

NANOPOROUS POLYCYANURATE FILMS VIA SYNTHESIS IN SITU WITH IONIC LIQUIDS

The article discusses characteristics of novel porous film materials of thermostable polycyanurates generated by polycyclotrimerization of dicyanate ester of bisphenol E in situ of 1-heptylpyridinium tetrafluoroborate, [HPyr][BF₄], ionic liquid (IL) followed by simple extraction of IL. The scanning electron microscopy and DSC-based thermoporometry analyses confirmed the formation of the nanoporous structure in the investigated CER samples. The pore size distribution varied from ~20 to ~180 nm with an average pore diameter of around 45 and 60 nm depending on the initial porogen content in the studied CERs.

Keywords: cyanate ester resins, ionic liquids, porous materials.

Introduction

Cyanate ester resins (CERs) – also known as polycyanurates (PCNs) – are commonly used in aerospace applications and electronic devices as high temperature polymer matrices. The specific interest in these high performance polymers arises from their unique combination of intrinsic properties, including thermal, fire, radiation and chemical resistance, high tensile moduli (3.1–3.4 GPa) and glass transition temperatures ($T_g > 250$ °C), low dielectric constants ($\epsilon \sim 2.5$ –3.2), high adhesion to conductor metals and composites as well as low water/moisture adsorption [1; 2].

Ionic liquids (ILs) are organic salts with melting points below or equal to room temperature that typically consist of bulky, asymmetric organic cations and inorganic anions. ILs have attracted widespread interest in polymer science, due to their unique properties, such as essentially near-zero vapour pressures, non-flammability, incombustibility, electrochemical and high-temperature stability, good stability to oxidation and recyclability [3]. Another application of ILs is as effective and reusable porogens in some polymerization reactions [3; 4]. In the case of membrane processes, ILs are being used in the design and modification of advanced materials that enable performance levels not typical of conventional materials [5].

Porous polymeric materials have a large variety of applications in many areas, as highly efficient membranes, porous substrates, selective adsorbents and filters, porous electrodes for fuel cells, sensors or insulators etc. Recently several papers have been published [6–9] on generation of porous structure in crosslinked CERs (polycyanurates) using different techniques.

This work is focused on the new approach – synthesis of novel nanoporous CERs using

1-heptylpyridinium tetrafluoroborate ionic liquids ([HPyr][BF₄]) as porogen, and investigation of effect of porogen content on their porosity characteristics.

Materials

1,1'-bis(4-cyanatophenyl) ethane (dicyanate ester of bisphenol E, DCBE), under the trade name Primaset™ LECy was kindly supplied by Lonza (Bazel, Switzerland). The following chemicals were used for the synthesis of the 1-heptylpyridinium tetrafluoroborate, [HPyr][BF₄]: pyridine, 1-chloroheptane, ethyl acetate, hexane, tetrafluoroboric acid (48 wt.% in H₂O), methylene chloride, and sodium sulfate. The chemicals were provided by Fluka and were used as received.

Ionic liquid synthesis

1-heptylpyridinium tetrafluoroborate [HPyr][BF₄] was synthesized using the following method. The mixture of dry pyridine and 1-chloroheptane in molar ratio 1.0:1.1 was heated at 140 °C for 20 h under stirring. The white solid product – 1-heptylpyridinium chloride precipitated after cooling the reactionary mixture to room temperature. It was purified by recrystallization from ethyl acetate-hexane mixture (1:1 v/v). 1-heptylpyridinium chloride (50 g, 0.23 mol) was dissolved in 300 ml of water and 30 ml of tetrafluoroboric acid was added to the solution. The water immiscible layer of ionic liquid [HPyr][BF₄] formed was extracted with methylene chloride (3×150 ml), washed with water and dried under sodium sulfate. The solvent was distilled off, and the resulting ionic liquid was dried under a reduced pressure of 1 mbar at 80 °C for 12 h.

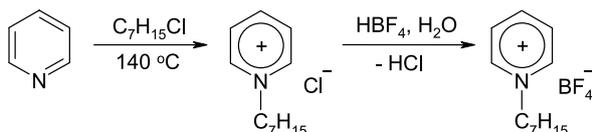


Fig. 1. Synthesis route of [HPyr][BF₄]

Preparation of CER films

DCBE was mixed with [HPyr][BF₄] in a given ratio (the content of [HPyr][BF₄] was varied from 20 to 40 wt.%) and the mixtures obtained were treated by ultrasound in ultrasonic bath at 60 °C for 30 min. Then the solutions of DCBE in [HPyr][BF₄] were poured into PTFE-coated mold and cured over the temperature range from 25 to 300 °C with heating rate of 0.5 °C/min. The polycyclotrimerization of DCBE monomer results in the formation of CER networks (Fig. 2).

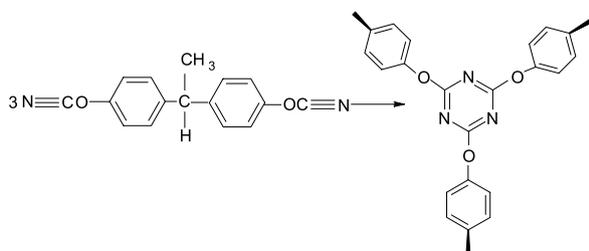


Fig. 2. Reaction scheme associated with polycyclotrimerization of DCBE

The films obtained with a thickness around 100 μm were subjected to extraction with ethanol in a Soxhlet apparatus for 16 h. During extraction of the [HPyr][BF₄] followed by drying of the samples up to a constant weight at 25 °C, the porous structure in the CER-based films was generated. The following codes were applied to the samples studied: CER_(ext), CER_(20ext), CER_(30ext), CER_(40ext) for extracted CER sample synthesized without IL and for CER samples synthesized in the presence of IL, where the subscripts indicate the initial content of the [HPyr][BF₄]. The code CER₍₄₀₎ was applied for the sample CER/[HPyr][BF₄] = 60/40 (wt.%) before extraction used as the non-porous film for comparison.

Methods

The experimental values of gel fractions, $w_{g(\text{exp})}$, were determined as the contents of insoluble part of the samples using following equation:

$$w_{g(\text{exp})} = \frac{m_1}{m_2} \cdot 100\%,$$

where m_1 and m_2 stand for the mass of the dried sample before and after extraction, respectively.

The theoretical values of gel fractions were determined with the conjecture that nonreactive inert [HPyr][BF₄] was completely extracted from CER films using following equation:

$$w_{g(\text{theor})\text{CER}} = w_{g(\text{exp})\text{CER}} - w_{g[\text{HPyr}][\text{BF}_4]},$$

where $w_{g(\text{exp})\text{CER}}$ and $w_{g[\text{HPyr}][\text{BF}_4]}$ stand for the experimental value of gel fraction for pure CER ($w_{g(\text{theor})\text{CER}} = 100.0$ wt.%) and the initial [HPyr][BF₄] content in the studied systems, respectively.

The morphology of the samples was examined by Scanning Electron Microscopy (SEM) using a LEO 1530 microscope with a high-vacuum (10⁻¹⁰ mmHg) Gemini Column equipped with an energy dispersive X-ray spectrometer (EDXS); it operated at accelerating voltage 4 kV. The materials studied were rather stable under electron beam. EDX spectra were obtained in control experiments for local element content analysis; electron beam was focused to a spot of about 2 nm in diameter. Prior to analyses, the samples were coated with a Pd/Au alloy (4 nm thickness) in a Cressington 208 HR sputter-coater. To determine the main porosity characteristics derived from SEM data (i.e. pore size and pore size distribution), 1000 pores for each sample were at least evaluated. Pores with area inferior to 20 nm² and superior to 1.25 × 10⁵ nm² were ignored to avoid counting of improbable values. Since pore circularity values revealed from *ImageJ* analysis varied from 0.80 to 0.90 (assuming that “0” corresponded to an infinitely elongated polygon and “1” was related to a perfect circle), pore diameters were calculated assuming circular pore shapes.

DSC-based thermoporometry was used as an independent quantitative technique for determining pore sizes and pore size distributions. Basic principles and methodology of DSC-based thermoporometry technique are well-known [10; 11].

In this study, thermoporometry was performed using water as a penetrating liquid. Since a cylindrical shape of pores was assumed, the following equations for determination of pore diameter (D_p), pore size distribution (dV/dR_p) and heat flow $\Delta H(T)$ were applied:

$$D_p (\text{nm}) = 2 \cdot \left(0.68 - \frac{32.33}{T_m - T_{m0}} \right)$$

$$dV/dR (\text{cm}^3 \cdot \text{nm}^{-1} \cdot \text{g}^{-1}) = \frac{dq/dt \cdot (T_m - T_{m0})^2}{32.33 \cdot \rho \cdot v \cdot m \cdot \Delta H(T)}$$

$$\Delta H(T) (\text{J} \cdot \text{g}^{-1}) = 332 + 11.39 \cdot (T_m - T_{m0}) + 0.155 \cdot (T_m - T_{m0})^2$$

where T_m and T_{m0} are the melting temperatures of confined and bulk water, respectively; dq/dt , ρ , v , m , and $\Delta H(T)$ are the heat flow recovered by DSC, the

water density, the heating rate, the sample mass and the melting enthalpy of water, correspondingly.

Due to the hydrophobicity of CER porous films, we resorted to an ethanol pretreatment in order to improve their hydrophilic character and favor the water penetration into the pores. Such a pretreatment using an organic solvent miscible with water, followed by its subsequent replacement by water, ensured pore accessibility to water. In addition, it was assumed that pore filling was predominant over the bulk polymer swelling either in ethanol or water, due to the high cross-link density of the CER network. The samples were first immersed to ethanol for 2 h, and then deionized water was gradually added to remove the ethanol. Afterwards, the samples were kept in pure water for 2 weeks. After surface wiping, the melting thermograms were recorded using TA Instruments 2010 calorimeter under nitrogen atmosphere in temperature range from -50 to 5 °C at a heating rate of 1 °C/min. Mass of the samples was about 10–15 mg.

Results and discussion

Generation of porous films was accomplished through forming of CER-based thin films by the *in situ* polycyclotrimerization of CER [1] in the presence of $[\text{HPyr}][\text{BF}_4]$ with the further removal of the latter. One can see from Fig. 3 that the experimental and calculated values of the gel-fraction content nearly coincide that shows a quantitative extraction of $[\text{HPyr}][\text{BF}_4]$ from the CER-based network and confirms the chemical inertness of $[\text{HPyr}][\text{BF}_4]$ towards CER.

Fig. 4 shows the morphology of CERs SEM images films with and without $[\text{HPyr}][\text{BF}_4]$. One

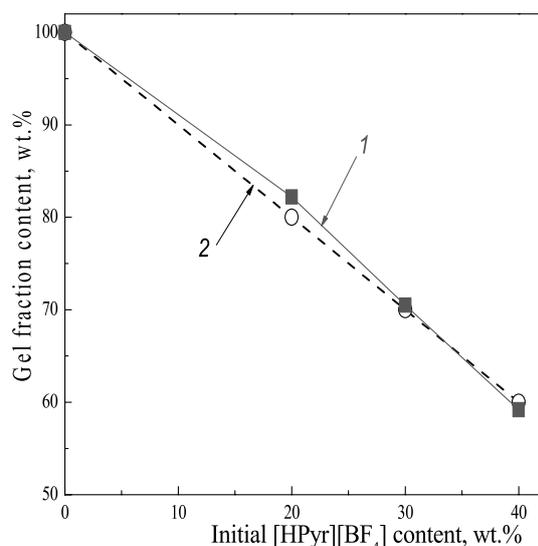


Fig. 3. Experimental (1) and theoretical (2) values of gel fraction content after extraction for the CER-based samples synthesized

can clearly see that both the $\text{CER}_{(\text{ext})}$ and $\text{CER}_{(40)}$ samples have uniform surface structure without any pores (Fig. 4, a and c, respectively), whereas the samples of $\text{CER}_{(20\text{ext})}$ and $\text{CER}_{(40\text{ext})}$ have well-defined porous structure of high regularity (Fig. 4, b and d, respectively). EDX spectra were obtained in control experiments for local element content analysis. Besides SEM micrographs, Fig. 4, e shows also four EDX spectra, which confirm the absence of B and F traces in the porous films. Table 1 shows the experimental and theoretical values of element content in CER-based samples studied. Importantly, the values obtained are similar.

The micrographs obtained were carefully analyzed using the *ImageJ* software. One can see that most of the area fractions are occupied by pores ranging from ~ 500 to 5000 nm² that corresponds to diameters of circle-shaped pores (D_p) from ~ 25 to 80 nm (Fig. 5). The quantity of larger pores (with pore area > 5000 nm², i.e. $D_p > 80$ nm) appeared to be solitary. The values of average pore diameters $D_{p(\text{av})}$ were found to be ~ 40 nm and 65 nm for the $\text{CER}_{(20\text{ext})}$ and $\text{CER}_{(40\text{ext})}$, respectively.

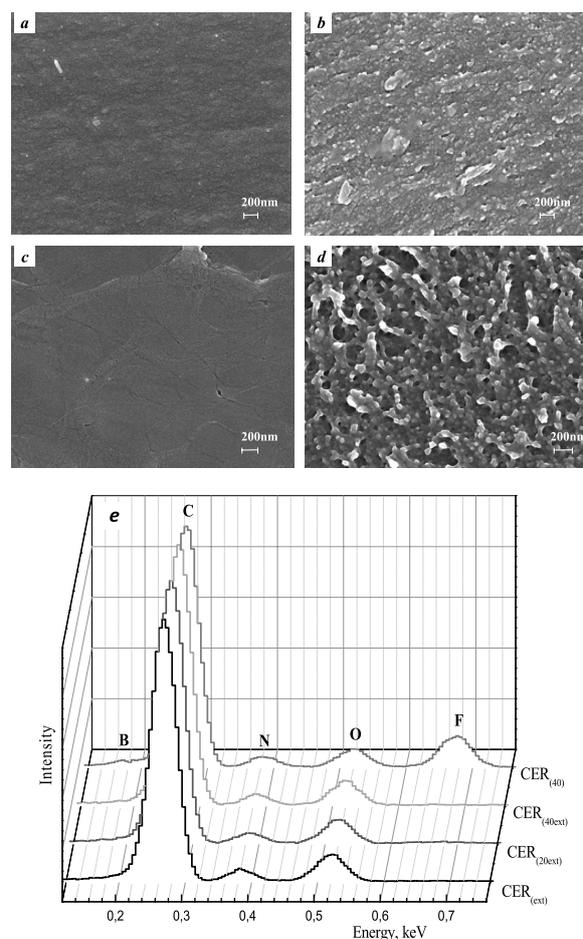


Fig. 4. SEM micrographs of the CER samples obtained: (a) $\text{CER}_{(\text{ext})}$; (b) $\text{CER}_{(20\text{ext})}$; (c) $\text{CER}_{(40)}$; (d) $\text{CER}_{(40\text{ext})}$ and EDX spectra for the CER films (e)

Table 1. Experimental and theoretical values of element content in CER-based samples studied

Samples	Element content, wt. %									
	Experimental (EDXS)					Theoretical (calculated)				
	C	N	O	F	B	C	N	O	F	B
CER _(ext)	76.0	12.0	12	0	0	76.2	11.1	12.7	0	0
CER _(20ext)	75.8	12.1	12.1	0	0	76.2	11.1	12.7	0	0
CER _(30ext)	76.8	11.5	11.7	0	0	76.2	11.1	12.7	0	0
CER _(40ext)	77.3	11.7	11.0	0	0	76.2	11.1	12.7	0	0
CER ₍₄₀₎	67.1	9.0	7.1	14.4	2.4	69.3	9.0	7.7	12.1	1.8

Table 2. Main porosity characteristics for porous PCN-based films after [HPyr][BF4] extraction

Samples	DSC-based thermoporometry			SEM	
	Average pore diameter, nm	Pore size distribution, nm	Total pore volume, V _p (cm ³ ·g ⁻¹)	Average pore diameter, nm	Pore size distribution, nm
PCN _(20ext)	45	~20–105	0.037	40	~25–100
PCN _(40ext)	60	~20–180	0.122	65	~25–170

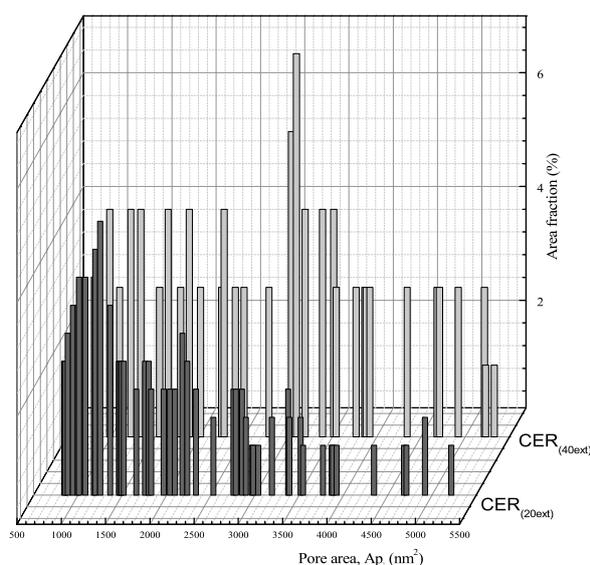


Fig. 5. Pore area distributions derived from SEM data (ImageJ analysis) for the nanoporous CER samples studied

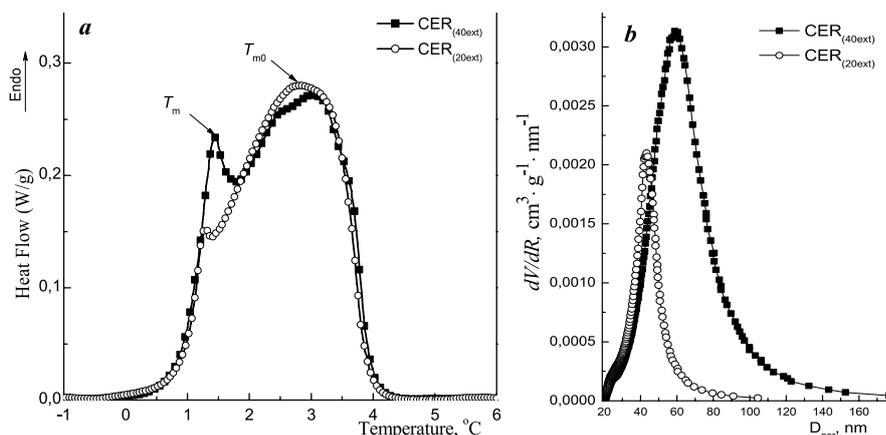


Fig. 6. Typical DSC melting thermograms of water (a) and corresponding pore size distribution profiles for porous samples (b) determined by DSC-based thermoporometry

As it can be seen from Fig. 6, the melting thermograms of water in the temperature region between -1 °C and 6 °C (Fig. 6, a) and the corresponding profiles of pore size distributions (Fig. 6, b) are given for porous CER samples. In the thermograms of CER samples, two endothermic peaks were detected, one with maximum, T_{m1} , between 1 and 2 °C corresponding to the melting of the water constrained within the pores of the films, and a second one with maximum, T_{m2} , between 2 and 4 °C related to the melting of bulk water (Fig. 6, a). It was found that the pore size distribution for the CER-based films studied was in the range of ~20–180 nm (Fig. 6, b) and their average pore diameters were around 45–60 nm (Table 2). It is also noteworthy that an increase in the [HPyr][BF4] content resulted in increasing pore diameters and extension of pore size distribution.

The results obtained by DSC-based thermoporometry clearly showed that pore characteristics were in a good agreement with those

determined by SEM (Table 2). Minor discrepancies between the pore characteristics obtained by both techniques could be explained by a difference between pore shapes of the real CER structures and those used for the mathematical data processing in SEM analyses.

Conclusions

Novel nanoporous film materials based on thermostable polycyanurates generated *in situ* by polycyclotrimerization of CER in the presence of [HPyr][BF₄] have been developed and characterized. Depending on the porogen content the average pore diameters values were found in the range of

45–60 nm with pore size distribution of ~20–180 nm. It is also noteworthy that an increase in the [HPyr][BF₄] content resulted in increasing pore diameters and extension of pore size distribution. It should be noted here that synthesis was carried out without using any solvents and specific catalysts and the ionic liquid used was high temperature tolerable and could be utilized repeatedly.

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СИНТЕЗ НАНОПОРИСТИХ ПОЛІЦІАНОУРЕТАНОВИХ ПЛІВОК IN SITU З ІОННИМИ РІДИНАМИ

Розроблено та охарактеризовано пористі плівкові матеріали на основі термостабільних поліціаноуретанів, одержаних поліциклотримеризацією диціанових естерів бісфенолу Е *in situ* з 1-гептилпіримідин тетрафлуороборатом, [HPyr][BF₄], іонною рідиною (IP) з подальшою простою екстракцією IP. За допомогою сканувальної електронної мікроскопії та ДСК-термопорометрії підтверджено формування нанопористої структури в зразках ЦЕС. Встановлено, що розподіл пор за розмірами варіюється в діапазоні від ~20 до ~180 нм із середнім діаметром пор приблизно 45 і 60 нм, що залежить від початкового вмісту пороутворювача в досліджуваних зразках.

Ключові слова: ціанатестерні смоли, іонні рідини, пористі матеріали.

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