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CONTROLLED FREE RADICAL POLYMERIZATION OF METHACRYLATES CONTAING CARBAZOLE AND CUMARIN PENDANT GROUPS

BADANIA NAD KONTROLOWANĄ POLIMERYZACJĄ METAKTYLANÓW ZAWIERAJACYCH UGRUPOWANIA KARBAZOLOWE I KUMARYNOWE

Abstract

This paper presents the results of synthesis copolymers based on 2-(9-carbazolyl)ethyl methacrylate (CEM) and 7- (diethylamino)coumarin-3-carboxylic acid 2-(methacryloyloxy) ethyl ester (MK) using ATRP technique. The reactions were carried out both under conventional and microwave conditions. Various activations system with organic ligand 1,10-phenanthroline monohydrate were tested. Obtained polymers were characterized by GPC and UV-VIS techniques.

Keywords: atom transfer radical polymerization, microwave irradiation, carbazole, coumarin, copolymer, luminescence

Streszczenie

W artykule przedstawiono wyniki reakcji kopolimeryzacji monomerów: metakrylanu 2-(9-karbazolilo)etylu (CEM) i 7-(dietyloamino)-3-(metakroilooksyetoksy)karbonylokumaryny. (MK). Syntezę kopolimerów przeprowadzono techniką ATRP w warunkach ogrzewania konwencjonalnego jak również pod wpływem promieniowania mikrofalowego. Testowano różne układy inicjujące z monohydratem 1,10-fenantroliny, stanowiącym ligand organiczny. Dla uzyskanych kopolimerów wykonano analizę GPC i UV-VIS.

Słowa kluczowe: polimeryzacja rodnikowa z przeniesieniem atomu, promieniowanie mikrofalowe, karbazol, kumaryna, kopolimery, luminescencja

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1. Introduction

Control radical polymerization (CRP) is one of the newer techniques of polymer synthesis. In recent years, numerous CRP techniques as ATRP, RAFT, SFRP have been developed to control over the synthesis of many new well-defined polymers [1, 2]. These methods gives possibility to obtain materials with predictable molecular weight and low polydispersity index (PDI). They also enabling a production (co)polymers with controlled architectures and compositions [2]. This allows to production of new functional materials and improve the properties currently available in industry. Among the available CRP techniques atom transfer radical polymerization (ATRP) has become one the most widely applied. ATRP process goes through dynamic equilibrium established between the dormant species and active propagating radical. Simple mechanism and commercially available reagents had an impact on the success of this method. ATRP is apply in all areas of synthesis polymers: in nanostructures, biomedical polymers, conductive polymers (also in the synthesis of semiconductor and insulators), structural polymers and others. So far ATRP was utilizing in synthesis wide range of vinyl monomers eg. styrene, methacrylates, acrylates, (metha) crylamides [3].

It is important to choose appropriate method of polymerization in the synthesis of luminescent polymers. The presence of chromophores in the main or/and side chain can influence on photo and electroluminescent properties. By changing the polymer repeat unit or using a side groups ranging from small to sterically demanding the different colors reveal by polymers can be achieved. A lot of conjugated polymers which are capable to conducting an electrical charge and exhibit luminescent properties can be used as: active layer, OLED, biomarkers, photovoltaic cells, anti-reflective filter [4–6].

Carbazole and it derivatives are well-known hole-transporting and electroluminescent unites. Polymers containing carbazole moieties in the main or side chains are widely used in OLED, solar cell and flat-panel displays [7–10]. Methacrylic derivatives of coumarins are known as blue light emitters what strongly depends on chemical structure of coumarin rings. Last synthesis of copolymers containing coumarin and carbazole units using ATRP techniques were conducted [11].

Microwave assisted synthesis is technique which provide to reduce reaction time, and increasing product's yields. In this article we reported a synthesis various 2-(9-carbazolyl)ethyl methacrylate (CEM) and 7-(diethylamino)coumarin-3-carboxylic acid 2-(methacryloyloxy) ethyl ester (MK) copolymers by ATRP polymerization using various catalyst and 1,10-phenanthroline monohydrate as organic ligands. All copolymerizations were carried out both under conventional and microwave conditions.

2. Experimental

2.1. Materials

Carbazole was purchased from MERCK. Methacrylic acid, 2-hydroxyethyl methacrylate (HEMA), 4-(diethylamino)salicylaldehyde, diethyl malonate, 2-chloroethanol, was supplied by Sigma-Aldrich. Dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane, toluene were dried according to procedures described in the literature [11]. HEMA and azobisisobutyronitrile (AIBN) were dried and purified. All other reagents and solvents were analytical grade and were used without further purification. Monomers CEM and MK used to synthesis of copolymers were carried out according to known procedures developed in our laboratory [11].

2.2. Methods

In order to obtain the CEM0.5MK (Fig. 1) copolymers, CEM and MK monomers were copolymerized in molar ratio 99,5:0,5 (mol/mol). All the substrates in appropriate molar ratio were placed in test tube. Each samples contained CEM, MK, azobisisobutyronitrile (AIBN) in molar ratio 50:0,5:1, respectively. The following compounds were used as an activating systems in ATRP technique: copper (II) chloride dihydrate $CuCl_2 \cdot 2H_2O$, bis(triphenylphosphine) nickel (II) bromide ($DTPNiBr_2$), iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) with organic ligand 1,10-phenanthroline. The activating system was added in molar ratio $CuCl_2 \cdot 2H_2O$:1,10-phenanthroline – 2:4 and $FeCl_3 \cdot 6H_2O$:1,10-phenanthroline – 2:6. In reaction with $DTPNiBr_2$, 1,10-phenanthroline was not used and the molar ratio to CEM was set to 2. All systems were dissolved in anhydrous toluene (4 cm^3). In the next step mixtures of reagents were flushed with argon for 15 min. Polymerization reaction were conducted at 70°C for 48 h in conventional heating. Finally, the copolymers were precipitated by the addition of methanol, filtered and dried. The purification process was repeated twice.

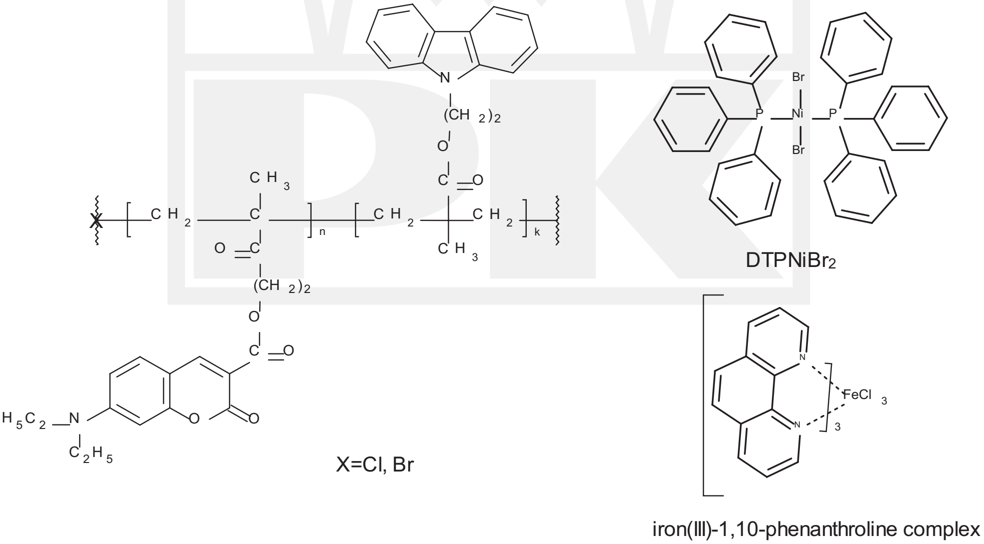

Fig. 1. The structure of CEMMK copolymers (*n*:*k* = 99,5:0,5) and ATRP catalysts

Rys. 1. Struktura kopolimerów CEMMK i katalizatorów ATRP

The second stage of experiment was concerned with the synthesis of CEM0.5MK copolymers using ATRP technique under microwave conditions. Reactions were carried out for the same systems and quantities as in conventional heating. Anhydrous toluene (4 cm^3) was placed into each of the tubes than vessels were sealed and flushed with argon for 15 min. Microwave experiments were carried out in Prolabo Synthewave® 402 in tubes with condenser, in the inert gas atmosphere at 70°C for 1 h (20% of power ~ 60W). As a result copolymers were obtained by the precipitation with methanol (50 cm^3). Afterwards the copolymers were dried and purified twice by re-dissolving in methanol.

The molecular weights M_n, M_w and polydispersity (PDI) of the products were calculated from chromatograms achieved from gel permeation chromatography (GPC) using Knauer chromatograph. Photoluminescence spectra data's were obtained using PG Instruments Ltd. T80$^+$ UV/Vis spectrometer and Ocean Optics USB2000 spectrophotometer.

3. Results and discusion

We achieved a various copolymers based on 2-(9-carbazolyl)ethyl methacrylate (CEM) with 7-(diethyloamino)coumarine-3-carboxylic acid 2-(methacyloyloxy)ethyl ester (MK) using ATRP method. Reactions were performed under conventional and microwave conditions using 3 different catalyst. The monomers were polymerize in molar ratio CEM:MK equals 99,5:0,5.

Table 1

The number and weight average molecular weights, yield of CEM0.5MK copolymers (under conventional conditions)

Catalyst system for CEM0.5MK copolymer*	Acronym	Mn [g/mol]	Mw [g/mol]	Pd	Yield [%]
None – the classic method	CEMMK	$5{,}62\cdot10^3$	$1{,}63\cdot10^4$	2,91	85
FeCl$_3$-Phen	2CEMMK	$6{,}41\cdot10^3$	$1{,}43\cdot10^4$	2,23	62
DTPNiBr$_2$	3CEMMK	$5{,}51\cdot10^3$	$1{,}25\cdot10^4$	2,26	82
CuCl$_2$-Phen	4CEMMK	$2{,}93\cdot10^3$	$5{,}28\cdot10^3$	1,80	72

* CuBr-Phen, CuCl-Phen, CuCl$_2$-Phen, FeCl$_3$-Phen, DTPNiBr$_2$ corresponds subsequently to the [CuCl$_2\cdot$2H$_2$O][1,10-phentanthroline x H$_2$O]$_2$, [FeCl$_3$6H$_2$O] [1,10-phentanthroline H$_2$O]$_{3,}$ C$_{36}$H$_{30}$Br$_2$NiP$_2$ Dibromobis(triphenylphosphine)nickel(II).

The GPC analysis data are presented in Tab. 1. The highest yield 82% was achieved in 3CEMMK where DTPNiBr$_2$ was used as the ATRP catalyst. Similar and relatively small degree of polydispersity were obtained for 2CEMMK and 4CEMMK. It was found that in the presence of catalytic amount of copper (II) and iron (III) chloride complex with 1,10-phentanthroline monohydrate the molecular weight control of formed chains is the highest. In other case the copolymers 1CEMMK (without catalyst) have a higher polydispersity and weight average molecular weights. Moreover, as a result of addition of copper chloride the number and weight average molecular weights were almost two times smaller than with other catalysts.

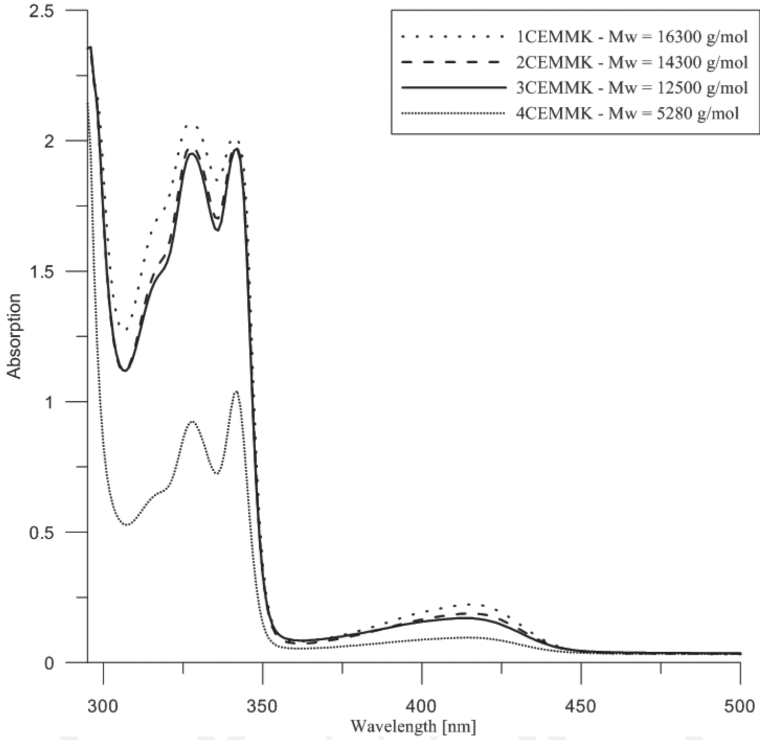

Fig. 2. The absorption bands of copolymers CEMMK (conventional heating) in 1,4-dioxane solution ($1{,}33 \cdot 10^{-5}$ mol/l)

Rys. 2. Widma absorpcji kopolimerów CEMMK (ogrzewanie konwencjonalne) w roztworze 1,4-dioxanu ($1{,}33 \cdot 10^{-5}$ mol/l, $\lambda_{ex.}$= 366 nm)

The absorption spectra of copolymers obtained by conventional heating were presented in the Fig. 2. In the spectra the wide absorption band in the range 360–440 nm caused by coumarin groups can be observed. There are also two characteristic maxims from carbazole chromophore at 328 nm and 341 nm. With the increase of weight average molecular weights the absorption from both chromophores increase.

Fig. 3 illustrates the emission spectra of copolymers synthesized under conventional conditions. The maximum observed at 364 nm comes from carbazole rings. The wide range from 420 to 550 nm with maximum at 452 nm is connection with emission from coumarin rings. The intensity of emission coumarin chromophore for copolymers obtain by using catalyst system (sample 2,3,4CEMMK) is much higher than the copolymer 1CEMMK where it wasn't used. The increase of emission intensity which was observed in 2,3,4CEMMK copolymers may be indicate by an energy transfer from the lowest singlet excited state of carbazole to the coumarin rings.

Copolymers obtained under microwave heating exhibit polydispersity index in the range 1,83–2,42 and have a molecular weights of the order of 10^3 (Tab. 2). Due to the nature of conventional and microwave heating it is very difficult to compare these two method but we try repeat selected parameters, such as temperature, catalyst, and solvent in order to

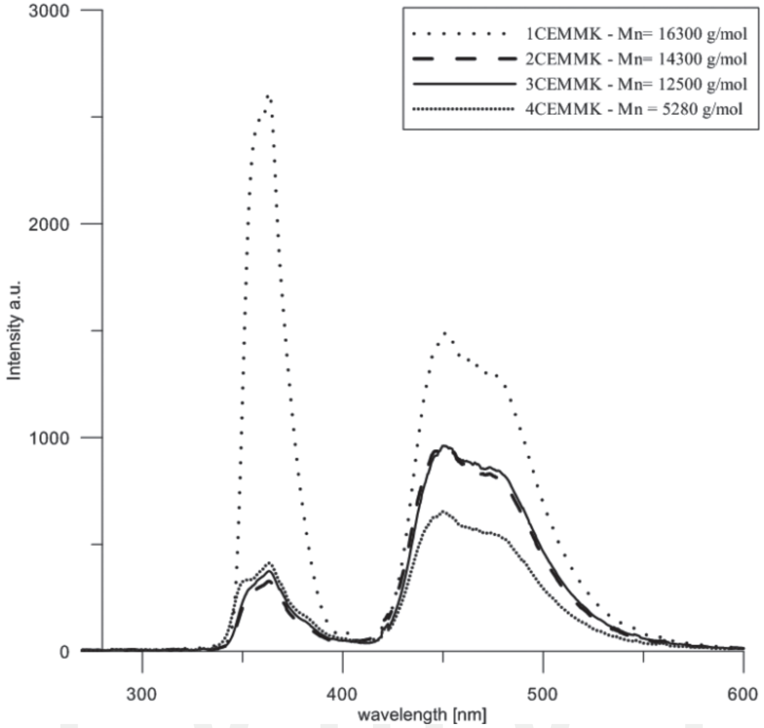

Fig. 3. The emission bands of copolymers CEMMK (conventional heating) in 1,4-dioxane solutions ($1{,}33 \cdot 10^{-5}$ mol/l, $\lambda_{ex.}$= 366 nm)

Rys. 3. Widma emisji kopolimerów CEMMK (ogrzewanie konwencjonalne) w roztworze 1,4-dioxanu ($1{,}33 \cdot 10^{-5}$ mol/l, $\lambda_{ex.}$= 366 nm)

Table 2

The number and weight average molecular weights, yield for CEM0,5MK copolymers (under MV conditions)

Catalyst system for CEM0.5MK	Abbreviation	M_n [g/mol]	M_w [g/mol]	Pd	Yield [%]
$FeCl_3$-Phen	1MVCEMMK	$2{,}81 \cdot 10^3$	$6{,}69 \cdot 10^3$	2,38	48
$CuCl_2$-Phen	2MVCEMMK	$2{,}59 \cdot 10^3$	$6{,}27 \cdot 10^3$	2,42	46
$DTPNiBr_2$	3MVCEMMK	$2{,}32 \cdot 10^3$	$4{,}27 \cdot 10^3$	1,83	15
NONE	4MVCEMMK	$3{,}60 \cdot 10^3$	$7{,}57 \cdot 10^3$	2,10	13

ensure the comparability of the processes. All reactions in MV were conducted for 1 hour which is a very short time for ATRP process. For example in conventional conditions we heated samples for 48 h. In ATRP technique reactions are carried out over several hours even up to several days. The idea of ATRP process is based on slow down the growth of the chain and extend the time of his life. Long duration of the polymerization process allows to achieve the dynamic equilibrium between active and inactive macro radicals. Such control over the polymerization process allows a simultaneous growth of all chains and thus provide to control over polymer molecular weight and polydispersity (PDI). The slight increase in polydispersity of the copolymers obtained by this method and their relatively low efficiency may be connection with short time of polymerization and the type of catalyst.

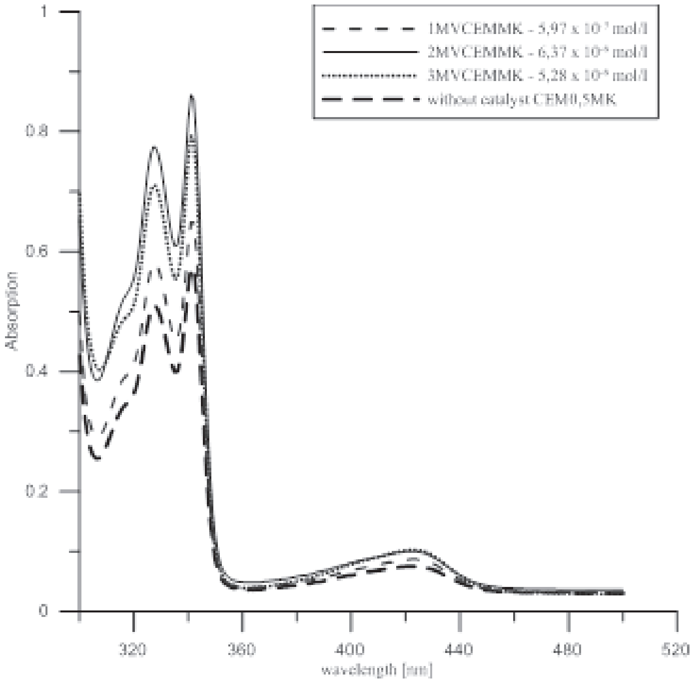

Fig. 4. The absorption of copolymers CEMMK (microwave heating) in 1,4-dioxane solution ($1,33 \cdot 10^{-5}$ mol/l)

Rys. 4. Widma absorpcji kopolimerów CEMMK (ogrzewanie mikrofalowe) w roztworze 1,4-dioxanu ($1,33 \cdot 10^{-5}$ mol/l)

Absorption spectra for copolymers obtain under microwave heating were made by the same procedure as previously (Fig. 4). It shows two characteristic emission bands come from carbazole and coumarin rings. Spectra of copolymers obtained in the conventional manner are similar to those made for copolymers which were synthesized using microwave irradiation. In earlier publications concerning the synthesis of copolymers CEMMK by free radical polymerization in solution the PDI = 2,8–3,1 [11] was obtained. In our experiment we achieved significantly reducing of the polydispersity index. Presented studies have confirmed the catalytic activity $CuCl_2 \cdot 2H_2O$ and $FeCl_3 \cdot 6H_2O$ in combination with 1,10-phentanthroline monohydreate as organic ligand.

4. Conclusions

The copolymers CEMMK were successfully synthesized by ATRP method. As a result of the synthesis were reduced polydispersity of copolymers compared to the previous work [11]. The absorption and emission spectra shows that luminescent properties of copolymers CEMMK are strictly connected with their chemical compositions. Even small amount of coumarine monomer could influences on electron structure.

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