

# RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



## Synthesis and properties of novel polyurethanes based on amino ethers of boron acid for gas separation membranes

I. M. Davletbaeva,<sup>a, b, c</sup> O. Yu. Emelina,<sup>a</sup> I. V. Vorotyntsev,<sup>a</sup> R. S. Davletbaev,<sup>a, d</sup> E. S. Grebennikova,<sup>c</sup> A. N. Petukhov,<sup>a</sup> A. I. Ahkmetshina,<sup>a</sup> T. S. Sazanova,<sup>a</sup> and V. V. Loskutov<sup>e</sup>

Received 00th June 2015,  
Accepted 00th January 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

Herein we present the structural and mechanical properties of polyurethanes synthesized from amino ethers of boric acid for gas separation. The polymers were characterized by light scattering methods, conductivity measurements, thermal gravimetric analysis, Fourier transform infrared spectroscopy, and atomic force microscopy. Additionally, the permeability of ammonia and carbon dioxide, as well as the selectivity for their diffusion and resultant impurity are presented. The results illustrate the steric hindrance, resulting in a branched architecture borate formation, leads to intermolecular complexation which may assist the polymer in ammonia diffusion selectivity.

### Introduction

Throughout recent decades, an increasing interest in membrane gas separation is seen due to its immense potential for the optimization of the manufacturing process which currently utilizes inefficient distillation and sorption methods<sup>1</sup>. The numerous polymers currently used as gas separation membranes have a tendency of permeability/selectivity relations that are limited by upper bond or Robeson line<sup>2-4</sup>. These novel polymers tested as gas separation membranes<sup>5-7</sup> present one of several ways of gas-separation membrane development. The next feature of membrane properties which is exploited to improve separation is a mixed matrix membrane containing additives such as nanoparticle, CNTs, metal-organic frameworks, or other materials which are distributed through the membrane<sup>8-10</sup>.

Considerable efforts have been aimed at improving membrane properties through the use of ionic liquids and its different type of distribution into polymeric chains of a membrane<sup>11-13</sup>. Additionally, a new trend in membrane design<sup>14</sup> is the alteration of membrane structure from two-dimensional geometry with a lower degree of potential application to three-dimensional membrane architectures in molecular ensembles<sup>15</sup>. One approach to design sterically hindered node fragments in macromolecular structure is the application of

amino ethers of boric acid<sup>16-18</sup>. The introduction of steric hindrance effect creates an opportunity to influence polymer architecture and, furthermore, a possibility to control intermolecular interactions, not only between amino ethers of the boronic acid, but also of polymer's macrostructure.

Boron-organic polymers present great potential for chemical production of stable constructive materials and surface protectants operating in aggressive media<sup>19,20</sup>. Moreover, the formations of coordinative bonds of boron-derivatives to nitrogen are used in the design of heterocyclic and macrocyclic precursors<sup>21,22</sup>. One example of facile synthesis of organoboron compounds is based on the etherification of boric acid, however, high hydrolytic instability of boronic acids presents an obstacle to conducting research. Overcoming this instability can be achieved by the alteration of acid structure by the introduction of steric hindrance upon these<sup>23,24</sup>.

The goal of the current work is to obtain hydrolytically stable amino ethers of boronic acid by introducing the aforementioned steric hindrance, and using these materials toward the synthesis of polyurethanes to be tested as a gas separation membranes for ammonia and carbon dioxide. As shown in previous literature<sup>25-29</sup> polyurethane one is the attractive polymer to make such composites.

Carbon dioxide, methane and ammonia were chosen as penetrants for testing gas separation properties, because of its importance to industrial application<sup>1-7</sup>. However, carbon dioxide removal from methane is one of the most discussed applications for polymeric membranes<sup>1-7,30,31</sup>. Regarding to ammonia it has the largest production capacity in the world. The ammonia production process, invented and industrially implemented by Haber and Bosch<sup>31</sup>, has not undergone dramatic changes for more than one hundred years. Certainly, in due course, process optimization must be accomplished, and membrane gas separation is one of the most promising ways to improve this classical process<sup>32-37</sup>. Also agriculture processes like treatment by product storages<sup>38,39</sup> where

<sup>a</sup> Nizhny Novgorod State Technical University n.a. R.E. Alekseev, 24 Minina str., Nizhny Novgorod 603950, Russian Federation

<sup>b</sup> Kazan National Research Technological University, 68 Karl Marks str, Kazan 420015, Republic of Tatarstan, Russian Federation.

<sup>c</sup> Kazan Federal University, 18 Kremlyovskaya St., Kazan 420008, Republic of Tatarstan, Russian Federation

<sup>d</sup> Kazan National Research Technical University n.a. A.N.Tupolev – KAI, 10 Karl Marks str., Kazan 420111, Republic of Tatarstan, Russian Federation

<sup>e</sup> Mary State University, 1 Lenin Sq, Yoshkar-Ola 424000, Russian Federation

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

gaseous emissions contain ammonia, carbon dioxide and methane might be improved by components separations these emissions. As has been previously noted<sup>40</sup>, there is a lack of experimental data on ammonia permeability through a polymeric membrane, which results not only from the hazardous nature of the process itself and the number of special requirements for testing equipment, but also from its ability to react with a polymeric matrix with further plasticization<sup>41-43</sup>. It is known that ammonia typically possesses high permeability, especially in polar polymers, because of its chemical structure and the presence of a lone pair of electrons. These factors led to our hypothesis of ammonia's high permeability in amino ethers of boric acid.

## Results and discussion

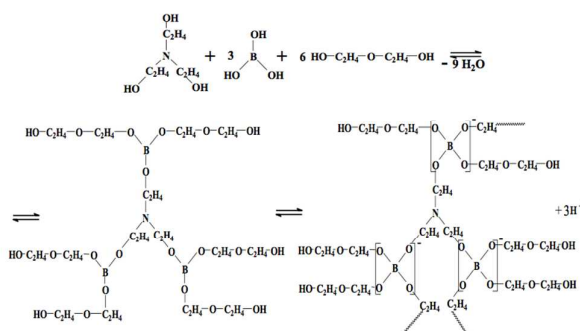
### A Handling of AEBA properties

The synthesis of hyperbranched AEBA, as described above, is shown in Scheme 1. The feature most apparent in this reaction is the increase of reacting mass viscosity and acidity at the initial stages. The comparison of hydroxyl group concentration determined by titration with the theoretical estimation shows good agreement, supporting the presence of a hyperbranched structure in the synthesis of AEBA.

The formation of intermolecular complexes in AEBA-DEG and AEBA-TEG were established by investigation of aqueous solutions of AEBA with the help of dynamic light scattering methods.

It was found that the most probable size of the formed complexes equated to 86 nm, as shown in Figure 1, where the cumulative frequency curve is presented. This is indicative of the AEBA-TEG complex forming massive cluster formations.

The measurements of the viscosity ratio of AEBA-TEG from its concentration in water solutions also informs of the presence of intermolecular complexes of AEBA-TEG. Also as a solvent TEG was used due to elimination the hydrolysis effect on the patterns of change in viscosity AEBA-TEG in water solution, because TEG was a component in the reaction systems of AEBA-TEG. The dependence in Figure 2 shows that when AEBA-TEG concentration decreases in aqueous as well as TEG solutions, the reduction of the viscosity ratio appears at rather high AEBA-TEG concentration.



Scheme 1. The reaction of TEA, boron acid and DEG

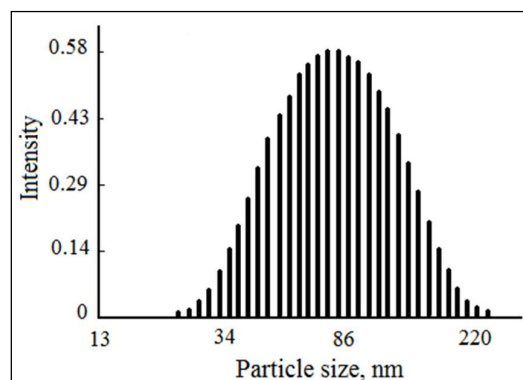


Fig. 1. Cumulative frequency curve of particle size distribution of AEBA-TEG in water.

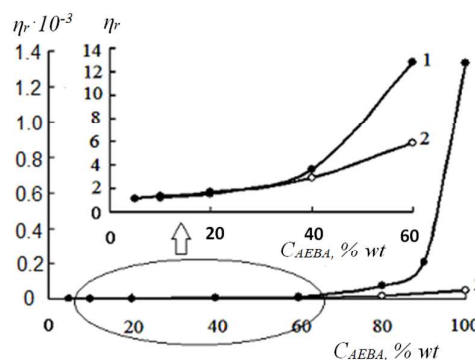


Fig. 2. Concentration dependencies of the viscosity ratio ( $\eta_r$ ) from concentration of AEBA-TEG solution; solvents: water (1) and TEG (2) @ 293 K.

The change of the gradient of character of viscosity ratio from AEBA-TEG concentration shows that a rheological modification occurs upon AEBA-TEG, likely caused by the degradation of intermolecular complexes. According to a ball-and-stick molecular modelling, intermolecular complexes of AEBA-TEG are characterized by a closer packing of atoms than intermolecular complexes of AEBA-DEG. In fact, AEBA-TEG appeared to be more stable to moisture and air at high temperature in comparison with AEBA-DEG. The signs of aging of AEBA-TEG are visible at 443 K, and for AEBA-DEG, this degradation starts at 403 K.

The dependence of the conductivity and viscosity of the AEBA-TEG water solution on the polymer content are shown on Figure 2. As can be seen, with increasing polymer concentration up to the concentrations corresponding to the maxima on the conductivity concentration dependences, the conductivity increased, despite the system viscosity increase; we predict that this was due to a decrease in the entropy contribution to the proton transfer process. The reduction of entropy in the confined geometry of the polymeric matrix resulted in an increase in the conductivity at the expense of the more ordered motion of the charge carriers inside the polymeric skeleton. The importance of this entropic influence has been previously shown<sup>44,45</sup>, where the ionic transport processes in membranes were studied. Further increases in the polymer concentration, higher than those corresponding to the

maximal conductivity (C=28%) led to a substantial viscosity growth and, as a consequence, a decrease in conductivity. The appearance of sharp increase of specific conductivity concentration dependences is often explained by the simultaneous effect of two opposite phenomena. On the one hand, the content of ionic species increases with increasing total water concentration (water acts as a proton donor); this, consequently, should result in conductivity growth. On the other hand, the strengthening of specific interactions and an increase in the viscosity occurs when the water concentration increases, thus depressing the ionic mobility.

### B Characterization of AEBA-TDI properties

It was found that the reactivity of hydroxyl groups and isocyanate groups of 2,4-toluenediisocyanate (TDI) is dependent on the nature of the glycol used for AEBA synthesis. It was also found that the interaction of TDI ([NCO]/[OH]=1) with AEBA-TEG or AEBA-DEG under intensive mixing at 373 K during 3 hours, the reaction of isocyanate groups is rather minimal, without any visible changes, according to FTIR. The absorption peak at 2274  $\text{cm}^{-1}$  which corresponding to N=C=O group is reducing by 30 % only, and there is the appearance of a slight increase in the band 1720  $\text{cm}^{-1}$  due to stretching vibrations of the C=O group of urethane.

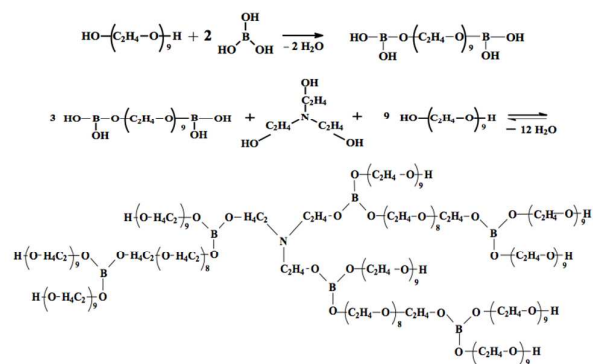
Furthermore, the reaction of AEBA-TEG or AEBA-DEG with a stoichiometric or excess of TDI does not lead to mixture solidification.

This observation supports the aforementioned theory that the reason of intermolecular complexation of AEBA is the reaction between hydroxyl groups and borate which are present in AEBA. As a result of such cluster formation, all hydroxyl groups are disposed within the polymer matrix and drawn into further association in between, which prevents the interaction of hydroxyl groups with the isocyanate group and, accordingly, their inability to form polyurethanes and avoid solidification of the mixture.

A possible method to decrease the influence of intermolecular complexation on the AEBA's possibility to form the node of hyperbranched molecular structure of polyurethanes is to use poly(ethylene glycol) with nine oxyethylene repeating units as a glycol based precursor. The two-stage synthesis of AEBA-PEG is shown in Scheme 2.

AEBA-PEG contains terminal hydroxyl groups. According to the comparison of experimentally found and theoretically calculated number of hydroxyl groups, AEBA-PEG possesses a hyperbranched structure.

Titration analysis of hydroxyl groups conducted in the course of reaction of AEBA-PEG formation shows that the reaction proceeds rather exothermically in high yield. In comparison with AEBA-DEG and AEBA-PEG, AEBA-PEG reacts with TDI. According to FTIR investigation at the stoichiometric ratio



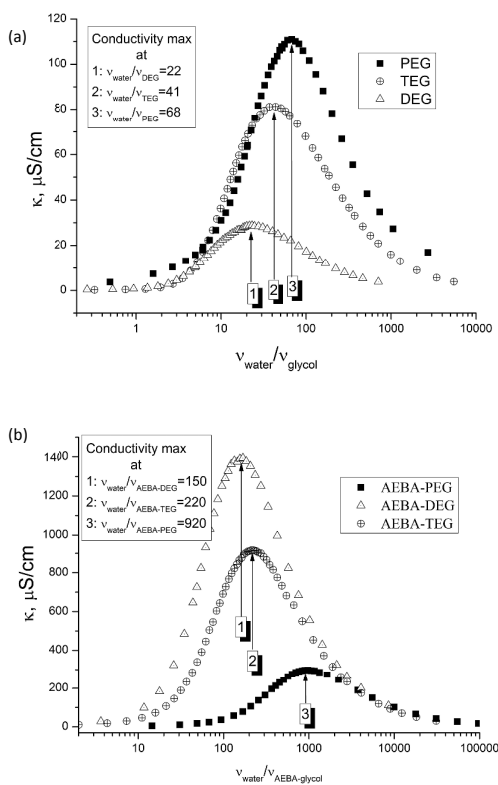
Scheme 2. The reaction of TEA, boron acid and PEG

[NCO]:[OH], the total conversion of isocyanate groups is obtained which is accompanied by the gelation of polyurethanes.

The FTIR spectra of AEBA-PEG shows peaks in the range of 3400-3600  $\text{cm}^{-1}$  which corresponding to associated hydroxyl groups (3400  $\text{cm}^{-1}$ ), as well as to monomeric water (3600  $\text{cm}^{-1}$ ). It was found that in the reaction between TDI and AEBA-PEG, only monomeric hydroxyl groups are consumed throughout the course of the reaction.

Experimentally it was determined that use of polyoxyethelen glycols with higher values of oxyethylene units for synthesis of AEBA-PEG breaks compactness of the macromolecular structure of AEBA-PEG and also leads to microphase separation processes in AEBA-PEG and in polymeric films made from AEBA-PEG with PIC. That is why such polymers are of no interest for solving the problems in the current investigation.

The Grotthuss mechanism<sup>46</sup> of proton transfer appeared to be possible due to hydrogen bonds formed in the system. In contrast to other ions, proton transfer will not occur in a single step, but can be reduced to a succession of jumps along the hydrogen bond and rotations of the proton-containing groups. As has been noted<sup>47</sup>, concentration maxima of conductivity, reflecting the particular state of the solution, are not determined by the number of charge carriers. This concentration corresponds to a transition region whereby the change in the structure from aqueous to non-aqueous solution, such as in glycols, results in variation of the morphology. At these concentrations, the water structure in solution is destroyed and a change occurs in the mechanism of proton transfers. The hydrogen-bond formation between water protons and AEBA is an established phenomenon<sup>44</sup>, however, the conductivity growth in the AEBA elucidates the participation of the polymeric matrix in the conductivity process as well. Until now, the mechanism of this participation was poorly understood, and no consensus on hydrogen bond formation between water protons and oxygen in the polymeric matrix was present. However, according to Figure 3a, the increase in conductivity glycol results from the increase in the number of  $-\text{H}_2\text{C}-\text{O}-\text{CH}_2-$  groups. Thus, the oxygen is



**Fig. 3.** Dependence of the specific conductivity for glycols (a) and AEBAs (b) on water to glycols/AEBAs mole ratios. Each figure contains the concentration of specific conductivity maximum, i.e. number of water molecules per molecule of the dissolved component.

participating directly in the process of formation of a hydrogen bond and proton transfer. Consequently, the maximum concentration values of electrical conductivity (Figure 3) can be regarded as the number of water molecules in the glycol hydrate shell. It is apparent that this issue requires further study. In particular, it can be assumed that these numbers refer to the second hydration shell, which establishes the network of the hydrogen bonds.

Figure 3 shows the concentration dependence of specific conductivity of AEBA. The comparison of Figure 3a and Figure 3b shows that the increase in molecular weight of AEBA leads to decrease in the value of its specific conductivity, as contrasted

**Table 1.** The maximum concentration (%), maximum specific conductivity ( $\kappa_{\max}$ ) and specific resistance ( $\rho_b$ ) of water solution of glycols and AEBA-glycols

Composition	Maximum concentration, % <sub>w</sub>	$\kappa_{\max}$ , $\mu\text{S}/\text{cm}$	$\rho_b$ , $10^{-4}$ Ohm-cm
DEG	20.3	28	344
TEG	15.9	81	500
PEG	25.3	102	47
AEBA-DEG	32.1	1380	10
AEBA-TEG	28.1	916	20
AEBA-PEG	22.7	296	66

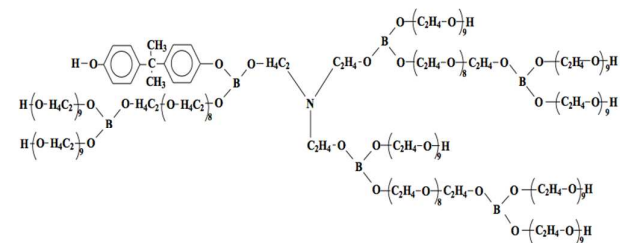
contrasted to glycols, for which the increase in its molecular weight from DEG to PEG leads to the increase in its specific conductivity. Thus, we may conclude that the increasing of glycol's molecular weight leads to steric hindrance toward borate formation, i.e. intermolecular complexes. The maximum concentration of water solution of glycols and AEBA-glycol composition and its conductivity and resistivity values are shown in Table 1. As shown in Table 1, the values of specific resistance of non-water AEBA-DEG and AEBA-TEG is rather small in comparison with AEBA-PEG. Also, there are several orders difference of its values for low-weight glycols with base on it AEBAs. And it is opposite; the specific resistance of PEG and AEBA-PEG is rather equal in values. We may reach a conclusion that proton concentration released during the complexation of AEBA is inverse to molecular weight of glycol which is used in AEBA synthesis. Water addition up to 1-2 % leads to a significant decrease in specific resistance. It is explained by the presence of small molecules of water in the system which facilitates proton transfer under the conditions of a superimposed electric field. The pattern in specific resistance change confirms the accuracy of the statements of AEBA intermolecular complex formation synthesized with low-weight glycols. This detail allows the classification of this material as an ionic liquid with proton conductivity.

The comparison of viscosimetric investigation of AEBA-TEG and AEBA-PEG also confirms a high probability of intermolecular complex formation in the case of AEBA prepared from low molecular weight glycols. As shown in Figure 4, a relatively high molecular weight of AEBA-PEG in comparison with AEBA-TEG is observed, and the value of viscosity ratio of AEBA-PEG is much less than this value of AEBA-TEG.

Due to the fact that the terminal hydroxyl groups of AEBA-PEG showed high reactivity towards isocyanate groups, these compounds were used as the basis for the synthesis of polyurethanes.

### C Chemical stability, thermal stability, and mechanical properties of AEBAs-PIC polymers

Polymer films obtained on the basis of AEBA-PEG and PIC were investigated. 4,4-dihydroxy-2,2-diphenylpropane (BPh) was used for the formation of hyperbranched AEBA-PEG, heretofore referred to as AEBA-PEG-BPh (Scheme 3).



**Scheme 3.** AEBA-PEG-BPh structure formula

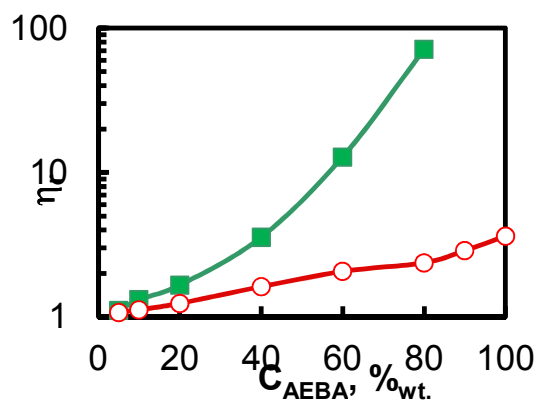


Fig. 4. Dependence of the viscosity ratio ( $\eta_0$ ) from concentrations AEBA-TEG (1) and AEBA-PEG (2) in aqueous solution at 293 K.

The polymeric films based on PEG and PIC were also prepared in order to compare them with AEBA-PEG and AEBA-PEG-BPh. According to thermal stability investigation of AEBA-PEG polymers by TGA, the thermal degradation begins at around 585 K, as shown in Figure 5, and this temperature range increases with the increase of boron concentration in the polymer. The polymeric films made from AEBA-PEG with PIC do not swell much in polar and non-polar organic solvents and the polymeric films made from AEBA-PEG-BPh with PIC swell to 5 % in toluene and to 15 % in acetone.

Also, polymeric films obtained from AEBA-PEG and AEBA-PEG-BPh and PIC are stable in alkaline conditions and possess high mechanical strain as is shown in Figure 6.

The glass transition temperatures ( $T_g$ ) of polyurethanes are determining by nature and molecular mass of soft components of polymer and also by the density of polymer network crosslinks<sup>48</sup>. In the current investigation there was used an approach, in which soft component (polyoxyethylene glycol of low molecular weight) is a part of hyperbranched structures of AEBA-PEG and AEBA-PEG-BPh. As a result the glass transition temperature of the polymer synthesised from PEG and PIC determined by TMA was around 363 K; for polymers obtained from AEBA-PEG-BPh with PIC the TMA curves shows two transitions temperatures equals to 336 K and 363 K; and for polymer obtained from AEBA-PEG with PIC  $T_g$  equals to 352 K.

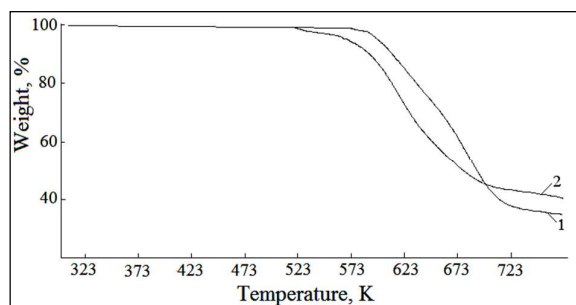


Fig. 5. TGA curves of polymeric films made from AEBA-PEG and PIC with different composition of [TEA]:[H<sub>3</sub>BO<sub>3</sub>]:[PEG] 1:6:15 (1) and 1:3:6 (2).

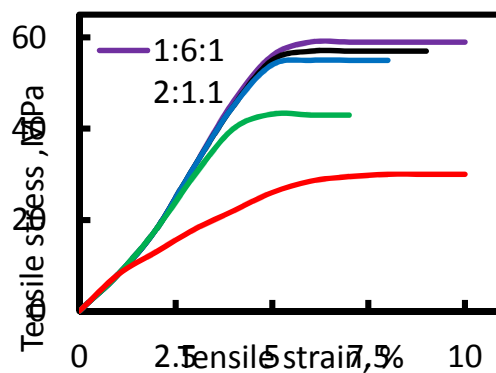


Fig. 6. Tensile test of polymers prepared from [AEBA-PEG]:[PIC]=1:1 and [AEBA-PEG-BPh]:[PIC]=1:1 with different composition of [TEA]:[H<sub>3</sub>BO<sub>3</sub>]:[PEG]:[BPh].

The flow temperature which usually characterized polyurethanes usually equals to 453 K, because of high temperature dissociation of urethanes groups. Indeed, for a polymer prepared from PEG with PIC, flow temperature is 452 K. For polymers obtained from AEBA-PEG-BPh with PIC the flow temperature is 480 K and for polymers based on AEBA-PEG with PIC this temperature increases up to 540 K.

Thus, the structure of the hyperbranched AEBA-PEG and AEBA-PEG-BPh creates conditions for screening of urethane groups by exposure to high temperatures and improving the heat resistance of polyurethanes derived from them.

The FTIR spectra of the investigated polymers are shown in Figure 7. Stretching vibrations of the -NH of the urethane groups appear in the region of  $\sim 3300$   $\text{cm}^{-1}$ . The substantial absence of the band at  $2274$   $\text{cm}^{-1}$  indicates that isocyanates are almost completely consumed in the urethane reaction. The PEG characteristic peaks found at  $2880$   $\text{cm}^{-1}$  and  $\sim 1020$ - $1170$   $\text{cm}^{-1}$ . The stretching vibration of B-O are characterized by an absorption band at  $768$   $\text{cm}^{-1}$ . Analysis of the measured IR spectra of the membrane before (Figure 7. Curve a) and after exposure to ammonia during the gas separation process (Figure 7, Curve b) has shown that the spectra have not changed, suggesting that the polymer exhibits a high resistance to ammonia.

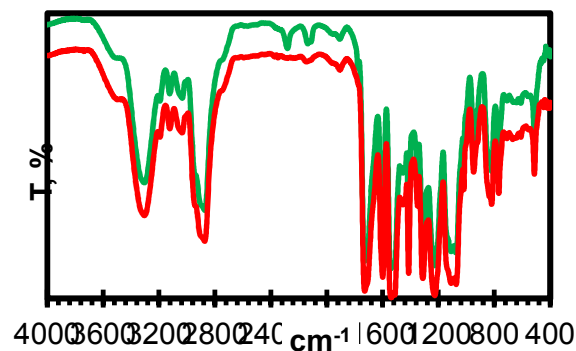


Fig. 7. FTIR-spectra of polymers [AEBA-PEG-BPh]:[PIC]=1:1, where the composition of [TEA]:[H<sub>3</sub>BO<sub>3</sub>]:[PEG]:[BPh] is 1:6:12:1 before (a) and after (b) ammonia treatment.

### D Characterization of separation performance of polyurethanes based on amino ethers of boronic acid

High mechanical strain, thermal stability, and chemical stability to organic and alkaline media are presented above. The presence of hyperbranched structure with spatially separated ion pairs (in the case AEBA-PEG) or single volume elements (in the case AEBA-PEG-BPh) are proposed to test these polymers as gas separation membrane for specific application. Carbon dioxide or ammonia removal can act as an example of such application.

Carbon dioxide and ammonia were chosen as compounds with an unusually high permeability value, especially in polar polymers<sup>31,32,41-43</sup> such as AEBA-PIC polymers. Also, ammonia membrane gas separation might be used in its synthesis, refrigeration cycle, and high purification for the needs of nano- and microelectronics. In comparison, for example, with carbon dioxide, hydrocarbons, and simple gases, there is relatively little experimental data on ammonia permeability through polymeric membranes that has been revealed<sup>33,37,40,41</sup>.

Polymeric films synthesized from AEBA-PEG and PIC has rather low permeability values for all measured gases as shown in Table 2. This observation represents features of its macromolecular architecture with structure-shared ionic pairs, causing a high cohesive interaction. This fact is leading us to conclude, that the high ammonia permeability is realized by

**Table 2.** The permeability of [AEBA-PEG-BPh]:[PIC]=1:1 polymers

p <sub>1</sub> , bar	P, Barrer*		
	CO <sub>2</sub>	CH <sub>4</sub>	NH <sub>3</sub>
BPh @ 1 stage			
1	90 043±7 362	122 011±9 381	110 373±2 001
2	83 751±5 817	111 512±4 855	168 429±4 279
3	71 699±3 344	116 088±12 061	133 963±6 036
2	70 592±6 597	123 785±11 371	19 217±157
1	71 111±2 178	105 428±6 674	20 022±930
BPh @ 2 stage			
1	11 439±478	20 268±1 625	n/d**
2	11 686±117	28 874±5 119	n/d
3	10 692±191	18 385±952	n/d
2	11 032±163	14 737±1 028	n/d
1	13 585±554	23 964±721	n/d

\* 1 Barrer = 3.348·10<sup>-19</sup> kmol·m·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>

\*\* n/d – not determined

**Table 3.** The ideal selectivity of [AEBA-PEG-BPh]:[PIC]=1:1 polymers

p <sub>1</sub> , bar	α(CH <sub>4</sub> /gas)		
	CO <sub>2</sub>	NH <sub>3</sub>	CO <sub>2</sub>
BPh @ 1 stage			
1	1.4±0.1	1.1±0.1	1.8±0.1
2	1.3±0.1	0.7±0.1	2.5±0.1
3	1.6±0.1	0.9±0.1	1.7±0.1
2	1.8±0.1	6.4±1.0	1.3±0.1
1	1.5±0.1	5.3±0.1	1.8±0.1

active transport like presented by Timashev etc.<sup>49</sup>. The small values of selectivity presented in Table 3 indicated the fact of

not solution-diffusion mechanism is presented, especially for the polymer generated from the addition of BPh at the first stage of the reaction. Also dramatically decreasing of ammonia permeability after decreasing the feed pressure shows possible realized by swelling of the membrane in the membrane module. That fact might be realized by a specific interaction of ammonia with polar centers of polymer which might be urethane groups. As an assumption we can suggest that the ration of active transport is decreasing by saturation of urethane group by ammonia. However, there are no any changes in structure like shown on FTIR spectras on Figure 7. That means only reversible decreasing of the permeability which shows us that membrane need be recover by regeneration.

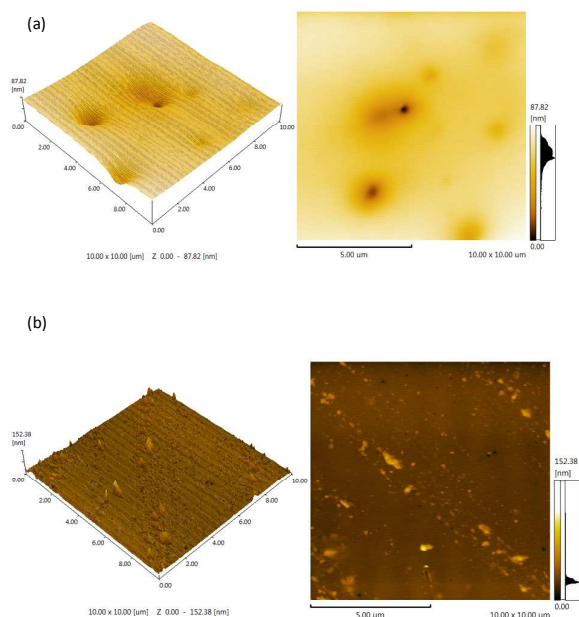
However, hyperbranched structure in combination with rigid aromatic branching is used for the design of hyperbranched structures. To achieve this goal, BPh was used in the current study. Nevertheless, ammonia in some cases has a lower permeability than methane. At present, some engineering techniques have allowed for the separation of these lower penetrating impurities<sup>50-52</sup>.

Steric hindrance resulting in a branched architecture of AEBA-PEG-BPh allows for gas permeability selectivity in the obtained polymer. Two approaches were used to synthesize AEBA-PAG-BPh. First, BPh was added at the first stage of synthesis, increasing the probability of BPh molecules appearing in the inner structure of AEBA-PEG-BPh. The second approach was realized when BPh was added at the second stage of the synthesis, which leads to a significant change in the polymer architecture. This fact is also proved by the permeability's values presented in Table 2. But the selectivity's of methane/carbon dioxide are rather higher for the polymer generated from the addition of BPh at the second stage of the reaction.

### E Correlation between surface topography and gas separation properties of polyurethanes based on amino ethers of boronic acid polymers

The surface topographies of the polymers are presented in Figure 8 by AFM data, allowing us to deduce the inner which BPh was added at the first stage leads to higher morphology of the polymer based on surface measurements. The larger number of pores on the surface of polymers in permeability in comparison with other polymer where BPh was added at the second stage. The root-mean-square roughness values were equalled 43 and 19 nm for polymers in which BPh was added on first and second stages, respectively.

Thus, this surface morphology obtained by AFM corresponds to data presented in Table 2, where the higher permeability is seen for the polymer generated from the addition of BPh at



**Fig. 8.** AFM images of [AEBA-PEG-BPh]:[PIC]=1:1 polymers in which BPh was added at the first (a) and second (b) stages of their synthesis.

the second stage of the reaction. And also the smaller pore size of polymer where BPh was added at the second stage generally leads to slightly increasing of selectivity, presenting in Table 3.

## Experimental

### A Materials

Whole glycols i.e. diethylene glycol (DEG), triethylene glycol (TEG), and poly(ethylene glycol) (PEG) were purchased from PJSC Nizhnekamskneftekhim (Nizhnekamsk, Russia). Triethanolamine (TEA) was purchased from OJSC Kazanorgsintez (Kazan, Russia). 4,4'-dihydroxy-2,2-dephenylpropane (BPh), boronic acid (99.99 %), and 2,4-toluenediisocyanate (TDI) (98%) were purchased from Sigma-Aldrich. Polyisocyanate "Cosmonate-200" (PIC) was purchased from Kumho Mitsui Chemicals, Inc. Glycols were additionally dried at low pressure at 5mmHg and 353 K down to 0.01 % moisture concentration. Crystal hydrates of  $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$  were decomposed by heating at 393 K for 48 hours.

In the gas separation investigation of prepared polymers were used gases (carbon dioxide and methane) with purity not less than 99.995 % (NII KM, Russia). And as ammonia we used high purity ammonia 99.99999 % (Firm HORST, Russia). Other reagents and solvents were used without further purification.

### B Synthetic procedures

**General procedure for synthesis of amino ethers of boronic acid (AEBA).** The syntheses of AEBA were carried out based on different glycols usage. For the synthesis of AEBA-DEG,

triethanolamine (1 mol), boron acid (3 mol), and DEG (6 mol) were added into a 250 mL three-necked rounded-bottom flask equipped with a magnetic stirrer. The mixture was heated to 353 K for 2 hours under low pressure (0.2-2.0 mmHg) in a vacuum oven. The synthesized liquid AEBA-DEG was collected into a ground-glass stoppered flask.

For the synthesis of AEBA-TEG, TEA (1 mol), boric acid (6 mol), TEG (12 mol), and  $\text{CuCl}_2$  as a catalyst (0.1 mol% w/w) were added into a 250 mL three-necked rounded-bottom flask equipped with a magnetic stirrer. The mixture was heated to 363 K for 2 hours under low pressure (0.2-2.0 mmHg) in a vacuum oven. The synthesized liquid AEBA-TEG was collected into a ground-glass stoppered flask.

AEBA-PEG was synthesized via a two-step process. In the first stage, boric acid (6 mol) and PEG (3 mol) were added to a 250 mL three-necked round-bottom flask equipped with a magnetic stirrer. The mixture was heated to 363 K for 2 hours under low pressure (0.2-2.0 mmHg) in a vacuum oven. In the second stage, the remaining PEG (6-12 mol) and TEA (1 mol) were added to the first mixture, followed by heating under similar conditions. The synthesized liquid AEBA-PEG was collected into a ground-glass stoppered flask.

AEBA-PEG-BPh was also synthesized using a similar two-step process. In the first stage, boric acid (6 mol) and PEG (3 mol) were added to a 250 mL three-necked rounded-bottom flask equipped with a magnetic stirrer. The mixture was heated to 363 K for 2 hours under reduced pressure (0.7-2.0 mmHg). In the second stage, the remaining PEG (9 mol), BPh (1 mol) and TEA (1 mol) was combined. The mixture was heated again under the identical conditions. The synthesized liquid AEBA-PEG-BPh was collected into a ground-glass stoppered flask. Eventually, the molar ratio of [TEA]:[ $\text{H}_3\text{BO}_3$ ]:[PEG]:[BPh] was 1:6:12:1. The further increasing of BPh ratio leads to significant increasing of the viscosity of AEBA-PEG-BPh.

The composition and structure of AEBAs is determined by the mole ratio of TEA, boric acid, and glycols. The reaction was quenched after the desired amount of hydroxylation toward the target product. Reaction progress was monitored by titration to determine hydroxyl group concentration.

**General procedure for synthesis of polyurethanes based on amino ethers of boronic acid.** Dense polymeric films were obtained by mass polymerization process. The synthesized AEBA-PEG-BPh was mixed with polyisocyanate (PIC) in a 1:1 ratio. The polymerization was carried out on a glass surface. Drying in a vacuum oven at 353 K for two hours afforded a dense film. The polymers were identified according to the molar ratio of TEA,  $\text{H}_3\text{BO}_3$ , PEG, and PIC, (e.g. sample [[TEA]:[ $\text{H}_3\text{BO}_3$ ]:[PEG]=1:3:6]:[PIC]=1:1 contains 1 mol of AEBA-PEG-BPh per 1 mol of PIC, and AEBA-PEG-BPh was synthesized from TEA (1 mol),  $\text{H}_3\text{BO}_3$  (3 mol), and PEG (6 mol). The flat-sheet polymeric films with diameter equal to 80 cm were obtained and used for further investigation in gas separation ability. The thicknesses of polymeric films were approximately 140 microns.

**B Light-scattering of AEBA water solution.**



The light-scattering of aqueous AEBA was measured by dynamic light scattering instrument (Photocor Complex (Photocor, Russia)) with the angle of deflection equal to 90°. An electrophoretic light scattering instrument (Zetasizer Nano Z (Malvern, UK)) was additionally used with the an angle of deflection equal to 173°. The light source for the experiments was a He-Ne laser (633 nm). The effective hydrodynamic radius of aggregates was calculated from diffusion coefficients by Stocks-Einstein equation for the case of spherical particles with the same radius<sup>53</sup>. The range of measurement varies from 2 nm to several microns with an accuracy of 5 %. Large time of signal storage (up to 600 s) allows for the decrease of this accuracy to 1 %. The water solutions of AEBA were drained from dust on Millipore filters immediately prior to measurements.

#### C Specific conductivity of AEBA water solution.

The glycols and AEBA specific conductivity ( $\kappa$ ) was determined using a logging microprocessor-based conductivity bench meter (HI 2300 (Hanna Instruments Inc., USA)) and HI 76310 sensor with error lower than 1%. All measurements were carried out in a cell with platinum electrodes. The temperature was measured with a thermostat within  $\pm 0.1$  K.

#### D Thermal gravimetric analysis.

Thermal gravimetric analysis (TGA) experiments were performed from derivatographes using STA 600 (Perkin Elmer). Samples (0.1 g) were loaded in alumina pans and ramped to 773 K at a heating rate of 5 K/min in nitrogen environment.

#### E Thermomechanical Analysis

TMA curves of the films were obtained using a Netzsch TMA 402 F thermomechanical analyzer in the pression mode. Films samples (thickness of 2 mm) were used for the TMA testing; a heating rate was 3 K/min from ambient temperature to 623 K in static mode.

#### F Viscosity ratio measurements.

Flow times of polymer solutions were measured using an Ubbelohde capillary viscometer. Viscosity ratio ( $\eta_r$ ) was obtained from the ratio of the flow times of a solution and the solvent<sup>54</sup>. Before each measurement, a solution in the viscometer was sealed and allowed to equilibrate with a thermostated water tank for at least 20 min. The temperature fluctuation of the water tank was smaller than 0.1 K. Each polymer solution was measured for three times so that the relative error was less than 0.2%.

#### G Fourier transform infrared spectroscopy analysis.

FTIR spectra were recorded at ambient temperature on an FTIR spectrometer (IRrfinity-1 (Shimadzu, Japan)). A minimum of 30 scans was signal-averaged with a resolution of 4  $\text{cm}^{-1}$  at the 4000-400  $\text{cm}^{-1}$  range. All other parameters were not controlled and corresponded to the testing characteristics established by the producer. The accuracy of measurement of

wave numbers was monitored by the spectrum of polystyrene, being  $\pm 0.2$   $\text{cm}^{-1}$ . The sample measurements were carried out using two varying methods; first, film spectra and films sample were treated in a potassium bromide matrix as was previously reported in our work<sup>38</sup>. Second, the testing procedure was repeated after treatment of films in ammonia.

#### H Atomic force microscopy topology analysis.

The topography of the membrane surface was determined by atomic force microscopy (AFM). The atomic force microscope SPM-9700 (Shimadzu, Japan) with scanner 30  $\mu\text{m}$  was used in the force modulation mode. Commercially available silicon tips were used (POINTPROBE FMR-20 S/N-71814F8L882 (Nano World Innovative Technologies, USA)) with a spring stiffness of 1.3 N/m, and the radius of the curve of the tip being rated at 8 to 12 nm. The surface characterization was carried out at ambient temperature. The samples were cleaned of dust with ethanol before measurement, then joined on a steel holder using the double-sided scotch tape. After image acquisition the root-mean-square roughness was obtained by a program in the AFM image processing toolbox (SPM Online, ver. 4.02).

#### I Permeability measurements.

The permeability of the obtained polymeric films was measured using a dead-end, vacuum regime<sup>39, 55</sup> at ambient temperature. The pressure of feed flow was changed from 1 to 3 bar, then from 3 to 1 bar, to determine the possible swelling of sample polymers. The pressure of permeate flow was less than 10 mbar. As a membrane module, a radial membrane module with porous mechanical support was used<sup>56</sup> which was vacuum-degassed before each measurement. The diameter of samples was 42.3 mm. Carbon dioxide, methane and ammonia, were tested in these studies. After ammonia analysis, the permeability of helium and argon were tested again to show the chemical stability of polymer. After permeability measurements, the ideal selectivity was calculated as a ratio of permeability values. Every sample was measured not less than tri times. The errors of permeability measurements were less 15 %.

## Conclusions

The polyurethane films were synthesized on a base of amino ethers of boric acid with the use of poly(ethylene glycol) and aromatic polyisocyanats as precursors. The obtained polyurethanes possess the following distinctive features: relatively high mechanical strength, heat resistance, and low degree of swelling in a broad array of media.

It was determined that the architecture of the polymers obtained on the basis of AEBA-PEG used is predetermined by the nature of the hydroxyl-containing compounds. Thus, their application in the synthesis of AEBA poly(ethylene glycols) produces gastight film materials. In the case of the additional

use of a hydroxyl-containing compound, such as 4,4'-dihydroxy-2,2-diphenylpropane, polymers exhibit high permeability values in combination with enough selectivity in the separation of ammonia and carbon dioxide containing gas mixtures.

## Abbreviation

DEG - diethylene glycol  
 TEG - triethylene glycol  
 PEG - poly(ethylene glycol)  
 TEA – triethanolamin  
 BPh - 4,4'-dihydroxy-2,2-dephenylpropane  
 TDI - 2,4-toluene diisocyanate  
 PIC - polyisocyanate "Cosmonate-200"  
 AEBA - amino ethers of boron acid

## Acknowledgements

This work was supported by the Russian Science Foundation (grant no. 15-19-10057).

## References

- E.Drioli, A.J.Stankiewicz, F.Macedonio, *J. Membr. Sci.*, 2011, **380**, 1.
- B.D. Freeman, *Macromolecules*, 1999, **23**, 375.
- L.M. Robeson, *J. Membr. Sci.*, 2008, **320**, 390.
- L.M. Robeson, G.Liu, B.D. Freeman, D.R. Paul, *J.Membr.Sci.*, 2015, **476**, 421.
- L.M. Robeson, W.F. Burgoyne, M. Langsam, A.C. Savoca, C.F. Tien, *Polymer*, 1994, **35**, 4970.
- L.M. Robeson, *Current Opinion in Solid State and Materials Science*, 1999, **4**, 549.
- P. Pandey, R.S. Chauhan, *Progress in polymer science*, 2001, **26**, 853.
- B. Zornoza, C. Tellex, J. Coronas, J.Garscon, F. Kapteijn, *Microporous and Mesoporous Materials*, 2013, **166**, 67.
- H. Vinh-Thank, S. Kaliaguine, *Chem.Rev.*, 2013, **113**, 4980.
- Yu.P. Yampolskii, L.E. Strannikova, N.A. Belov, *Petroleum Chemistry*, 2014, **54**, 637.
- L.J. Lozano, C. Godínez, A.P. de los Ríos, F.J. Hernández-Fernández, S. Sánchez-Segado, F.J. Alguacil, *J. Membr. Sci.*, 2011, **376**, 1.
- P. Cserjési, N. Nemestóthy, K. Bélafi-Bakó, *J. Membr.Sci.*, 2010, **349**, 6.
- J.E. Bara, C.J. Gabriel, T.K. Carlisle, D.E. Camper, A. Finotello, D.L. Gin, R.D. Noble, *Chem.Eng.*, 2009, **147**, 43.
- D.F. Sanders, Z.P. Smith, R. Guo, L.M. Robeson, J.E. McGrath, D.R. Paul, B.D. Freeman, *Polymer*, 2013, **54**, 4729.
- T. Femmer, A.J.C. Kuehne, J. Torres-Rendon, A. Walther, M. Wessling, *J. Membr. Sci.*, 2015, **478**, 12.
- H. Hyung, J.-H. Kim, *J. Membr. Sci.*, 2006, **286**, 269.
- S.J. Kang, G.H. Lee, Y.J. Yu, Y. Zhao, B. Kim, K. Watanabe, T.Taniguchi, J. Hone, P. Kim, C. Nuckolls, *Adv. Mater.*, 2014, **2** 092511.
- R. N. Gadel'shin, A. D. Khusainov, Yu. N. Khakimullin, R. S. Davletbaev, O. Yu. Emelina, I. M. Davletbaeva, *Russian Journal of Applied Chemistry*, 2013, **86**, 1430.
- F. Jäkle, *Coordination Chemistry Reviews*, 2006, **250** 1107.
- N.P. Patel, J.M. Zielinski, J. Samseth, R.J. Spontak, *Macromol. Chem. Phys.*, 2004, **205**, 2409.
- M. Sanchez, O. Sanchez, H. Hopfi, M.E.Ochoa, D. Castillo, N. Farfan, S. Rojas-Lima, *J. Organometall. Chem.*, 20004, **689**, 811.
- F. Cheng, F. Jäkle, *Polym. Chem.*, 2011, **2**, 2122
- N. Du, G.P. Robertson, J. Song, I. Pinnau, S. Thomas, M.D. Guiver, *Macromolecules*, 2008, **41**, 9656-9662.
- M.M. Khan, V. Filiz, G. Bengtson, S. Shishatskiy, M.M. Rahman, J. Lillepaerg, V. Abetz, *J. Membr. Sci.*, 2013, **436**, 109.
- R. S. Davletbaev, I. M. Davletbaeva, R. Ya. Deberdeev, I. I. Zaripov, M. N. Kayumov, O. R. Gumerova, *Russian Journal of Applied Chemistry*, 2014, **87**, 861.
- I. M. Davletbaeva, A. I. Akhmetshina, R. S. Davletbaev, I. I. Zaripov, A. M. Gumerova, R. R. Sharifullin, *Polymer Science, Series B*, 2014, **56**, 781.
- G. Wang, Z. Zeng, X. Wu, T. Ren, J. Hana and Q. Xuea, *Polym. Chem.*, 2014, **5**, 5942
- R. Davletbaev, A. Akhmetshina, A. Gumerov, I. Davletbaeva, V. Parfenov, *Composite Interfaces Special Issue:The Fourth Asia Symposium on Advanced Materials (ASAM-4)*, 2014, **21**, 611.
- E. Ameri, M. Sadeghi, N. Zarei, A. Pournaghshband, *J.Membr.Sci.*, 2015, **479**, 11
- P. Budd, N.B. MaKeown, *Polym. Chem.*, 2010, **1**, 63
- P. Bernardo, E. Drioli and G. Golemme, *Ing. Eng. Chem. Res.*, 2009, **48**, 4638
- S.A. Topham, The history of the catalytic synthesis of ammonia, in: J.R. Anderson, M. Boudart (Eds.), *Catalysis Science and Technology*, Springer- Verlag, Berlin-Heidelberg, 1985, pp. 1-50.
- V. Tricoli, E.L. Cussler, E.L., *J. Membr. Sci.*, 1995, **104**, 19.
- F. Siavashi, M. Saidi, M.R. Rahimpour, *J.Pow.Source*, 2014, **267**, 104.
- S. Klinsrisuk, S. Tao, J.T.S. Irvine, *Membrane Reactors for Energy Applications and Basic Chemical Production*, 2015, 543.
- M.R. Karami, P. Keshavarz, M. Khorram, M. Mehdipour, *J. of Hazardous Mat.*, 2013, **250**, 576.
- C. Makhloufi, B. Belaisaoui, D. Roizard, E. Favre, *Procedia Eng.*, 2012, **44**, 143.
- L. Loyon, F. Guiziou, F. Belinem P. Peu, *Int. Congress Series*, 2006, **1293**, 299
- A.B. Leytem, R.S. Dungan, D.L. Bjerneberg, A.C. Koehn, *J. Environ Qual.*, 2011, **1383**, 94
- C. Makhloufi, D. Roizard, E. Favre, *J.Membr.Sci.*, 2013, **441**, 63.
- S.I. Semenova, S.I. Smirnov, H. Ohya, *J.Membr.Sci.*, 2000, **172**, 75.
- I. V. Vorotyntsev, P. N. Drozdov, N. V. Karyakin, *Inorg. Mat.*, 2006, **42**, 231.
- I.V. Vorotyntsev, I.I. Grinwald, I.Yu. Kalagaev, N.A. Pethukhova, A.N. Petukhov, *Petroleum Chemistry*, 2013, **53**, 564.
- I.S. Elashmawi, N.A. Hakeem, *Polym. Eng. Sci.*, 2008, **48**, 895.
- A.A. Ivanov, *Rus. J. Inorg. Chem.*, 2008, **53**, 1948.
- S. Cukierman, *Biochim. Biophys. Acta*, 2006, **1757**, 876.
- S-W. Kuo, *J. Polym. Res.*, 2008, **15**, 459.
- Prisacariu, C., *Polyurethane Elastomers. From Morphology to Mechanical Aspects*, New York: Springer, 2011.
- S.F. Timashev, A.V. Vorobiev, V.I. Kirichenko, Yu.M. Popkov, V.I. Volkov, R.R. Shifrina, A.Ya. Lyapunov, A.G. Bondarenko, L.P. Bobrova, *J.Membr.Sci.*, 1991, **65**, 31
- V.M. Vorotyntsev, P.N. Drozdov, I.V. Vorotyntsev, D.V. Murav'ev, *Doklady Chemistry*, 2006, **411**, 243.
- V.M. Vorotyntsev, P.N. Drozdov, *Desalination*, 2002, **147**, 433
- V.M. Vorotyntsev, P.N. Drozdov, I.V. Vorotyntsev, E.S. Belyaev, *Petroleum Chemistry*, 2011, **51**, 595.

## ARTICLE

RCS Advances

- 53 L.Ya. Zakharova, A.R. Ibragimova, L.A. Kudryavtseva, *Langmuir*, 2007, **23**, 3214.
- 54 Principles of colloid and surface chemistry, by Paul C. Hiemenz, Marcel Dekker, New York, 1977, 516 pp
- 55 V. M. Vorotyntsev, P. N. Drozdov, I. V. Vorotyntsev, K. Yu. Smirnov, *Inorg. Mat.*, 200, **45**, 1263.
- 56 P.N. Drozdov, Y.P. Kirillov, E.Y. Kolotilov, I.V. Vorotyntsev, *Desalination*, 2002, **146**, 249.

RSC Advances Accepted Manuscript