less conjugated structures, where this bond was more distanced from perimidine system, demonstrated higher activity in the radical polymerizations. The incorporation was complicated by limited solubility and chain transfer properties of the perinones, however, fluorescent colored copolymers of high molecular weights were obtained.

1. Introduction

Fused heterocyclic compounds of perinone type are known as dyes and pigments recommended for a wide range of industrial plastics [1–3]. Thanks to their highly conjugated structures these compounds have excellent resistance to heat and light and thus are able to sustain high plastic processing temperatures without destruction and to maintain the brightness of color even under long term sun exposure. If compounds additionally to the bright color demonstrate luminescent properties it significantly broadens possible applications for these dyestuffs [3,4]. Polymers filled with such compounds are of interest as potential materials for luminescent sensors of various purposes, for organic light emitting diodes and other optoelectronic devices [5,6]. Colorants are usually incorporated into plastics by dry blending prior to the processing or mixing previously prepared dispersed concentrate at an appropriate stage of the processing. However, the applications of such prepared polymer–colorant systems may be restricted mostly because of possible coagulation and migration of the dye out of the polymer matrix that results in loss of emitting efficiency, color brightness and commodity value. The restriction is especially severe when colored polymers are used for food packaging, drug and cosmetic applications; only a very few pigments are certified

for these purposes [2]. Modification of polymers by bonding covalently the colorant compound as a pedant group or as a part of backbone chain is a common practice to avoid the problems of the coagulation and migration and thus to overcome this drawback. For luminescent substances it helps to enhance the luminescent properties of the material by preventing dye selfquenching via the formation of nonemitting agglomerates, phase separation and some of the thermal relaxation limitations [7].

In order to use the covalent modification approach and incorporate the fused heterocyclic colored molecules into the polymer chain, the original parent structures must be modified by the addition of some functional groups which are active in polymerization reactions or may form chemical bonds reacting with the polymer matrix. However, because of the conjugated structure of the perinones the functional groups introduced do not demonstrate high reactivity in the reactions. Such synthesis of a series of functionalized perinones with high yields and their incorporation into polystyrene, polyolefins and polyesters by reactive extrusion have been reported [8–11]. In all the cases the incorporation occurred at quite elevated temperatures, 240–250 °C, and the temperature not depending on the nature of the polymer matrix. On the other hand using functionalized reagents in synthesis of the perinones is also restricted because of aggressive conditions of the synthesis. The most typical synthetic procedure is a reflux of the corresponding diamines with the anhydrides or acids in acetic acid or anhydride for several hours [4,8–12]. Sometimes reflux in solutions of sulfuric acid or such high boiling solvents as 1-chloronaphthalene,

nitrobenzene, phenol or *N*-**MP** was applied [3,4,12–15]. Under such severe conditions the functional groups may be easily affected by undesirable chemical reactions.

Much milder synthetic route was reported by Zimmer and Al-Khathlan [16], where the perinones were obtained in two steps. At first 1,8-diaminonaphthalene and appropriate acid anhydrides were refluxed in THF to give corresponding amino-imides, which then were converted into the perinones via intramolecular aza-Wittig cyclization in boiling methylene chloride. Though the conditions of the synthesis were mild enough it required more than 20 h to complete the reaction and the yield of the resulting product was quite low (about 25%). Moreover bromine used in this cyclization might react with double bonds or with another functional group.

The chemistry of *N-ortho*-hydroxy- and amino- substituted polyimides and their precursors, poly(amic acid)s, was investigated in detail by our group with the use of low molecular weight model compounds [17–21]. It was shown, for example, that the temperature of the imide to benzoxazole rearrangement depends on a leaving group nature and thus may be decreased by the substitution of the OH group with *o*-acetoxy or *o*-methoxy. The rearrangement started at much lower temperature when thermodynamically less stable isoimide structure was used instead of imide. Detailed investigation carried out on the model compounds revealed that *N-o*-substituted isoimides may even spontaneously rearrange to pyrrones, forming two fused five-membered heterocycles, in solution at room temperature with yield of 35%, as it is shown in Scheme 1. Moreover, the conversion dramatically increased almost to 100% yield, if the size of one of the fused heterorings formed during the secondary cyclization was raised from five- to six-members to afford thus fully cyclized five, six-membered fused heterocycle molecule of the perinone type [22]. Thus, the effect of the cycle size along with isoimide instability allowed us to design a highly effective low temperature synthetic route for perinone type molecules. The route easily permits including potentially reactive double bond in the perinone structure.

Here we described the synthesis of various perinones using this new method. Several of thus synthesized perinones have carbon–carbon double bond in their structures which may be active in addition polymerization reactions. Copolymerizations of these perinones with styrene and methyl methacrylate by free radical mechanism have been investigated; specific features of these copolymerizations and properties of the copolymers are discussed.
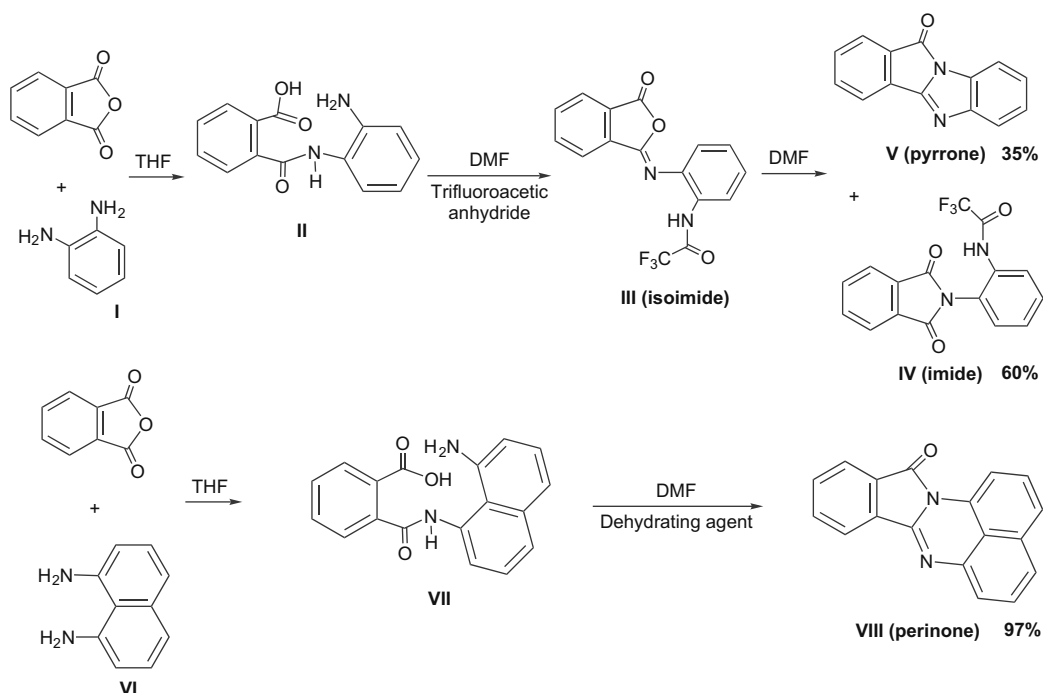
2. Experimental

2.1. Materials

All reagents were supplied by Aldrich, except initiators, Trigonox-22 and Trigonox-23, which were supplied by Akzo Nobel. 1,8-Diaminonaphthalene was recrystallized from ethanol; styrene (St) and methyl methacrylate (MMA) were distilled in vacuum prior to use. All other reagents and solvents were used as-received.
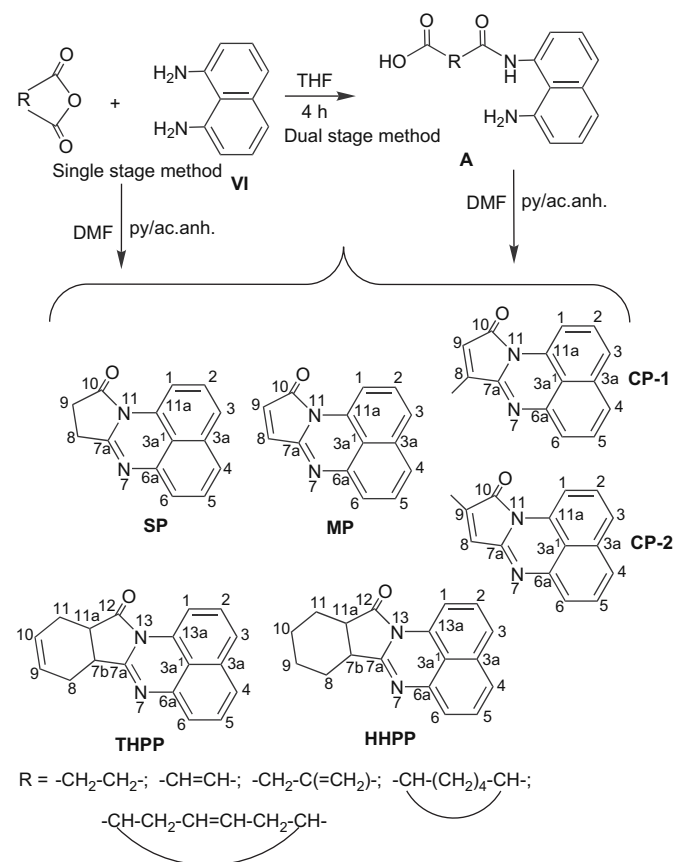
2.2. Synthesis of perinones

Synthetic route to the perinones is shown in Scheme 2.

The final fused heterocyclic structures were synthesized via catalytic cyclization of the appropriate precursors, the corresponding amic acids (**A** in Scheme 2). Detailed investigation of the mechanism was realized for **MP** and **SP** structures only. These two compounds were obtained by two routes: (1) two-step synthesis with separation and characterization of the precursor **A** and, when the mechanism of the formation of the perinones through the corresponding amic acid was established, (2) their synthesis was simplified and carried out in DMF from the very beginning without separation of the intermediates (see the descriptions below). Other perinones used in the study were obtained only by direct, single stage synthesis in DMF. All the structures synthesized were characterized by ^{1}H and ^{13}C NMR, FTIR and UV–vis spectroscopies, m.p. and elemental analysis.

Dehydrating agent: Trifluoroacetic anhydride, Dicyclohexylcarbodiimide, Acetic anhydride/pyridine

Scheme 1.

Scheme 2.

2.3. Maleiperinone

The synthesis procedure for maleiperinone (**MP**, IUPAC name 10H-pyrrolo[2,1-a]perimidin-10-one) was as follows.

2.3.1. Dual stage method

Maleic anhydride (1.915 g, 0.0195 mol) was added to a solution of 1,8-diaminonaphthalene (**VI**) (3.09 g, 0.0195 mol) in 50 ml of THF and the reaction mixture was stirred for 4 h at room temperature. The precursor **A**, N-(8-aminonaphthyl)maleamic acid, was formed as a brown precipitate. It was filtered off, washed repetitively with THF and dried in vacuum to a constant weight. The yield was 98%. The formation of the amic acids was confirmed by FTIR spectroscopy. FTIR (KBr, wavenumbers, cm^{-1}): 3400 (ν NH$_2$); 3060 (ν OH), 1690 (ν acidic C=O), 1654 (Amide I), 1526 (Amide II).

The resulted **MP** was produced by adding 20 ml of a 50/50 by volume mixture of acetic anhydride and pyridine (Ac.anh/py) to a suspension of N-(8-aminonaphthyl)maleamic acid (5 g, 0.0195 mol) in 20 ml of DMF. After 2 h stirring the intensively red colored solution was poured in aprox. 70 ml of water and a dark red precipitate was filtered off, twice recrystallized from ethanol to afford wine red crystals, which were dried under vacuum to a constant weight. Yield: 92% (calculated on original reagents).

2.3.2. Single stage method

Both, maleic anhydride (2.227 g, 22.7 mmol) and **VI** (3.950 g, 22.7 mmol) were dissolved in 10 ml of DMF and the solution was permitted to stir for 4 h at room temperature. Then 5 ml of the mixture Ac.Anh./py (50/50 by vol.) was added and the reaction was left stirred for another 2 h and then poured in aprox. 40 ml of water. After filtration the obtained dark red powder was twice recrystallized from ethanol and dried, giving the same crystals as those

obtained in the two-step method. Yield: 97%; m.p. = 161–162 °C. Anal. calcd. for C$_{14}$H$_8$N$_2$O: C 76.36%, N 12.73%, H 3.64%; found: C 76.57%, N 12.66%, H 3.73%. FTIR (KBr, wavenumbers, cm^{-1}): 1709 (ν C=O), 1636 (ν C=N), 1588 (γ heteroc. syst.), 1413 (ν C–N). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm) (see Scheme 2 for atom assignment): 6.74 (d, J = 5.87 Hz, 1H) (8), 7.26 (d, J = 5.87 Hz, 1H) (9), 7.42 (m, 4H), 7.55 (dd, J = 5.38 Hz, 1H), 8.24 (dd, J = 6.36 Hz, 1H); ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 166.35 (quart) (10), 151.95 (quart) (7a), 139.2 (quart), 134.26 (tert) (9), 133.75 (quart), 131.14 (quart), 130.44 (tert), 127.89 (tert), 127.82 (tert) (8), 126.92 (tert), 123.81 (tert), 122.59 (tert), 117.98 (quart), 109.37 (tert).

2.4. Succinoperinone (**SP**, IUPAC name dihydro-10H-pyrrolo[2,1-a]perimidin-10-one)

2.4.1. Dual stage method

N-(8-Aminonaphthyl)succinamic acid, precursor **A** in the case of succinic anhydride and **VI**, was obtained using the same procedure as those described for the precursor **A** of maleic anhydride and **VI**. The yield was 76%. FTIR (KBr, wavenumbers, cm^{-1}): 3400 (ν NH$_2$), 3100 (ν OH), 1710 (ν acidic C=O), 1660 (Amide I), 1545 (Amide II). The final **SP** was produced after 2 h stirring of N-(8-amino-naphthyl)succinamic acid (5 g, 0.0194 mol) in a mixture of 20 ml of DMF and 20 ml Ac.Anh./py (50/50 by vol.) at room temperature. After the separation and recrystallization procedures green brownish needle crystals of **SP** were obtained. Yield: 62% (calculated on original reagents).

2.4.2. Single stage method

SP was obtained analogously to the described procedure for **MP** from succinic anhydride and **VI**. Yield: 68%; m.p. = 176 °C. Anal. calcd. for C$_{14}$H$_{10}$N$_2$O: C 75.68%, N 12.61%, H 4.50%; found: C 75.59%, N 12.57%, H 4.56%. FTIR (KBr, wavenumbers, cm^{-1}): 1743 (ν C=O), 1647 (ν C=N), 1587 (γ heteroc. syst.), 1404 (ν C–N). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 2.76 (m, 2H) (8), 2.88 (m, 2H) (9), 7.00 (dd, J = 4.89 Hz, 1H), 7.22 (m, 3H), 7.39 (dd, J = 7.34 Hz, 1H); 8.16 (dd, J = 6.36 Hz, 1H); ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 173.89 (quart) (10), 157.18 (quart) (7a), 139.64 (quart), 134.14 (quart), 131.93 (quart), 128.07 (tert), 127.17 (tert), 123.62 (tert), 123.25 (tert), 119.63 (quart), 118.26 (tert), 109.16 (tert), 28.21 (sec) (9), 25.05 (sec) (8).

2.5. Citraconoperinones

Citraconoperinones (**CP**s, mixture of isomers of 1:1 ratio, 8-methyl-10H-pyrrolo[2,1-a]perimidin-10-one, **CP-1**, and 9-meth-yl-10H-pyrrolo[2,1-a]perimidin-10-one, **CP-2**) were obtained analogously by single stage method from itaconic anhydride and **VI**. Yield: 65%. Anal. calcd. for C$_{15}$H$_{10}$N$_2$O: C 76.92%, N 11.97%, H 4.27%; found: C 77.11%, N 12.07%, H 4.35%. FTIR (KBr, wavenumbers, cm^{-1}): 1708 (ν C=O), 1637 (ν C=N), 1583 (γ heteroc. syst.), 1411 (ν C–N) cm^{-1}.

CP-1: ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 2.36 (d, J = 2.01 Hz, 3H) (CH$_3$), 6.44 (q, J = 2.00 Hz, 1H) (9), 7.45 (m, 4H), 7.58 (dd, J = 2.52 Hz, 1H), 8.25 (dd, J = 6.04 Hz, 1H); ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 166.55 (quart) (10), 152.63 (quart) (7a), 145.92 (quart) (8), 139.35 (quart), 133.91 (quart), 131.55 (quart), 129.09 (tert), 127.89 (tert), 127.77 (tert), 126.41 (tert), 125.52 (tert) (9), 123.22 (tert), 118.11 (quart), 108.75 (tert), 11.37 (CH$_3$); m.p. = 194 °C.

CP-2: ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 2.24 (d, J = 2.01 Hz, 3H) (CH$_3$), 6.96 (q, J = 2.01 Hz, 1H) (8), 7.45 (m, 4H), 7.60 (dd, J = 2.52 Hz, 1H), 8.30 (dd, J = 8.06 Hz, 1H); ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 167.21 (quart) (10), 151.45 (quart) (7a), 141.36 (quart) (9), 139.22 (quart), 133.78 (quart), 131.02 (quart), 128.16 (tert) (8), 127.85 (tert), 127.73 (tert), 126.37 (tert), 123.21 (tert), 122.42 (tert), 117.81 (quart), 109.16 (tert), 11.29 (CH$_3$); m.p. = 183 °C.

2.6. Tetrahydrophthaloperinone

Tetrahydrophthaloperinone (**THPP**, 7b,8,11,11a-tetrahydroiso-indolo[2,1-*a*]perimidin-12-one) was synthesized by the same single stage method in DMF from *cis*-1,2,3,6-tetrahydrophthalic anhydride and **VI**. Yield: 90%; m.p. = 161 °C. Anal. calcd. for $C_{18}H_{14}N_2O$: C 78.83%, N 10.22%, H 5.11%; found: C 78.76%, N 10.27%, H 5.26%.

FTIR (KBr, wavenumbers, cm^{-1}): 1716 (ν C=O), 1635 (ν C=N), 1582 (γ heteroc. syst.), 1413 (ν C–N). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 2.38 (m, 2H), 2.69 (m, 2H), 3.18 (m, 1H), 3.33 (m, 1H), 5.95 (t, 2H), 7.06 (dd, J = 4.89 Hz, 1H,), 7.31 (m, 3H), 7.42 (d, J = 8.31 Hz, 1H), 8.22 (d, J = 7.82 Hz, 1H); ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 176.72 (*quart*), 160.91 (*quart*), 139.99 (*quart*), 134.28 (*quart*), 131.96 (*quart*), 128.12 (*tert*), 128.06 (*tert*), 127.81 (*tert*), 127.22 (*tert*), 123.57 (*tert*), 123.21 (*tert*), 119.88 (*quart*), 118.38 (*tert*), 109.27 (*tert*), 39.32 (*tert*), 36.25 (*tert*), 25.47 (*sec*), 23.56 (*sec*).

2.7. Hexahydrophthaloperinone

Hexahydrophthaloperinone (**HHPP**, 7b,8,9,10,11,11a-hexahy-droisoindolo[2,1-*a*]perimidin-12-one) was obtained analogously from 1,2-cyclohexanedicarboxylic anhydride and **VI**. Yield: 62%; m.p. = 56 °C. Anal. calcd. for $C_{18}H_{16}N_2O$: C 78.26%, N 12.96%, H 7.41%; found: C 78.80%, N 12.39%, H 7.01%. FTIR (KBr, wavenumbers, cm^{-1}): 1716 (ν C=O), 1654 (ν C=N), 1591 (γ heteroc. syst.), 1402 (ν C–N) cm^{-1}; ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 175.75 (*quart*), 159.95 (*quart*), 139.86 (*quart*), 134.31 (*quart*), 132.18 (*quart*), 128.03 (*tert*), 127.20 (*tert*), 123.24 (*tert*), 123.19 (*tert*), 120.06 (*quart*), 118.53 (*tert*), 109.08 (*tert*), 40.38 (*tert*), 37.29(*tert*), 26.46 (*sec*), 23.12 (*sec*), 22.11 (*sec*), 22.05 (*sec*).

2.8. Copolymerization

Copolymerizations of St and MMA with the perinones having carbon–carbon double bond apart from the aromatic system in their structures, such as **MP**, **CP**s and **THPP**, were carried out in bulk and in solution under N$_2$ using radical initiators Trigonox-22 and Trigonox-23 for St and MMA correspondingly. The bulk co-polymerizations were conducted with 0.01 M initiator at 110 °C for St and at 80 °C for MMA. However, the perinones used have a limited solubility in both monomers even at high temperature. Thus, in order to verify how solubility of the perinone affects its insertion into the polymer chains, the solution copolymerizations of **MP** with St and MMA were carried out in two solvents toluene (St) and DMF (St and MMA) using 50/50 by volume monomer to solvent mixtures and the same temperature conditions and the initiators as in the case of the bulk polymerizations, but the initiator concentrations were 10 times higher, 0.1 M. The copolymers obtained were dissolved in THF and then precipitated in methanol. The procedure was repeated three times to wash the copolymer from an unreacted perinone.

2.9. Analytical techniques

FTIR spectra were recorded on a Bruker Equinox 55 Fourier transform infrared spectrometer. UV–vis spectra were obtained on a Varian Cary 400 UV–vis spectrophotometer. NMR spectra were recorded using a Bruker Avance 400 spectrometer. ^{1}H–^{1}H COSY and HMQC spectra were used for the assignment of all proton resonance and HMBC was used for the assignment of the carbon resonances. Fluorescence spectra were recorded on a Perkin–Elmer LS50B fluorescent spectrometer using Rhodamine 6G as a standard. The concentrations of the luminophores were within (4.5–6.0) × 10^{-5} mol L^{-1}. The molecular weights were determined by GPC on a Waters 717 apparatus with a refraction index detector. PSt

and PMMA samples of low polydispersities were used for calibration and THF as an eluent. Monomer conversion was determined gravimetrically. Thermal analysis was performed on Thermogravimetric Analyzer, TGA 2950, and DSC measurements were done using a TA Instruments Differential Scanning Calorimeter, Model 2100 at a heating rate of 20 °C/min. The amount of the perinone in copolymers was estimated from analytical (nitrogen content) or UV–vis data using the extinction coefficient of its analogue but without the carbon–carbon double bond, for example, **SP** in the case of **MP** and **CP** and **HHPP** in the case of **THPP**. The results obtained by both methods showed a good match.

3. Results and discussion

3.1. Synthesis of perinones

The synthetic approach applied here to obtain the perinones was developed based on our previous researches of rearrangement and cyclization reactions of *N-o*-substituted imide and isoimide structures [17–22] as it was mentioned in Section 1. The main results related to this research are summarized in Scheme 1. As it is known *N*-(*o*-aminophenyl)phthalamic acid, **II** in Scheme 1, could be converted to aroylenbenzimidazole or pyrrone structure **V** via high temperature treatment in melt or refluxing solvents above 100 °C through the phthalimide or benzimidazole as the main intermediates. However, the cyclization may proceed spontaneously at ambient temperature when thermodynamically unstable isoimide **III** was used as intermediate, as it is shown in Scheme 1, giving the final heterocyclic structure **V** as one of the products with 35% yield. Further study of the catalytic cyclization process revealed that the number of atoms forming the fused heterocyclic system has a substantial effect on the ease of the secondary cyclization. Application of 1,8-diaminonaphthalene, **VI**, instead of a phenyl based diamine, **I**, in order to pass from five, five-membered fused heterocycles to five, six-membered fused structure resulted in a dramatic increase in the yield of the corresponding fully cyclized molecule **VIII** (see Scheme 1).

In this case, a partially cycled intermediate analogous to **III** was not isolated, suggesting that the second cyclization step (formation of perimidine, a six-membered heterocycle) is so favorable that occurs directly without formation of any stable transitional compound between **VII** and **VIII**. The effect of the ring size on the conversion is rather an attribute of a strain release when a six-membered ring is formed comparing to a formation of five-membered heterocycle (benzimidazole in our case). Thus, taking into account such features of the catalytic cyclization reaction as the generated leaving group, the participating intermediates and the size of the formed heterocycles, a new highly effective low temperature route for synthesis of fully cycled structures of perinone type has been designed. The novel synthetic method depicted in Scheme 2 permitted a use of reagents having active carbon–carbon double bond in their structures and the bond was not affected under very mild synthetic conditions. Thus, two new perinones, **CP**s and **THPP**, with polymerizable double bond have been synthesized. The synthesis of the third perinone which may be active in addition polymerizations, namely **MP**, was reported earlier [16], but its yield was dramatically improved from less than 30 up to 97%. Such perinones as **SP** and **HHPP**, analogous to **MP** and **THPP** correspondingly but without the polymerizable double bond, have also been synthesized with high yields by this route and used for comparison studies.

It is worth to give more details of the **CP** synthesis. The synthetic procedure started with itaconic anhydride in an attempt to obtain itaconoperinone, the structure where the polymerizable carbon–carbon double bond would be located out of the five-membered cycle and thus would be less conjugated and more active in radical

addition reactions than **MP**. At least it has been demonstrated by various authors that itaconic derivatives are more reactive in radical co- and homo-polymerizations compared to maleic derivatives [23–26]. However, under the cyclization conditions an isomerization of the itaconic to citraconic structure occurred with 100% conversion. No secondary carbons were observed in the ^{13}C DEPT 135 NMR spectrum of the product, only the signals of methyl carbons at δ 11.37 and 11.29 ppm instead. Similarly, two doublets of approx. equal intensities were seen in saturated aliphatic area of the ^{1}H NMR spectrum at 2.36 and 2.24 ppm. The integrations gave three for each of them relatively to one aromatic proton either at 8.25 or 8.30 ppm. There were also two methylene proton signals at 6.44 and 6.96 ppm in the spectrum, each corresponding to one proton according to the integration. In general we saw much more signals in both ^{13}C and ^{1}H NMR spectra than it should be for one citraconic compound. The melting point determined by DSC method revealed that the product is a mixture of two different compounds. The product was passed through the silica column; a mixture of hexane/ethyl acetate (97/3 for the first and 95/5 for the second fraction) was used as an eluent, and thus two citraconoperinone compounds were separated and each of them was characterized by NMR and DSC (melting point) methods. Analysis of their NMR spectra showed that the original non-separated citraconoperinone was a 50/50 mixture of the two isomers differing from each other by the position of the methyl group either at 8 or 9 carbon atom (see Scheme 2); they were referred as **CP-1** and **CP-2** correspondingly. The assignment of each of these structures was made based on HMQC and HMBC NMR methods.

It is known that itaconic anhydride isomerizes to citraconic anhydride at temperatures above 100 °C [27]. The isomerization is also takes place at lower temperatures during reactions of itaconic anhydride with amines, especially with aliphatic ones [28,29]. Studies showed that the isomerization rate depends on the amine basicity and concentration as well as solvent polarity [28,29]. Such triethylamine causes complete isomerization in 5 min at room temperature in both polar and non-polar solvents, whereas tertiary aromatic amines, such as pyridine, require 23–25 h at room temperature for the complete isomerization, but in the last case the isomerization was notably faster in the polar acetone. Under our single stage conditions even the reduction of the reaction time from 4 to 2 h resulted to citraconoperinones, no notable amounts of itaconoperinone structures were obtained. Probably the itaco- to citraco- isomerization in DMF is even faster than in acetone. More acceptable conditions for itaconoperinone synthesis are under investigation in our group now.

3.2. Spectral properties of the perinones

The main characteristics of electronic absorption and fluorescence spectra, such as the wavelength of the maximum absorptions (λ_{max}^{abs}), the corresponding extinction coefficients (ε), as well as values of fluorescent maxima (λ_{max}^{fl}), Stock's shift ($\Delta\nu$) and quantum efficiency of fluorescence (Φ_{fl}), of the synthesized compounds are given in Table 1. As it could be seen from the data only two structures, **MP** and **CP**s, showed absorption bands with λ_{max} in visible region at 480 nm, while the other compounds have just two structured absorption bands, both with maximums in UV area, the first at 220–240 mn and the second at 330 mn, that is typical for perimidine system [30]. The lower wavelength band is ascribed to electronic transitions within naphthalene ring, and the 330 mn absorption is attributed to n–π^* transition into the naphthalene ring. The visible area bands, which are responsible for the color of the perinones, appear as shoulders on the major band with maximum at 330 nm. These visible absorptions are the most probable due to π-electron transfer from the naphthalene to the pyrimidine heteroring. The broad structureless bands centered at 480 nm

Table 1
Basic electronic absorption and fluorescence (exited at 350 nm) features of the perinones

Compound	λ_{max}^{abs} nm	$\varepsilon \times 10^{-3}$ L mol^{-1} cm^{-1}	λ_{max}^{fl} nm	$\Delta\nu$ cm^{-1}	Φ_{fl}
MP	226	41.4	No	–	–
	293	14.7			
	480	6.3			
CPs	229	46.1	No	–	–
	293	15.3			
	480	6.8			
SP	247	25.5	468	8843	0.06
	331	12.4			
THPP	222	22.6	456	8281	0.08
	231	12.2			
HHPP	229	20.5	468	8843	0.08
	231	13.7			

All spectra were measured in ethanol solutions.

observed for **CP**s and **MP** look as typically charge transfer (CT) absorptions and could be ascribed to a charge transfer complex between the electron rich perimidine system and the electron deficient five-membered ring. As expected from the structures **MP** and **CP**s demonstrated very similar electronic features. **SP**, which is similar to **MP** but does not contain carbon–carbon double bond in the five-membered ring, does not exhibit this high wavelength CT band. Another compound, **THPP**, where carbon–carbon double bond in anhydride fragment is more separated from perimidine system does not show such CT absorption either. This also explains the difference in the color between **MP**, **CP**s and all of the other perinones. The first two have an intense wine-red color in solution while the solutions of the others are of orange brown color.

Simple perimidines rarely fluoresce on irradiation with UV light [30], and the perinone type dyes are not known as luminescence compounds. Nevertheless the fluorescence properties of the synthesized structures were also verified, and as it can be seen from Table 1, three from the five synthesized perinone are able to emit visible light.

Quantum yields of their fluorescence are not as high as quantum yield of such known fluorescent dyes, as Coumarin 6H, for example. Its quantum yield is close to 80% in ethanol solution, but it is one of the most intensively fluorescent compounds. Very few dyes show this level of fluorescence. For many other luminescent colorants intensity of fluorescence is close to the data reported here [31,32]. The absorption and emission spectra are separated quite far one from another, thus the big values of Stock's shifts mean that the exited states of the molecules are much better stabilized in polar ethanol than the ground states. Generally it may be concluded that the electronic and fluorescence properties of the **SP**, **THPP** and **HHPP** molecules are very similar and almost do not depend on anhydride moiety. In spite of even their more rigid structures, both **MP** and **CP**s do not exhibit any notable luminescence and this is because of the CT absorption in this area.

## 3.3. Copolymerization of St and MMA with MP, CPs and THPP

Most of the copolymerizations were carried out in bulk, however, solubility of the perinones, especially **MP** and **CP**s, were limited in both monomers, MMA and St. In order to improve the solubility and evaluate influence of this on insertion of the perinone into the polymer chains several solution copolymerizations of St and MMA with **MP** were also carried out in two solvents, toluene and DMF. The results on the perinone incorporations and molecular weight characteristics of the copolymers are given in Table 2. As it is seen from the table that the oligomeric products of M_n between 6000 and 3000 were obtained in the solutions even when as low concentration of **MP** in the monomer feed as 5 mol% was used. Moreover, the polymerization rates decreased significantly when

Table 2
Radical copolymerization of the perinones (M_1) with St and MMA (M_2) in bulk and solution (toluene, DMF) at 100 °C for St and 80 °C for MMA

System	M_1 in the monomer feed, mol%	Conversion, %	M_1 in Copolymer, mol%	$M_n \times 10^{-3}$, GPC	M_w/M_n, GPC
St, bulk	0	28	0	197	1.66
St–**THPP**-5, bulk	5	13	3.6	186	1.63
St–**THPP**-10, bulk	10	12	7.2	164	1.67
St–**THPP**-15, bulk	15	13	8.2	150	1.70
		66	9.6	151	1.73
St–**MP**-2, bulk	2	14	1.2	158	2.07
St–**MP**-3, bulk	3	14	1.6	132	2.21
St–**MP**-5, bulk	5	13	2.5	121	2.10
		60	2.9	121	2.09
St–**CP**-2, bulk	2	12	0.7	140	2.34
St–**CP**-5, bulk	5	11	2.0	110	2.26
		33	2.1	108	2.28
St, toluene	0	41	0	61	2.01
St–**MP**-5, toluene	5	17	2.2	6	2.37
MMA, bulk	0	37	0	181	2.21
MMA–**THPP**-5, bulk	5	12	3.4	150	2.12
MMA–**THPP**-10, bulk	10	12	6.2	133	1.97
MMA–**THPP**-15, bulk	15	14	7.2	111	2.21
		47	8.1	113	2.22
MMA–**MP**-2, bulk	2	11	0.8	165	2.33
MMA–**MP**-3, bulk	3	11	1.2	132	2.39
MMA–**MP**-5, bulk	5	13	1.8	114	2.19
		36	2.0	115	2.23
MMA–**CP**-5, bulk	5	24	1.4	101	2.18
MMA, toluene	0	36	0	46	2.99
MMA–**MP**-5, toluene	5	34	1.6	5	2.87
MMA–**MP**-5, DMF	5	34	1.6	3	3.04

the perinone was added to the reaction mixture, meanwhile the insertion was not improved at all: the content of **MP** units in the polymer chains was lower than the content of the perinone incorporated under the bulk conditions at the same monomer feed composition (see data in Table 2). The bulk copolymerizations in general have similar tendency as those observed for the solution polymerizations in the presence of **MP** but much less pronounced. Thus, the polymerizations were slower and the molecular weights decreased in the presence of the perinones. Conversion vs time curves for MMA and St copolymerizations in bulk with different amounts of **MP**, **CP**s and **THPP** are shown in Figs. 1 and 2. As it can be observed the polymerization rate gradually decreased with
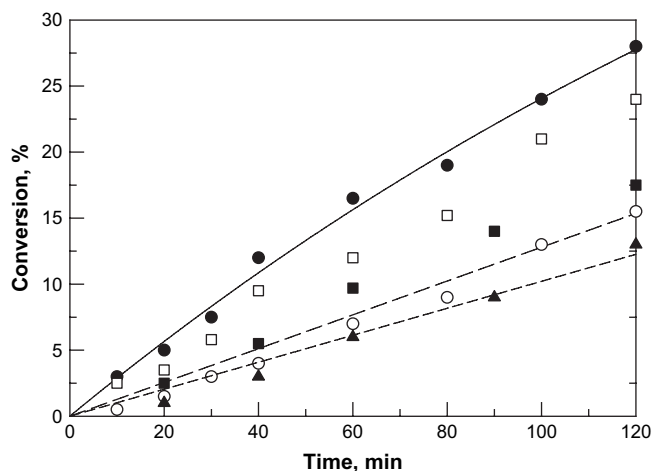

Fig. 1. Conversion vs time curves for bulk copolymerizations of St with various amounts of perinones in the monomer feed at 100 °C: (●) polymerization of pure St, $[St]_0 = 8.7$ M, $[Trigonox-22]_0 = 0.087$ M; (□), $[St]_0/[THPP]_0 = 95/5$; (○)$[St]_0/[THPP]_0 = 85/15$; (■)$[St]_0/[MP]_0 = 98/2$; (▲) $[St]_0/[MP]_0 = 95/5$.
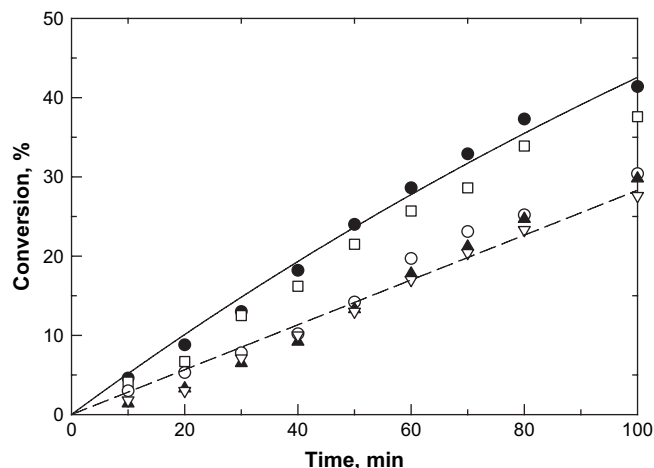
Fig. 2. Conversion vs time curves for bulk copolymerization of MMA with various amounts of perinones in the monomer feed at 80 °C: (●) polymerization of pure MMA, $[MMA]_0 = 9.3$ M, $[Trigonox-23]_0 = 0.094$ M; (□) $[MMA]_0/[THPP]_0 = 95/5$; (○) $[MMA]_0/[THPP]_0 = 85/15$; (▲)$[MMA]_0/[MP]_0 = 95/5$; (△) $[MMA]_0/[CPs]_0 = 95/5$.

increase of the perinone concentration in the monomer feed. The molecular weights diminished as well with enhance of the perinone concentrations (see data in Table 2), but their diminution was not as dramatic as in the case of the solution copolymerizations. The more conjugated **MP** and **CP**s affected both the polymerization rate and the molecular weights much stronger than **THPP** where the carbon–carbon double bond in anhydride moiety is isolated from the fused perimidine system. Such that the presence of only 2 mol% of **MP** had the same effect on the polymerization rate as the presence of 10 mol% of less conjugated **THPP**. The presence of 5 mol% of **MP** or **CP**s affected the polymerization rate more than the presence of 15 mol% of **THPP**: the rate decreased more than 2 times compared to that of pure St. The molecular weights were also dropped in about two times when 5 mol% of **MP** or **CP**s was added into the monomer mixture, from almost 200,000 till 120–100,000 (Table 2). The decrease in molecular weights was less when **THPP** was used as a co-monomer. However, under the bulk conditions high molecular weight copolymers of St and MMA with the perinones were obtained (see data in Table 2). After careful washing all the copolymers have similar orange brown color but with different intensities. As it could be concluded that **THPP** is more active than **MP** in polymerization reactions and it better incorporates into the copolymers. The concentration of the incorporated **CP** units is even less than that of **MP**. The same difference in activities in addition reactions was noted between maleic and citraconic anhydrides and assigned by the steric effect because of α-methyl group of the later [33]. Because of the limited solubility of the perinones in both MMA and St, we could not add more than 5 mol% of **MP** and **CP**s, and 15 mol% of **THPP**. The influence of the perinones on the molecular weights and polymerization rate may be explained by the chain transfer properties of these compounds. Because of the conjugated structure they should form quite stable radicals and thus the energy of the radical formation should be low. The propagating radical of St or MMA may easily abstract hydrogen from the perinones to afford the radical derived from the perinone as shown in Scheme 3. These radicals are little active in propagating reactions that result in the decrease of the polymerization rate. As it can be seen that the more conjugated **MP** and **CP**s lead to more significant decrease in molecular weights and slowing polymerization than less conjugated **THPP**. The effect is stronger in solvents, especially polar ones, such as DMF because of radical stabilization. Additionally toluene is also quite susceptible for chain transfer reactions [34]. Taking into account the very insignificant incorporation of the perinone units in
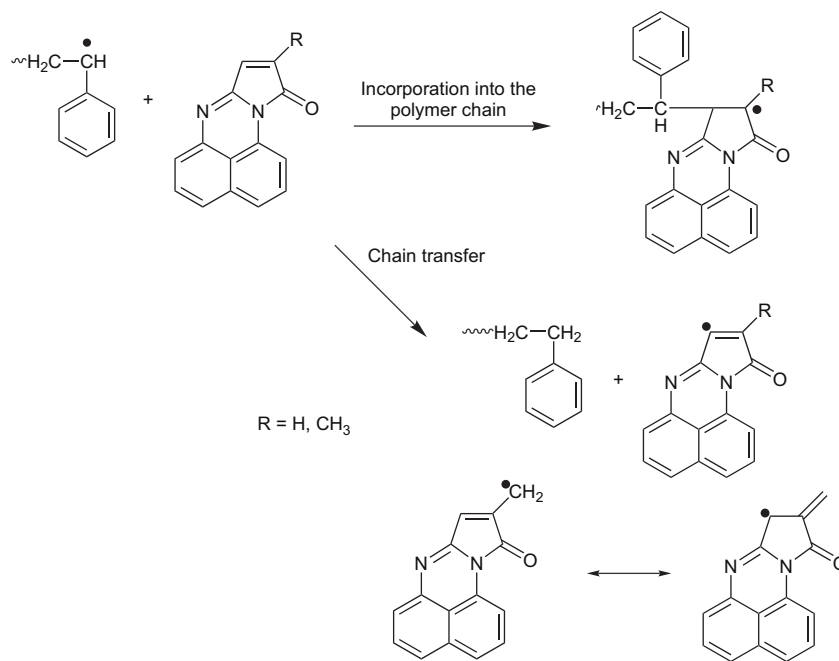
Scheme 3.

the polymer chains and the equality of the polymerization conditions we roughly estimate the chain transfer constants of the perinones to the monomers applying equation for a chain transfer agent [34] with use of the data obtained at early stage of the polymerizations:

$$\frac{1}{X_n} = \left(\frac{1}{X_n}\right)_0 + C_{tr}\frac{[\text{Perinone}]_0}{[\text{Monomer}]_0}$$

where $1/X_n$ and $(1/X_n)_0$ are polymerization degrees in the presence and absence of the perinone correspondingly. The plots for bulk polymerizations of St are presented in Fig. 3. For St polymerization the following values of the chain transfer constants were obtained: $C_{THPP} = 1.03$, $C_{MP} = 6.04$ and $C_{CP} = 11.27$. Slightly higher values of C_{tr} were obtained for polymerization of MMA: $C_{THPP} = 2.11$, $C_{MP} = 6.46$ and $C_{CP} = 12.34$. The highest C_{tr}s for both St and MMA polymerizations were observed for **CP**s that may be
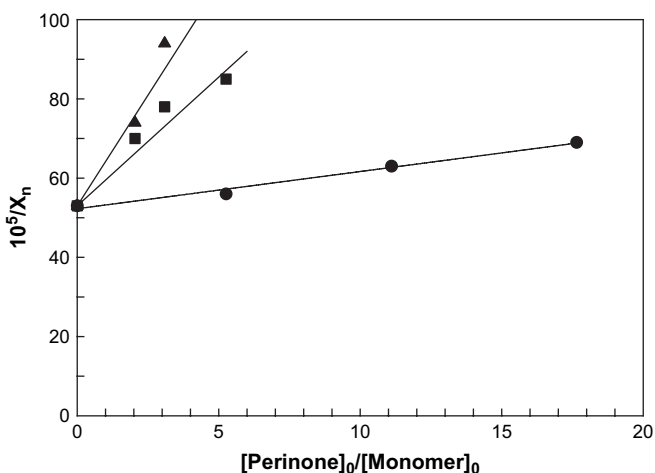

Fig. 3. The effect of the perinones on the degree of polymerization of St in bulk at 100 °C: (●) **THPP**; (■) **MP** and (▲) **CP**s.

explained by the resonance stabilization of the radical because of the α-methyl group as shown in Scheme 3.

Chemical incorporations of the perinones into PSt and PMMA were confirmed by FTIR and UV–vis spectroscopies. Fig. 4 demonstrates the FTIR spectra of the homopolymer (PSt) (a), the perinone (**THPP**) (b) and their copolymer obtained with 15 mol% of **THPP** after its washing from the unreacted perinone (c). Comparison between the spectra of the homopolymer (a) and the copolymer (c) reveals a considerable difference in the range of 1800–1400 cm^{-1}, where the characteristic bands of the perinone, such as 1716 (ν C=O), 1635 (ν C=N), 1582 (γ heteroc. syst.) and 1413 (ν C–N) cm^{-1}, are clearly seen in the spectrum of the latter. The same difference between the spectra was noted for the homo and co-polymers of MMA, as well as in the case of **MP** and **CP** copolymers. Only intensities of the perinone bands in the last two were less pronounced because of the small concentration of the perinone incorporated. Thus, the FTIR data confirm the existence of the perinones in copolymer compositions even after several solution and precipitation cycles of the later, but it does not give direct evidence of a covalent bond formation between the monomer (St or MMA) and the perinone.

More clear evidence of covalent bonding between the perinones and the monomers comes from UV–vis analysis of the copolymers.

The electronic absorption and emission spectra of the copolymers of MMA with **THPP** and **MP** are presented in Figs. 5 and 6, respectively. The spectra of the copolymers based on St look very similar. The new band with maximum at 330 nm which belongs to the perinone absorption appears in the copolymer absorption spectra. This band does not exhibit in homo-PMMA or -PSt spectra. The fluorescence spectrum of the MMA–**THPP** copolymer ((B) in Fig. 5) shows the emission with maximums at 460 mn. This spectrum is very similar to the emission spectra of pure **THPP** and **HHPP** since the spectra of these two compounds are practically identical because the carbon–carbon double bond in anhydride moiety of **THPP** does not give any notable impact in the electronic properties.

However, the remarkable difference was noted during comparison of the spectra of the **MP** and **CP** copolymers with those of the pure perinones. Electronic spectra of MMA–**MP** copolymer and
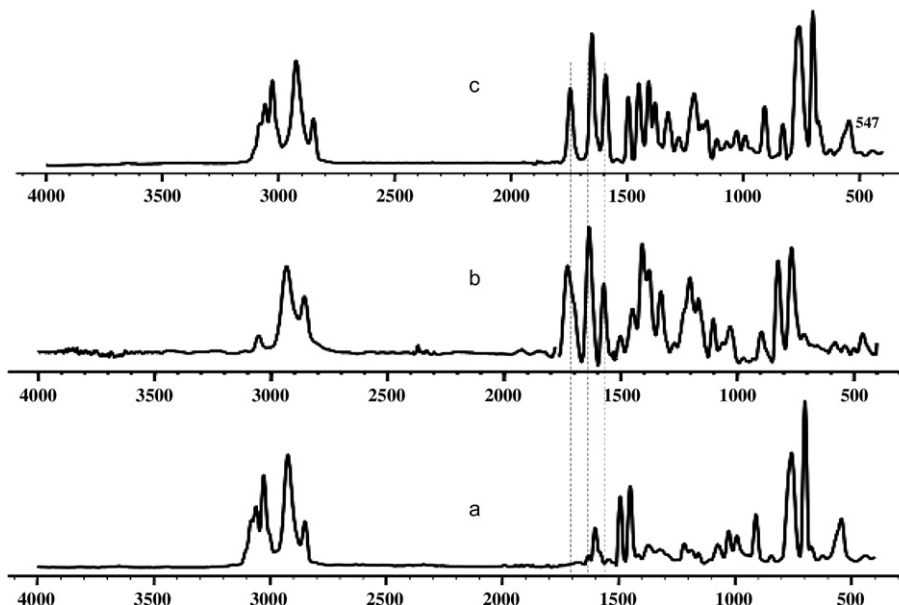
Fig. 4. FTIR spectra of the pure PSt (a), **THPP** (b) and the St–**THPP** copolymer obtained from [St]$_0$/[**THPP**]$_0$ = 85/15 monomer feed (c).

pure **MP** in ethanol solution are shown in Fig. 6. No broad CT absorption at 480 nm which is characteristic for both **MP** and **CP** structures is seen; meanwhile the shorter wavelength absorption at 331 nm is present in the copolymer spectra ((A) in Fig. 6). Thus, the absorption spectra of the copolymers very strongly remind the spectrum of **SP**, shown in Fig. 7, the structure analogue to **MP** but without carbon–carbon double bond in anhydride moiety. Moreover the copolymers fluorescent and their emission spectra are also completely coincide with the emission spectrum of the **SP**. Therefore it may be concluded that the incorporation of **MP** and **CP**s occurs by homolytic cleavage of the carbon–carbon π-bond in the anhydride moiety and thus the incorporated **MP** or **CP**s converted into less conjugated structures analogous to **SP**. It is logically to propose the same mechanism for **THPP** incorporation, even if it is not so obvious from the spectral data since the absorption and emission spectra of **THPP** and its more saturated analogue, **HHPP**, are very similar. From the point of view of the proposed mechanism the location of the reactive carbon–carbon π-bond is very important. Since this bond in **THPP** is isolated from the perimidine system in contrast to **MP** or **CP**, the radicals derived from **THPP** are

much more active and this explains its better incorporation in the copolymers.

The data presented in Table 2 were used for the estimation of the copolymerization reactivity ratios between the perinones and MMA and St. The estimation was made with the help of RREVM computer program [35]. The calculated ratios were $r_1 = 0.14$ and $r_2 = 29.71$ for **THPP**–St; $r_1 = 0.11$ and $r_2 = 62.21$ for **MP**–St couples. For the MMA systems the ratios were $r_1 = 0.13$ and $r_2 = 39.08$ for **THPP** and $r_1 = 0.09$ and $r_2 = 72.78$ for **MP**. Since **CP**s incorporated into the polymers are worse than **MP**, the difference in ratios between **CP**s and St or MMA should be even bigger. However, it should be noted that this is very rough estimation since we could not vary much the monomer compositions and additionally the data were obtained not at very low conversions. So thus obtained reactivity ratios are not very useful for deep conclusions, they just confirmed a low activity of the perinones in the addition
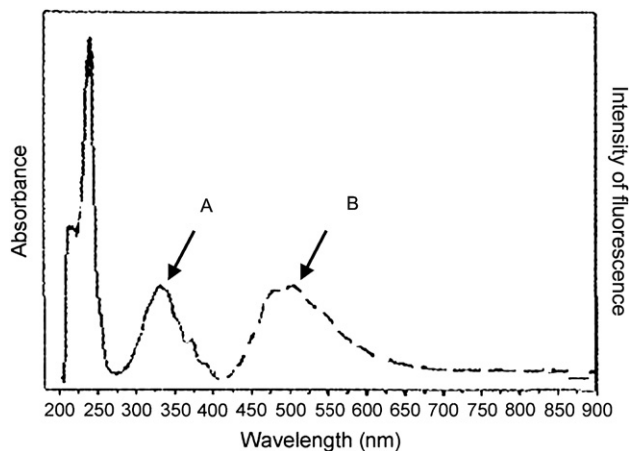

Fig. 5. Absorption (A) and fluorescence (B) spectra of the MMA–**THPP** copolymer.
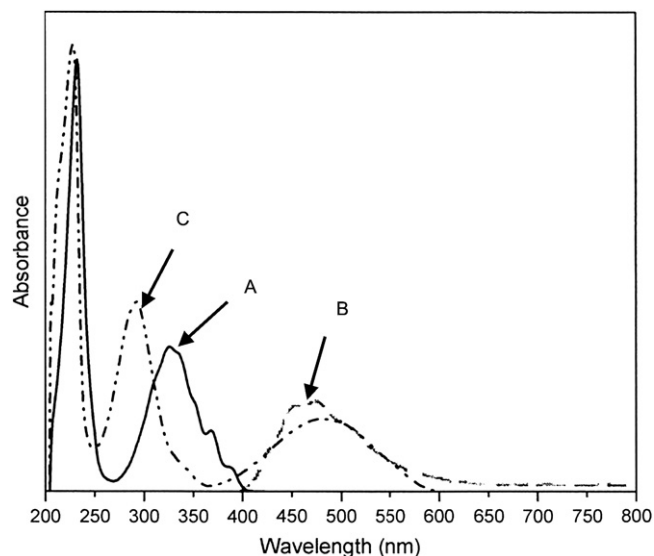

Fig. 6. Absorption (A) and fluorescence (B) spectra of the MMA–**MP** copolymer. The absorption spectrum of **MP** (C) in ethanol solution is given for comparison.
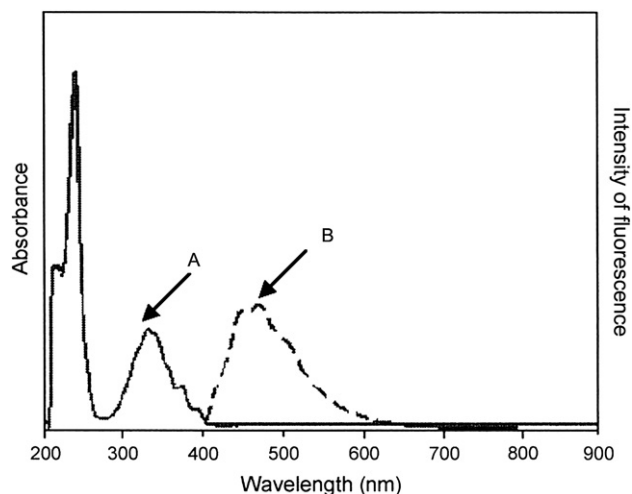
Fig. 7. Absorption (A) and fluorescence (B) spectra of the **SP**.

polymerizations, showed that more conjugated **MP** is less active than **THPP**, and that both MMA and St prefer to react with their own radicals.

Because of the low concentrations of the perinone units in the copolymers their T_gs determined by DSC method almost do not differ from those of the homopolymers. The maximum raise in T_gs was 4 °C and observed for the copolymers with the highest **THPP** content.

4. Conclusions

The new low temperature highly effective route for the synthesis of fused perinone structures based on catalytic cyclization reactions was developed. The synthetic conditions are mild and permit to include polymerizable carbon–carbon π-bond in the synthesized structures. These perinones were incorporated chemically into PSt and PMMA and the fluorescent colored copolymers were obtained by radical process. The less conjugated **THPP** was incorporated into the polymers in larger amounts than more conjugated **MP** and **CP**s. The perinones were incorporated into the copolymer by homolytic cleavage of the carbon–carbon π-bond in anhydride moiety that clearly was demonstrated for the **MP** and **CP** structures. A steric hindrance of this bond makes **CP**s the least active in copolymerizations.

References

[1] Herbst W, Hunger K. Industrial organic pigments. 3rd ed. Wiley; 2004.
[2] Hays BG, Bindra AP. In: Salamone JC, editor. Polymeric materials encyclopedia. Boca Raton: CRC Press; 1996. p. 1321–32.
[3] Nagao Yu, Tsuda K, Kozawa K, Uchida T. Heterocycles 2001;54(2):757–64.
[4] Jaffe E. US Patent, US 3,622,581; Nov 23 1971.
[5] Barashkov NN, Gunder OA. Fluorescent polymers. New York: Ellis Horwood; 1994.
[6] Arici E, Greiner A, Raubacher F, Wendorff JH. Macromol Chem Phys 2000;201: 1679–86.
[7] Winnik FW. Chem Rev 1993;93:567–614.
[8] Burdeska K. US Patent, US 3,819,632; 1971.
[9] Roschger P. US Patent, US 5,466,805; 1995.
[10] Roschger P, Hederich V, Michaelis S. US Patent, US 5,530,130; 1996.
[11] Herzog H, Wunderlich K, Hohmann W. EP 0,104,530; 1984.
[12] Dietz E, Kapaun G, Schiessler S. US Patent, US 5,074,919; 1991.
[13] Kalz D, Arlt D, Reinhardt K.-H. Eur Patent, EP 827,986; 1998.
[14] Michaelis S, Stawitz J-W. Eur Patent, EP 1,245,645; 2002.
[15] Tikhonov VI, Rogovik VI. Chem Heterocycl Comp 1973;9(10):1257–9.
[16] Al-Khathlan H, Zimmer H. J Heterocycl Chem 1988;25(3):1047–9.
[17] Likhatchev D, Gutierrez-Wing C, Kardash I, Vera-Graziano R. J Appl Polym Sci 1996;59:725–36.
[18] Guzman-Lucero D, Likhatchev D. Polym Bull 2002;48:261–9.
[19] Likhatchev D, Valle L, Canseco M, Salcedo R, Gaviño R, Martinez Richa A, et al. J Appl Polym Sci 1998;67:609–19.
[20] Likhatchev D, Granados-Focil S, Gaviño R, Canseco M, Alexandrova L. High Perform Polym 1999;11:405–15.
[21] Salcedo R, Valle L, Alexandrova L, Likhatchev D. J Mol Struct (Theochem) 1999; 463:231–5.
[22] Granados-Focil S. Nuevos enfoques sinteticos para la obtencion de estructuras heterociclicas tipo 1,2-benzoilenbencimidazol. Tesis de licenciatura, Facultad de Quimica, Universidad Nacional Autonoma de Mexico; 2001.
[23] Hartford SL, Subramanian S, Parker JA. J Polym Sci Polym Chem Ed 1978;16: 137–53.
[24] Anand V, Choudhary V. J Appl Polym Sci 2001;82:2078–86.
[25] Solanki A, Choudhary VI, Varma K. 2002; 84: 2272–2282.
[26] Watanabe H, Matsumoto A, Otsu T. J Polym Sci Part A Polym Chem 1994;32: 2073–89.
[27] Tate BE. In: Leonard EC, editor. Vinyl and diene monomers. Part 1. Wyley Interscience; 1970. p. 224–6.
[28] Galanty MG, Galanti AV. J Org Chem 1982;47:1572–4.
[29] Galanti AV. J Polym Sci Polym Chem Ed 1981;19:2243–53.
[30] Katritzky AR. Comprehensive heterocyclic chemistry II. UK: Pergamon Press; 1996. p. 102–3.
[31] Filipova TZ, Grabchev I, Petkov I. J Polym Sci Part A Polym Chem 1996;35: 1069–76.
[32] Barashkov NN, Sakhno TV, Nurmukhametov RN, Khakhel OA. Polymer 1996; 37(7):1109–16.
[33] Yang J-Z, Otsu T. Macromolecules 1992;25:102–7.
[34] Odian G. Principles of polymerization. 3rd ed. NY: J. Wiley & Sons, Inc.; 1991.
[35] Hakim M, Verhoeven V, McManus NT, Dube MA, Penlidis A. J Appl Polym Sci 2000;77:602–9.