Preparation of poly(ethylcyanoacrylate) nanofibers by vapor phase polymerization using alcohol initiators

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Anionic initiators, containing either hydroxyl or thiohydroxyl group as initiating moieties, were used for preparation of poly(ethylcynoacrylate) (PECA) nanofibers by vapor phase polymerization. The hydroxyl (alcohol) and thoalcohol groups as nucleophilic entities are capable to attack the double bond of monomer resulting in polymerization in vapor phase and formation of nanofibers at high relative humidity atmosphere. Different techniques such as scanning electron microscopy, thermogravimetric analysis, differential scanning calorimetry, gel permeation chromatography and Fourier transformed infrared spectroscopy were used for characterization of the morphology, thermal behavior, molecular weight and structure of polymer nanostructures (nanofibers).

The results obtained show differences in the properties of PECA nanofibers formed via vapor phase polymerization more probably due to the different nucleophilicity of both initiating species.

Key words: Nanofibers, poly(ethylcyanoacrylate), vapor phase polymerization, alcohol initiators

1. INTRODUCTION

Alkyl-2-cyanoacrylates (ACA) are known as one of the most reactive monomers that easily undergo anionic polymerization by nucleophilic attack of strongly activated double bond even by traces of nucleophiles or weak bases such as water or alcohols [1]. The high susceptibility to anionic polymerization of the ACA originates from the monomer property of the 1,1 di-substituted strong electron withdrawing groups, nitrile (CN) and ester (COOR). The attacking nucleophile causes strong electromeric effects, which make the nitrile and ester groups highly negative. This leads to the polarization of the double bond and activates the monomer to the nucleophilic attack. Polymerization of cyanoacrylate vapors is used in forensic science for development of latent fingerprints [2,3] and for replication of ice crystals [4]. In the recent years, Mankidy et al. [5,6] were prepared nanofibers of poly(ethyl-2-cyanoacrylate) (PECA) by a vapor phase polymerization directly on surface modified glass substrates. The vapor phase polymerization of ethyl-2-cyanoacrylate (ECA) accomplished under high relative humidity conditions resulted in different polymer morphologies depending on the type of initiator used [7]. As the best of our knowledge mercaptoethanol is not investigated as initiator of ECA vapor phase polymerization.

2. EXPERIMENTAL

2.1 Materials

Ethyl-2-cyanoacrylate monomer was purchased from Specialty Polymers Ltd, Bulgaria. Ethanol (96%), sulfuric acid (97%) and hydrogen peroxide (30%) were from Valerus Ltd, Bulgaria. 1N–(3-methoxy silyl propyl)diethylenetriamine was obtained from Sigma Aldrich (USA) and mercaptoethanol (96%) was from Merck (USA). Tetrahydrofuran (THF) was from Merck (Germany). All chemicals were of laboratory grade purity and used as obtained.

Microscope slides (coverglasses) with size of 18x18 mm were from Knittel Glass (Germany).

2.2. Methods

2.2.1. Preparation of poly(ethylcyanoacrylate) (PECA) nanofibers by vapor phase polymerization. The closed glass chamber was used at room temperature with a humidity of 89.6-90.3% for preparation of PECA nanofibers. Glass substrates used for nanofibers deposition were cleaned by immersing for 30 min in a freshly prepared Piranha etching solution, then rinsed carefully with deionized water followed by ethanol and dried. Silanation of the cleaned substrate surfaces was performed by 2% aqueous solution of 1N–(3-methoxy silyl propyl)diethylenetriamine in deionized water. For this purpose the cleaned substrates were immersed in this silane solution for

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45 min and after that were removed and immediately rinsed with ethanol. The substrates were then placed in a drying-oven maintained at 110°C for 2 hours. Both anionic initiators at a volume of 0.3-0.5 ml were scattered onto processed glass substrates and dried. The substrate was then placed in the chamber with humidifying solution (8 % aqueous solution of sulfuric acid) and humidified for about 10 hours at 89-90% RH. Subsequently (after wetting of substrates), 50 μl of liquid ECA monomer was placed in a plate inside the chamber and vapor phase polymerization was carried out for 12 hours. The circulation in the gas phase inside the chamber was provided by a fan. Humidity was monitored by a Thermo-/Hygrometer model 306 (Germany).

The nanofibers samples were carefully scraped away from the glass substrates, washed by distilled water and dried before characterization by Infra Red Spectroscopy, Gel Permeation Chromatography and Thermal analyses.

2.2.2. Scanning electron microscopy (SEM). The morphology of PECA nanofibers was examined using a scanning electron microscope SEM 515 Philips (Holland) operated at 25 kV of acceleration voltage. Before the observation the samples were coated with thin gold film by BH-30 coater (Philips).

2.2.3. Fourier Transformed Infrared Spectroscopy Fourier Transformed Infrared (FT-IR) spectra of the PECA nanofibers were recorded on an IR Affinity-1 "SHIMADZU" FTIR spectrometer with MIRacle Attenuated Total Reflectance Attachment. A total of 50 scans were used and data were recorded with a spectral resolution of 4 cm^{-1} over the range 4000–400 cm^{-1} spectral region.

2.2.4. Gel Permeation Chromatography. Molecular weight and molecular weight distribution of the PECA nanofibers were determined by Gel Permeation Chromatography (GPC). GPC was performed on a Waters chromatographic system equipped with a double detection - Differential Refractometer M410 and an UV M484 (254 nm) detector. The analyses were performed on Phenogel 50Å, Phenogel 100Å and Phenogel 10000Å columns (Phenomenex) calibrated with polystyrene standards. THF was used as a mobile phase with a flow rate of 1.0 ml/min at 40°C. Data collection and processing were done by the Clarity software.

2.2.5. Thermal analyses. Thermogravimetric (TGA) – Differential Scanning Calorimetry (DSC) analyses were performed using DSC-TGA Perkin-Elmer Sapphire machine in flowing N_2 with an average heating rate of 10°C/min between 25 and 300°C.

Thermal degradation and the weight loss of the nanofibers samples were obtained by TGA. The TGA experiments were carried out under a nitrogen flow from 25°C to 300°C at a scan rate of 10°C/min. The glass transition temperatures (Tg) of the PECA nanofibers were measured with DSC. For each measurement, a sample of approximately 5 mg was used, placed in aluminum pan and sealed. The samples were firstly heated from 25°C to 170°C and cooled down (2.5°C/min) to 25°C. Then the analyzed samples were heated to 300°C at a scan rate of 10°C/min. Glass transition temperatures were determined from the first derivative of second scan and the midpoint of the transitions was taken as Tg.

4. RESULTS AND DISCUSSIONS

Poly (ethyl 2-cyanoacrylate) nanofibers were synthesized via vapor phase polymerization initiated either by ethanol or mercaptoethanol. ECA monomer introduced in the vapor phase polymerizes on a glass substrate coated with the alcohol initiators of polymerization. The formation of PECA nanofibers was observed using scanning electron microscopy. SEM analyses of the surface morphology of the obtained polymer nanostructures substantiate the availability of nanofibers deposited on the glass substrates (Figs. 1-2).

The examination of the micrographs shows that the glass substrates with deposited PECA nanofibers initiated with mercaptoethanol are more densely populated (Fig.2-A,B) as compared to these, on which nanofibers initiated with ethanol are deposited (Fig. 1). However there were observed areas, in which the nanofibers deposited are not homogenous in diameter as shown in Fig. 2-A,B. The reason for this higher nanofibers yield could be the different rate of polymerization. The diameters of nanofibers initiated with ethanol were between 125-250 nm (mean diameter of 175.75 nm), while these of nanofibers initiated with mercaptoethanol were between 100-200 nm (mean diameter of 141.75 nm).

IR spectra show no differences between the two vapor phase synthesized polymer nanofibers regarding their chemical structure (Fig. 3). The characteristic bands for PECA are well seen in both spectra: CH_3 at 2988 and 2880 cm^{-1}, CH_2 at 2943 cm^{-1}, CN at 2250 cm^{-1}, C=O at 1745/6 cm^{-1}, C-O-C at 1247 and 1013 cm^{-1}. The C-CN band was observed at 1156 cm^{-1}.
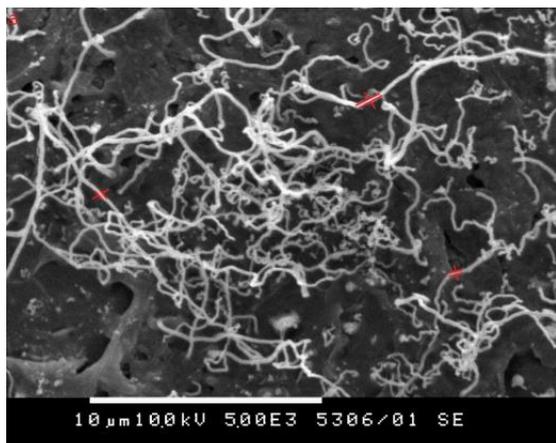
Fig. 1. SEM micrograph of PECA nanofibers prepared by vapor phase polymerization initiated with ethanol
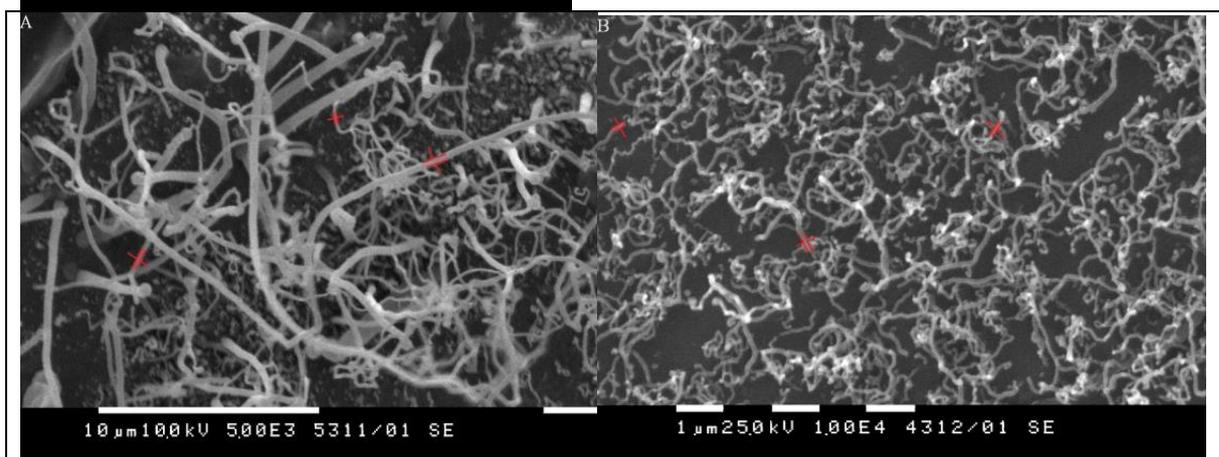
Fig. 2A,B. SEM micrographs of PECA nanofibers prepared by vapor phase polymerization initiated with mercaptoethanol

and mercaptoethanol initiated sample, respectively) there are significant differences in the number
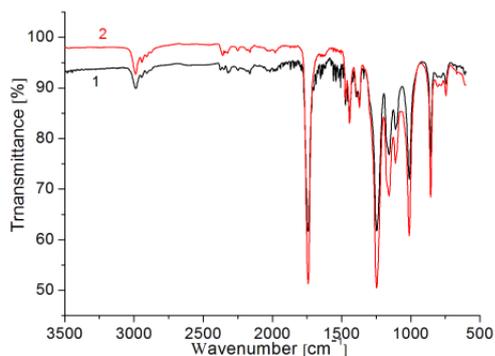
Fig. 3. FT-IR spectra of PECA nanofibers prepared by vapor phase polymerization initiated by ethanol (1) and mercaptoethanol (2)
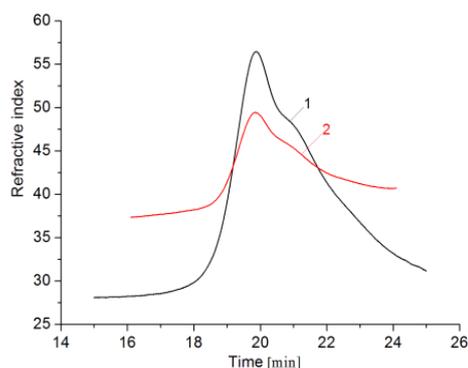
Fig. 4. GPC traces of PECA nanofibers made via vapor phase polymerization using ethanol (1) and mercaptoethanol (2) as initiators.

Molecular weight estimations of PECA nanofibers analyzed were made out using universal polystyrene calibration curve as the standard. Figure 4 depicts the traces obtained from the Refractive Index (RI) detector on the GPC as a function of elution time for both PECA nanofibers samples.

Although the peak molecular weights (Mp) are almost the same (Mp=15163 and 15581 for ethanol

average (Mn) and weight average (Mw) molecular weight values, as well as in the molecular weight distribution (polydispersity, PD) of the two nanofibers samples (Table 1). PECA nanofibers made using mercaptoethanol as initiator have higher Mn and Mw than these made using ethanol as initiator. Furthermore, the initiated by mercaptoethanol nanofibers show more than twice

narrow PD (1.5) in comparison to initiated by concentration of both initiators as well as the time of polymerization (about 12 hours) were the same, the differences are probably due to the differences in the rates of initiation, propagation or chain transfer (termination) during the polymerization. The lower molecular weight for PECA nanofibers prepared with ethanol as initiator could be due to a slower rate for initiation in contrast to the PECA nanofibers obtain in the presence of mercaptoethanol as initiator. This finding is in good accordance with the nucleophilicity of $^-$OH and $^-$SH species. HO$^-$ is smaller, more solvated, and less nucleophilic than HS$^-$ [8]. The IR data analysis indicated that transfer or termination reactions are identical in the two PECA nanofibers since no differences were observed in the IR spectra (Fig. 3). If so the lower molecular weight for PECA nanofibers obtained with initiator ethanol could be a result of a slower rate of initiation.

Table 1. Molecular weight characteristics of PECA nanofibers prepared by vapor phase polymerization initiated with ethanol and mercaptoethanol.

Initiator	Mp g/mol	Mn g/mol	Mw g/mol	PD (Mw/Mn)
Ethanol	15163	2857	10898	3.81
Mercaptoethanol	15581	8462	12749	1.50

Mn, Mw and Mw/Mn values relative to PS standards.

The thermal stability of the synthesized PECA nanofibers was studied by TGA. The TGA curves of PECA nanofibers prepared by two alcohol initiators differing by the nucleophilicity of their initiating species, $^-$OH and $^-$SH respectively, are shown in Fig. 5. Both curves appeared in the same temperature interval showing similar shapes. The initial (2%) and the maximum mass loss temperatures for PECA nanofibers studied are set in Table 2. The PECA nanofibers samples obtained by vapor phase polymerization initiated by ethanol and mercaptoethanol are relatively stable until 143 and

ethanol ones (3.8). As the quantity and 146°C, respectively. Nanofibers obtained with ethanol as initiator start degrading at slightly lower temperature than these prepared with mercaptoethanol. Their maximum degradation rate is registered significantly earlier (at 247°C) than that of mercaptoethanol initiated nanofibers (at 297°C). The two nanofibers samples completely degraded at around 300°C. The results obtained are in accordance with the suggestion of a previous study that the stability of the PACA depends on the nature of initiator and polymerization method [9].
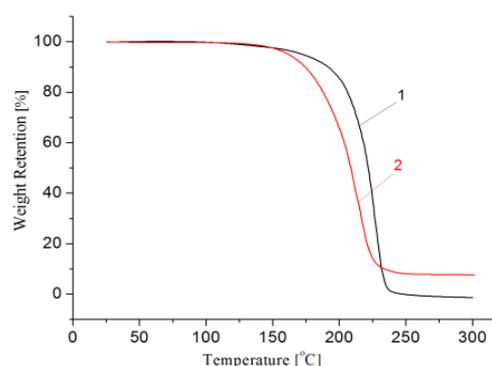
Fig. 5. TGA curves at a heating rate of 10°C/min of PECA nanofibers prepared by vapor phase polymerization with initiators ethanol (1) and mercaptoethanol (2).

The glass transition temperature of PECA nanofibers samples synthesized by vapor phase polymerization process initiated with ethanol and mercaptoethanol were determined by DSC analysis. The PECA nanofibers synthesized using initiator ethanol showed rather unclear glass transitions during the 1st DSC scan (Fig 6).

During the first DSC scan, two endothermic processes/peaks can be identified in the nanofibers sample obtained with initiation by mercaptoethanol. The first one, weak and relatively wide peak was registered around 64°C. The second relatively narrow and sharp endothermic peak superimposed over the Tg transition is registered at 138°C.

Table 2. Temperatures of initial (2%) and maximal weight loss and transition temperatures of PECA nanofibers, prepared by vapor phase polymerization depending on the initiator used.

Weight loss temperatures and transition temperatures* of PECA nanofibers					
Ethanol			Mercaptoethanol		
2% loss, °C	Max. loss, °C	Tg, °C	2% loss, °C	Max. loss, °C	Tg, °C
143.05	247.19	104	146.28	297.66	128.5

*Tg values were determined after the second DSC scan.

Denchev and co-authors [10] described the same behavior of PECA films synthesized in bulk assuming that neither of these transitions could be due to degradation with weight loss. They attributed the endothermic peak close to Tg rather to structural relaxation due the intensified chain mobility often found in other polymer systems [11].
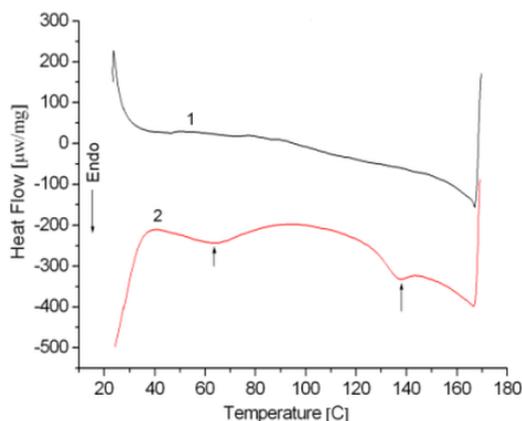
Fig. 6. DSC thermogramms of PECA nanofibers prepared by ethanol (1) and mercaptoethanol (2) used as initiators of vapor phase polymerization, 1st DSC scan.

To more exact determination of the Tg, the first derivative of the second DSC scan was calculated, showing a step instead of a peak. Glass transition temperatures were determined from the first derivative of second scan and the midpoint of the transitions was taken as Tg (figures are not shown). The individual data for both nanofibers are listed in Table 2. The glass transition temperatures in the PECA nanofibers increase with increasing the nucleophilicity of the initiating species of the alcohol used and the molecular weight of the respective nanofibers. Thus PECA nanofibers, depending on the initiator of vapor phase polymerization used and the molecular weight display a Tg between 104 and 128.5ºC. As a linear polymer chain PECA has two chain ends, on decreasing molecular weight, the concentration of chain ends increases and the mobility averaged over all repeat units is enhanced, resulting in decrease Tg.[12].

5. CONCLUSIONS

Poly(ethylcynoacrylate) nanofibers were successfully synthesized by vapor phase polymerization initiated by anionic (alcohol) initiators differing by the nucleophilicity of their initiating species, $^-$OH and $^-$SH, as documented by SEM. Mercaptoethanol was used for the first time for initiation of vapor phase polymerization of ECA aiming to synthesize polymer nanofibers.

Characterization of the morphology, termal behavior, molecular weight and structure of polymer nanofibers by different techniques clearly showed strong dependence of the properties of PECA nanofibers on the nucleophilicity of the initiator used for the vapor phase polymerization process.

Investigations dealing with preparation of PACA nanofibers by vapor phase polymerization initiated by different initiators are in progress.

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ПОЛУЧАВАНЕ НА ПОЛИЕТИЛЦИАНАКРИЛАТНИ НАНОВЛАКНА ЧРЕЗ ПОЛИМЕРИЗАЦИЯ В ПАРОВА ФАЗА С АЛКОХОЛНИ ИНИЦИАТОРИ

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(Резюме)

Анионни инициатори, съдържащи хидроксилна или тиохидроксилна група като инициращи групи, са използвани за получаване на полиетилцианакрилатни (ПЕЦА) нановлакна чрез полимеризация в парова фаза. Хидроксилната (алкохолна) и тиоалкохолна групи като нуклеофилни единици са способни да атакуват двойната връзка на мономера, в резултат на което протича полимеризация в парова фаза и формиране на нановлакна в атмосфера с висока относителна влажност. Различни техники като сканираща електронна микроскопия, термогравиметричен анализ, диференциална сканираща калориметрия, гелово-проникваща хроматография и инфрачервена спектроскопия с Фурие трансфомация са използвани за охарактеризиране на морфологията, термичното поведение, молекулната маса и структурата на полимерните наноструктури (нановлакна).

Получените резултати показват различия в свойствата на ПЕЦА нановлакна, формирани чрез полимеризация в парова фаза, най-вероятно поради различната нуклеофилност на двете инициращи групи.