Crosslinking Benzotriazolylimides and Polymeric Materials on Base of Them

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ABSTRACT: A new kind of crosslinking oligobenzotriazolylimides with terminal maleimide groups has been synthesized via an interaction of an excess of bismaleimides with 5,5′-bisbenzotriazoles in melt. Conditions of obtaining these oligomers were optimized via the syntheses of model compounds. Oligomers, according to dynamic thermogravimetric analysis (DTGA), fuse at 135–160°C, crosslink at 175–250°C, and possess the high thermal stability in air up to 410°C. Using these oligomers as thermosetting binders or crosslinking agents, tough laminate plastics reinforced by a glass-fiber cloth as well as crosslinked films on base of a linear polybenzimidazole (PBI) matrix were obtained. The plastics and the crosslinked films possess high mechanical characteristics. It has been proved that the crosslinked films on base of the PBI matrix are perspective precursors to design the phosphoric acid electrolyte membranes for the medium temperature fuel cells. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2011

Key words: composites; membranes; crosslinking; high performance polymers; oligomers; benzotriazoles; maleinimides

INTRODUCTION

At present, maleinimides are perspective compounds which are used as reactive and crosslinking components to develop specific materials.[1,2] The fundamental interest in maleinimide monomers is shown because the maleinimide cycle possesses the good reactivity in following reactions: nucleophilic additions,[3,4] Diels–Alder cycloadditions,[4–6] photoaddition,[7] and "ene"-reactions.[8,9] Moreover, the maleinimide cycle has a proneness to thermal, photo, anionic, and radical polymerizations.[6,9–11] The described above reactions of maleinimides are passed through opening the maleimide olefinic double bond, and no by-products evolve. All this promotes the wide popularity of maleinimides in the field of polymer chemistry. In the polymer chemistry and the technology of materials, maleinimides are generally used to develop thermoreactive oligomers which are widely applied as thermosetting binders for different filled plastics. In addition, the availability of maleic anhydride which is known to be the maleinimide precursor favors a wide use of maleinimides also.

Up to now, the benzotriazolyl-containing polymers are usually carbon-chain ones with pendant benzotriazole heterocycles and have been synthesized by either chain polymerizations[12] or polymer analogous transformations.[13] The main applications of those polymers are as the polymeric ligands for the complex compounds[13] and as a component of coatings used for the corrosion protection.[12]

For heterochain polybenzotriazoles where a polymer chain contains benzotriazolyl cycles, there is a single example for synthesis of them.[14] Such polybenzotriazoles had been prepared via an oxidative process of *ortho*-aminodiazopolymers, using Cu(II) salts in the presence of ammonia or oxide-resistant amines. The main chain of such polymers contains both symmetrical 2-benzotriazolyl fragments and nonfused diazo-links with near *ortho*-substituents. *ortho*-Aminodiazopolymers, in turn, had been synthesized via an interaction of aromatic diamines with aromatic bisdiazonic salts. The drawbacks of this method are following: the synthetic procedures are complex, and no full formation of the 2-benzotriazolyl cycles occurs; the final polymers contain impurities and possess low molecular weights, high softening temperatures, and are very poor soluble in common solvents. Hence, those polymers are not suitable to manufacture the industrial wares.

In our opinion, an adaptation of monomers with formed previously benzotriazolyl cycles for synthesis of heterochain polybenzotriazoles permits to avoid

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the abovementioned drawbacks. To date, the reactions of 1H-benzotriazoles and derivatives from them, including the Michael addition reactions, have been widely known.[15–17] To the best of our knowledge, information about a nucleophilic addition of 1H-benzotriazoles to the maleinimide olefinic bond is absent. Therefore, it was important to study this addition reaction in detail. Information about three-dimensional polymers containing benzotriazole links between knots of the polymer network is absent as well.

Hence, the main tasks of our work lie in a synthesis and an investigation of model benzotriazolylsuccinimides, in a synthesis and a study of the thermosetting benzotriazolylimide oligomers from bisbenzotriazoles and an excess of bismaleinimides, and in a design of materials on base of these thermosetting oligomers.

EXPERIMENTAL

Measurements

Fourier-transform infrared (IR)-spectra were recorded with an IFS25 instrument in KBr tablets. ^{13}C and ^{1}H-NMR spectra were obtained on a Varian VXR-500S spectrometer at 126.7 and 500 MHz, respectively, in DMSO-d_6 and CDCl$_3$; the signals of residual protons for DMSO-d_6 (δ 2.5 ppm), CDCl$_3$ (δ 7.24 ppm) in ^{1}H-NMR spectra and for carbon atoms of DMSO (δ 39.7 ppm) in ^{13}C-NMR spectra served as internal standard. Melting points were determined on an "IA9100" instrument and not corrected. Thermogravimetric analysis was performed with "Q-1000" derivatograph ("MOM" Hungary) at a heating rate of 10 grad min^{-1} in air.

A doping level of a membrane was calculated according to equation:

$$DL = \frac{(W_1 - W_0) \cdot MW_{PBIunit}}{W_0 \cdot \omega_{PBI} \cdot MW_{H_3PO_4}} \cdot 100\% \qquad (1)$$

where DL is doping level (mol %), W_1 and W_0 are weights of a doped membrane and an undoped film, respectively (g), ω_{PBI} is weight fraction of PBI in a film, and $MW_{H_3PO_4}$ and $MW_{PBIunit}$ are molar weights of H$_3$PO$_4$ (98.00 g mol^{-1}) and repeating unit of PBI (324.24 g mol^{-1}), respectively.

A proton conductivity of a membrane was measured by van der Pauw four-probe method at current frequency of 500 Hz under dry or moist argon flow and calculated according to equation:

$$\sigma = \frac{I_{12}}{4.53 \cdot h \cdot U_{34}} \qquad (2)$$

where σ is a proton conductivity (S sm^{-1}); I_{12} is a current between flank probes of 1 and 2 (A); U_{34} is a

voltage between flank probes of 3 and 4 (V); h is a thickness of a sample (sm). A square sample of 1 $\times$ 1 sm^2 dimension was used. The probes were located on centers of the sides of this square sample. When the conductivity depending on temperature was being measured, argon was being bubbled through water with temperature of 21.3°C before an inlet into a measuring cell.

Auxiliary compounds and monomers

N-Phenylmaleimide was prepared according to the method cited in the article.[18]

Ice CH$_3$COOH, HCOOH, NaHSO$_3$, NaNO$_2$, and NaOH of the chemical pure grade were used as received. All the solvents applied were purified according to the known procedures.[19]

Isophtalic acid of the chemical pure grade was dried *in vacuo* at 70–80°C before a synthesis.

Benzotriazole was crystallized from benzene. M.p. is 98–99°C.

Thionyl chloride was distilled under dry argon flow and in the presence of a trap filled with sodium hydroxide pellets. A fraction boiling at 70–72°C (atmospheric pressure) was collected.

Phenol was distilled under dry argon flow. A fraction boiling at 180–182°C (atmospheric pressure) was collected.

Isophtalic acid dichloride. Isophtalic acid was refluxed in an excess of thionyl chloride in the presence of a small quantity of DMF until complete dissolution of solids. Thionyl chloride unreacted was removed by a distillation and isophtalic acid dichloride obtained was crystallized from dry hexane. M.p. is 44–45°C.

bis-Maleimides were synthesized similar to the procedures.[20]

Isophtalic acid diphenyl ester was synthesized from isophtalic acid dichloride and a small excess of phenol in melt according to the procedures.[21] This compound was purified by crystallization from DMF. M.p. is 138–139°C.

3,3′,4,4′-Tetraaminodiphenylmethane was supplied from Nesmeyanov Institute of organoelement compounds (Moscow) and purified by refluxing in distilled water in the presence of NaHSO$_3$ and charcoal. After a hot filtration and cooling, crystals were filtered and rinsed with distilled water and dried *in vacuo* at 40–50°C. M.p. is 140–142°C.

3,3′,4,4′-Tetraaminodiphenyl ether was supplied from Novosibirsk Institute of organic chemistry and purified as 3,3′,4,4′-tetraaminodiphenylmethane. M.p. is 150–151°C.

bis(1H-benzotriazol-5-yl)methane. 3,3′,4,4′-Tetraaminodiphenylmethane (22 g, 0.076 mol), ice CH$_3$COOH (110 mL), and distilled water (55 mL) were placed into a 0.5 L three-neck flask equipped

TABLE I
^{13}C NMR Spectroscopy Data of Compounds IIa–c (DMSO-d$_6$)

Compound	$\underline{C}(4')$	$\underline{C}(4''')$	$\underline{C}(3')$	$\underline{C}(3''')$	$\underline{C}(7)$	$\underline{C}(4)$	$\underline{C}(5)$	$\underline{C}(6)$	$\underline{C}(1a)$	$\underline{C}(3a)$	$\underline{C}(4'') +$ $\underline{C}(7'')$	$\underline{C}(5'') +$ $\underline{C}(6'')$	$\underline{C}(1a'') +$ $\underline{C}(3a'')$
IIa	35.33	36.16	55.80	63.40	110.51	119.69	124.72	128.30	133.17	145.35	118.16	127.42	144.19
IIb	35.40	36.27	56.28	63.71	110.67	119.71	124.76	128.37	133.07	145.41	118.20	127.51	144.21
IIc	35.13	36.01	55.72	63.20	109.97	119.45	124.13	127.76	133.05	145.32	117.84	126.83	144.16

Carbon indexes are correspond to ones on Scheme 1.

with a stirrer, an inlet and an outlet of argon, and a thermometer. Flask content was heated under stirring until complete dissolution of solids. Solution was cooled to 13–14°C. Then, after removing the cooling bath, solution of NaNO$_2$ (18 g, 0.261 mol) in distilled water (40 mL) was quickly added to the flask content intensively stirred. After an addition of NaNO$_2$ solution, temperature rose up to 60–70°C. The content was stirred for about 1 h, with a suspension precipitating throughout this period. The suspension was poured into cold distilled water (500–600 mL) and stirred. A product was filtered and rinsed with distilled water and dried *in vacuo* at 50–60°C. Crude bis(1H-benzotriazol-5-yl)methane was dissolved in ice CH$_3$COOH under heating and refluxed in the presence of small quantities of distilled water and charcoal. After a hot filtration, filter liquor was poured into cold distilled water (500–600 mL) and stirred. A deposit was filtered, rinsed several times with distilled water, and dried *in vacuo* at 70–80°C. The yield of purified compound was 19.02 g (85%). M.p. is 240–241°C. ^{1}H-NMR (δ, ppm): 4.29 (s, 2H, CH$_2$), 7.34–7.42 (d, J = 19.5 Hz, 1H, H$_{arom}$), 7.78 (s, 1H, H$_{arom}$), 7.81–7.89 (d, J = 19.5 Hz, 1H, H$_{arom}$), and 15.46 (br s, 1H, NH). IR (KBr, tablet, cm^{-1}): 1400 (CH$_2$, bend), 3070 and 2950 (CH$_2$, stretch), and 3333–3400 (N—H, stretch). Anal. calctd for C$_{13}$H$_{10}$N$_6$: C, 62.39; H, 4.03; N, 33.58. Found: C, 62.15; H, 3.90; N, 33.16.

bis(1H-benzotriazol-5-yl)oxide was synthesized similar to bis(1H-benzotriazol-5-yl)methane. The yield of purified compound was 15.72 g (82%). M.p. is 263–264°C. ^{1}H-NMR (δ, ppm): 7.34–7.42 (d, J = 19.5 Hz, 1H, H$_{arom}$), 7.78 (s, 1H, H$_{arom}$), 7.81–7.89 (d, J = 19.5 Hz, 1H, H$_{arom}$), and 15.54 (br s, 1H, N—H). IR (KBr, tablet, cm^{-1}): 3325–3410 (N—H, stretch) 1247 (—O—, bend). Anal. calctd for C$_{12}$H$_8$N$_6$O: C, 57.14; H, 3.20; N, 33.32. Found: C, 57.03; H, 3.28; N, 33.12.

Model compounds

1-(2,5-Dioxo-1-phenylpyrrolidin-3-yl)benzotriazole (I). A mixture of benzotriazole (1.1913 g, 0.01 mol)

and *N*-phenylmaleimide (1.7937 g, 0.01 mol) in a fluoroplast cup was placed into a preheated to 120°C bath (Wood's alloy). Next the temperature was gradually increased up to 220°C, and the reaction mixture was kept additionally for 5 min. Then the reaction mixture was cooled to ambient temperature, and the glassy product was removed from the cup by cooling it with liquid nitrogen and knocking on the bottom. The yield was 90% (crude product). The product was dissolved in a mixture of HCOOH and H$_2$O, refluxed for 10 min in the presence of activated charcoal, then filtered, and compound **I** was precipitated by adjusting pH to 5 with 0.5% aqueous NaOH solution. The precipitate was filtered after solidification, dissolved in boiling ethanol, and gradually cooled, the isomer **I** was crystallized as small needles. The crystals were filtered off and dried *in vacuo* at 50–70°C. The yield of purified compound was 71%. M.p. is 145–147°C. IR (KBr, tablet, cm^{-1}): 1717.5 (C=O, stretch); 1187.5 (C—N—C, bend); 2930, 2979 (C—H aliph., stretch). Anal. calctd for C$_{16}$H$_{12}$N$_4$O$_2$: C, 65.74; H, 4.14; N, 19.17. Found: C, 65.90; H, 4.15; N, 18.98. ^{13}C-NMR data of this compound are shown in Table I.

Compounds IIa–c (mixture of isomers). Benzotriazole (2.3826 g, 0.02 mol) and either N,N′-hexamethylene-bismaleinimide (2.7629 g, 0.01 mol) (for **IIa**) or 4,4′-diphenylmethane-bismaleinimide (3.5835 g, 0.01 mol) (for **IIb**) or 4,4′-bis(maleimido)-diphenyl ether (3.6032 g, 0.01 mol) (for **IIc**) was placed in a fluoroplast cup. The reaction was carried out as described above for compound **I**. The products were precipitated as amorphous powders after purification with activated charcoal, then filtered and dried *in vacuo* at 50–70°C. ^{13}C-NMR data of these compounds are shown in Table I.

Compound IIa. Yield was 85%. IR (KBr, tablet, cm^{-1}):1714 (C=N, stretch); 2941, 2860 (C—H aliph., stretch); 746 (1,2-Ph, bend). Anal. calctd for C$_{26}$H$_{26}$N$_8$O$_4$: C, 60.69; H, 5.09; N, 21.78. Found: C, 60.09; H, 4.98; N, 19.86.

Compound IIb. Yield was 88%. IR (KBr, tablet, cm^{-1}): 1721, 1731 (C=N, stretch); 2944, 2854 (C—H aliph., stretch); 746 (1,2-Ph, bend); 1386 (C—N—C of succinimide, bend). Anal. calctd for C$_{33}$H$_{24}$N$_8$O$_4$: C,

66.44; H, 4.05; N, 18.78. Found: C, 64.89; H, 4.13; N, 17.60.

Compound IIc. Yield was 91%. IR (KBr, tablet, cm^{-1}): 1715, 1732 (C=N, stretch); 1242 (—O—, bend); 746 (1,2-Ph, bend); 1393 (C—N—C of succinimide, bend). Anal. calctd for $C_{32}H_{22}N_8O_5$: C, 64.21; H, 3.70; N, 18.72. Found: C, 63.46; H, 3.74; N, 17.94.

Oligomers and PBI

Oligomers 1–5. Conditions for the syntheses of oligomers were similar to ones for model compounds **I** and **IIa–c**. Grounded carefully and mixed bisbenzotriazole and bismaleinimide was put into a fluoroplast cup. Then this cap was placed into a bath (Wood's alloy) preheated to 120°C. The temperature of the bath was gradually increased up to 220°C, and reaction mixture was kept additionally for 5 min. After reaction, mixture was cooled to ambient temperature; a crude product was removed from the cup by cooling it with liquid nitrogen and knocking on the bottom. Crude oligomers were used in form of powders and without purification.

Oligomer-1. A mixture of N,N′-hexamethylene-bis-maleinimide (2.7629 g, 0.0100 mol) and bis(1H-benzotriazol-5-yl)oxide (0.6306 g, 0.0025 mol) was used.

Oligomer-2. A mixture of N,N′-hexamethylene-bis-maleinimide (2.0722 g, 0.0075 mol) and bis(1H-benzotriazol-5-yl)oxide (0.6306 g, 0.0025 mol) was used.

Oligomer-3. A mixture of 4,4′-diphenylmethane-bismaleinimide (1.7918 g, 0.0050 mol) and bis(1H-benzotriazol-5-yl)methane (0.6256 g, 0.0025 mol) was used.

Oligomer-4. A mixture of 4,4′-diphenylmethane-bismaleinimide (3.5835 g, 0.0100 mol) and bis(1H-benzotriazol-5-yl)methane (0.6256 g, 0.0025 mol) was used.

Oligomer-5. A mixture of 4,4′-bis(maleimido)-diphenyl ether (3.6033 g, 0.0100 mol) and bis(1H-benzotriazol-5-yl)methane (0.6256 g, 0.0025 mol) was used.

Oligomer-6 was supplied from "Karbolit" plant (Kemerovo city) and was used as received.

Polybenzimidazole. This polymer was obtained according procedure described in article[21] from equimolar amounts of 3,3′,4,4′-tetraaminodiphenyl ether and isophtalic acid diphenyl ester. PBIs with reduced viscosities (η_{red}) of 2.0–4.0 dL g^{-1} (HCOOH, 20°C, 0.5 g dL^{-1}) were used.

Making membranes

All membranes were made similar to the procedures described in the article[22] with some modifications. Uncured films precursors were made via a process of solubilization of PBI together with Oligomer-2 in DMF. Solution concentrations of PBI and weight ratio of PBI:Oligomer-2 were 10–15 wt % and 9:1, respectively. This viscous solution was poured into a glass substrate. The solution distributed on the substrate surface was dried in air at first, and then a crude film was postdried *in vacuo* at 40–70°C to remove remains of DMF. The film was separated from the substrate and sandwiched between sheets of a carbon-fiber cloth and pressed slightly between two metallic plates. This film was cured in an oven at 240–250°C for 4–6 h.

Membranes were obtained by soaking cured films into water solutions of H_3PO_4 with concentrations of 7M, 9M, 12M, and 13M for 5 days. After soaking, the membranes were removed from solutions of H_3PO_4, and acid residues were wiped with a filter paper. The membranes were dried *in vacuo* at room temperature up to a constant weight.

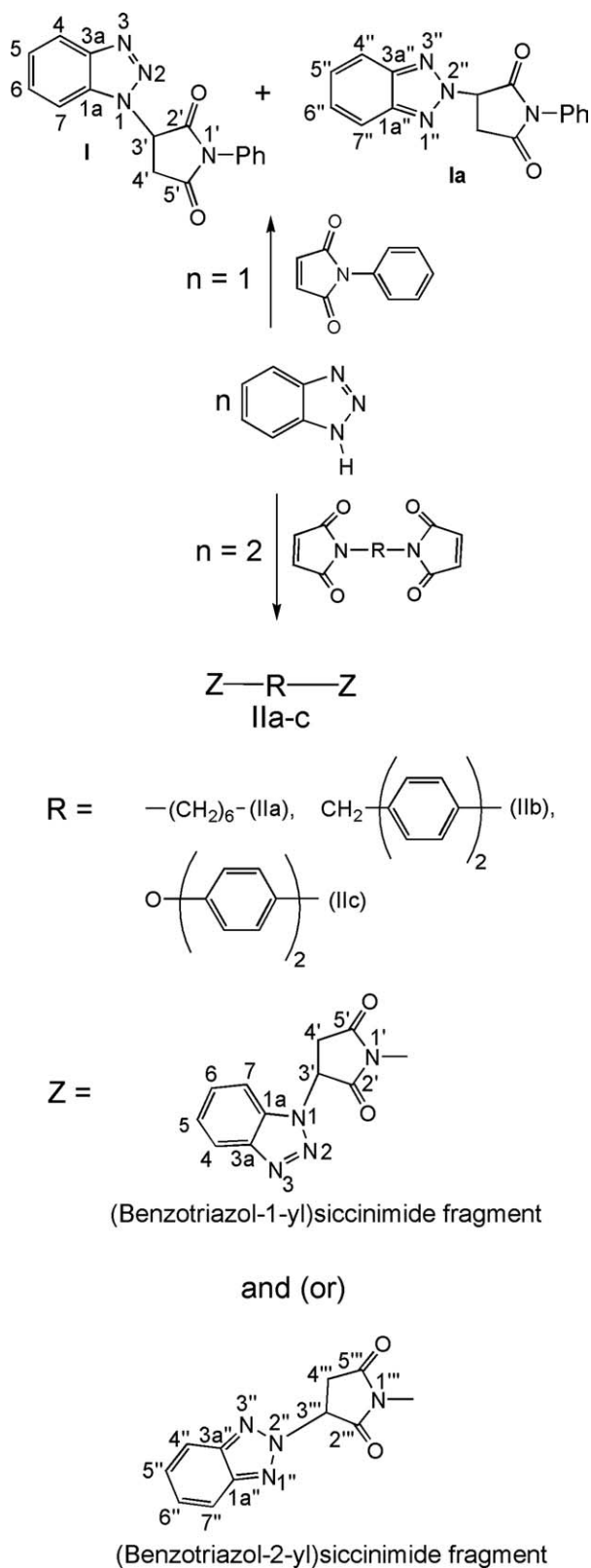### Making glass-fiber cloth laminate plastics

Prepregs were made via dipping sheets of an annealed glass-fiber cloth into oligomer solution in DMF or $CHCl_3$. Solution concentrations of oligomers were 5–10 wt %. The wet prepregs were dried in air at first and then *in vacuo* at 40–70°C to remove a solvent. These prepregs dried were assembled as a pack where fibers were located orthogonally. The pack was sandwiched between sheets of a carbon-fiber cloth treated with graphite dust, and then it was placed between two metallic plates. After, the pack was pressed at 150–200°C, and then it was cured in oven at 240–250°C for 4–6 h to afford a laminate plastic.

RESULTS AND DISCUSSION

Model compounds

A possibility of benzotriazoles to react with maleimides as Michael addition was studied on model compounds, namely, benzotriazolylsuccinimides. Benzotriazolylsuccinimides were obtained via melt syntheses at 120–210°C in a fluoroplastic cap according to Scheme 1.

In the ^{1}H-NMR spectrum (CDCl$_3$; Fig. 1) of the isolated product **I**, the protons of the group C(4′)H$_2$ give well resolved signals at δ 3.59–3.65 and 3.82–3.87 (both dd, 1 H, J_{vic} = 18.5 Hz, J_{trans} = 9.61 Hz, J_{cis} = 5.52 Hz) ppm, and the methine proton C(3′)H resonates at δ 5.94–5.97 (dd, 1 H) ppm. Aliphatic protons of an analog of this compound based on benzimidazole and N-phenylmaleinimide, that is, 1-(2,5-dioxo-1-phenylpyrrolidin-3-yl)benzimidazole, give similar spectral pattern.[23] In the ^{13}C-NMR spectrum (DMSO-d$_6$) (Fig. 2), the signals for aliphatic carbons C(4′) and C(3′) were observed at δ 35.43 and 56.34 ppm, respectively, and two signals for

R = $-(CH_2)_6-$ (IIa), CH_2 ⟨ ⟩$_2$ (IIb),

O⟨ ⟩$_2$ (IIc)

Z =

(Benzotriazol-1-yl)siccinimide fragment

and (or)

(Benzotriazol-2-yl)siccinimide fragment

Scheme 1

The presence of two signals for the aromatic protons in the 1H NMR spectrum of **I** (DMSO-d_6) (Fig. 1) at δ 7.95–7.96 and 8.14–8.16 (both d, 1 H each, H(7), H(4), J = 8.24 Hz, J = 8.55 Hz) ppm, and six signals for the carbon atoms of the benzotriazole fragment in the ^{13}C-NMR spectrum (Fig. 2) at δ 110.71 (C(7)), 119.72 (C(4)), 124.78 (C(5)), 128.38 (C(6)), 133.09(C(1a)), and 145.43 (C(3a)) ppm prove the formation of succinimide with nonsymmetrical benzotriazol-1-yl substituent.

Thus, the data from NMR spectroscopy prove compound **I** to be 1-(2,5-dioxo-1-phenylpyrrolidin-3-yl)-benzotriazole. The choice of reaction conditions is explained by the proneness of maleinimides to anionic homopolymerization across the olefin bonds and ring opening under classical Michael conditions in solution in the presence of a base. We have shown that, in contrast to benzimidazole,[23] benzotriazole is not added to the electron-deficient double bond of N-phenylmaleinimide under acidic conditions. In addition, synthesis in melt is environmentally and fire safe. If the reaction is carried out in glass reactors (melting at 210°C), then during 2–4 min a side reaction of homopolymerization of maleinimides (in the case of bismaleinimides, the formation of crosslinked polymers) occurs. According to our suggestions, the homopolymerization of maleinimides in this case can be catalyzed by $\equiv$Si—O$^-$Kat$^+$ (where Kat$^+$ is an alkali metal cation) groups on the glass surface. That is, why we have chosen a reactor made of an inert fluoroplast material.

Additionally, we have carried out condensation of bismaleimides, namely, N,N′-hexamethylene-bis-maleimide, 4,4′-diphenylmethane-bismaleinimide, and 4,4′-bis(maleimido)diphenyl ether with benzotriazole under analogous conditions according to Scheme 1. In the ^{13}C-NMR spectra of model compounds **IIa–c** (Table I), besides the signals for carbon atoms of (benzotriazol-1-yl)-succinimide, there are signals for the (benzotriazol-2-yl)-succinimide fragment.

Moreover, the ^{13}C-NMR spectrum of compound **IIb** is shown on Figure 3. As seen from this spectrum, aliphatic, aromatic, and carbonyl areas contain the peaks for the carbons of both benzotriazol-1- and -2-yl succinimide fragments. The peaks for the carbons of the major benzotriazol-1-yl succinimide fragment at δ 35.40, 56.28, 110.67, 119.71, 124.76, 128.37, 133.07, 145.71, 172.31, and 173.19 ppm are analogous ones for the carbons of model compound **I**. The peaks for the benzotriazol-2-yl succinimide fragment at δ 36.27, 63.71, 118.20, 127.51, 144.21, 171.40, and 173.24 ppm are low intensity ones due to the lesser content of this fragment. Splitting of the peaks for the aromatic carbons of diphenylmethane residue at
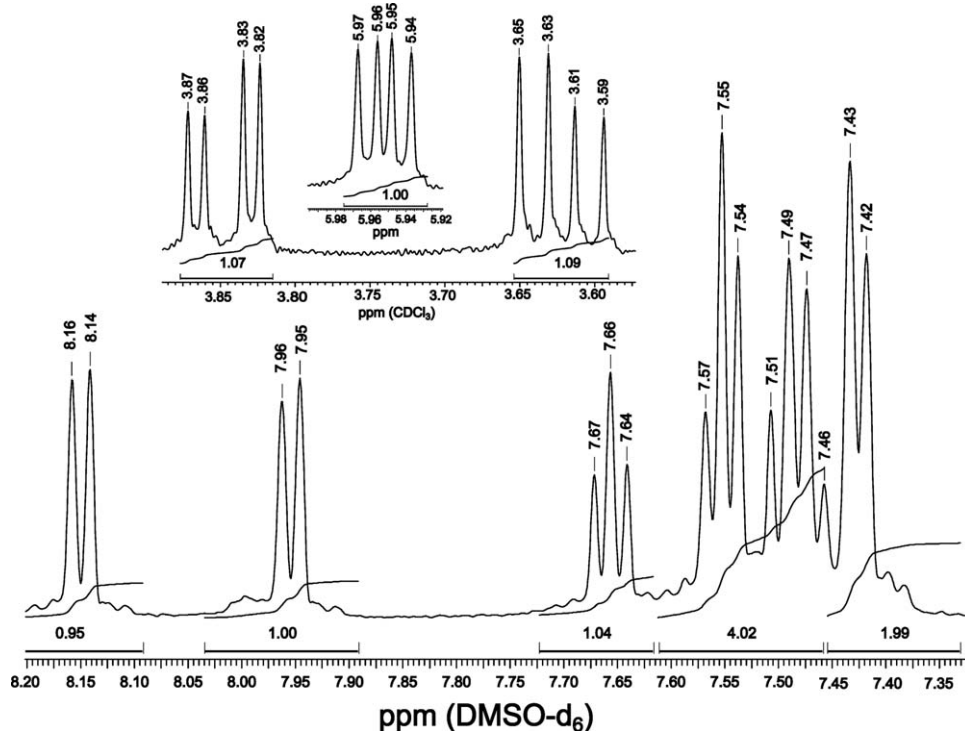
carbonyl atoms C(2′) and C(5′) at δ 172.33 and 173.19 ppm. These data altogether prove the formation of 3-substituted succinimide.

Figure 1 ^{1}H-NMR spectrums of Compound **I** in DMSO-d$_6$ and CDCl$_3$.

δ 127.20, 129.59, 130.10, and 141.76 ppm may be due to the formation two isomers of the position of benzotriazolyl fragments.

In the ^{1}H-NMR spectra of compounds **IIa–c**, the integral intensity ratios of C(3′)H and C(3‴)H protons are equal to 7.0, 4.5, and 7.0, respectively, which correspond to the molar ratios of benzotriazol-1- and -2-yl succinimide fragments in these products. The presence of the (benzotriazol-2-yl)succinimide fragments in compounds **IIa–c** suggests that under the conditions of the formation of compound **I** 2-(2,5-dioxo-1-phenylpyrrolidin-3-yl)benzotriazole (compound **Ia**) forms also. Compound **Ia** seemed to be lost in processes of the purification and the crystallization. The facts of a formation of benzotriazol-2-yl cycles in reactions where 1H-benzotriazoles taken part were cited in other works.[15–17]

Thus, we have established that benzotriazoles interact with maleinimides according to Michael in melt at elevated temperatures to afford both minor (benzotriazol-2-yl)- and major (benzotriazol-1-yl)succinimides.
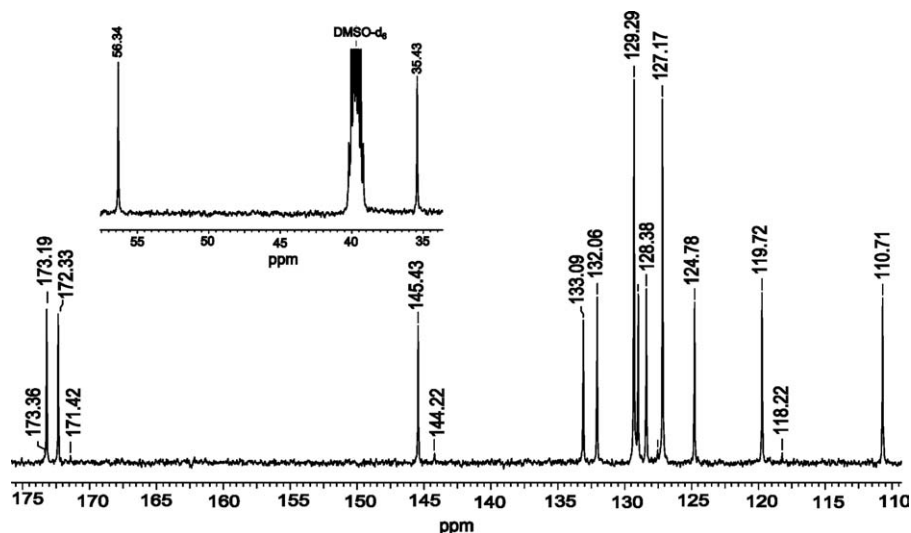

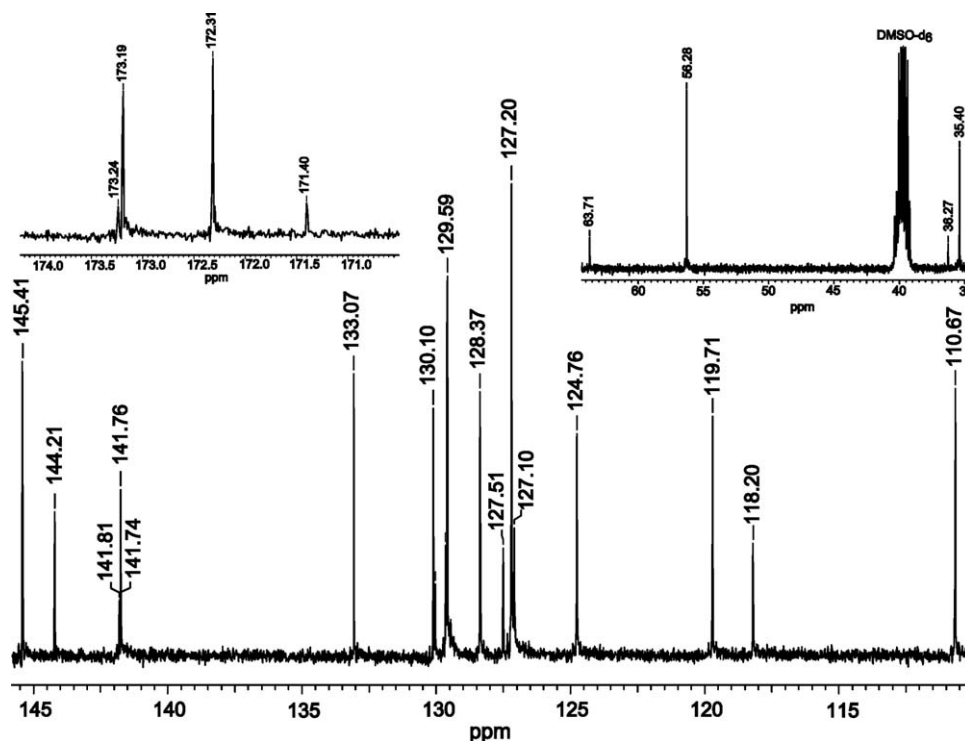**Figure 2** ^{13}C-NMR spectrum of Compound **I** in DMSO-d$_6$.

Figure 3 ^{13}C-NMR spectrum of Compound **IIb** in DMSO-d$_6$.

Benzotriazolylimide thermosetting oligomers and materials on base of them

The model compounds study data have assisted us to carry out the syntheses of a series of benzotriazolylimide thermosetting oligomers. These oligomers were synthesized via the interaction of 5,5′-bisbenzotriazoles with a molar excess of bismaleinimides in melt.

Oligomer synthesized from bis(1H-benzotriazol-5-yl)oxide and 4 mol of N,N′-hexamethylene-bismaleinimide (**Oligomer-1**) was chosen as the main object for the investigation. N,N′-hexamethylene-bismaleinimide as bismaleimide monomer was selected due to the presence of the hexamethylene group N-CH$_2$ reference protons for the estimation of a conversion of the maleimide olefinic bonds. It was proposed also that the presence of the soft hexamethylene groups in a final product would favor a best solubility and a processability of oligomer.

Oligomer-1, according to the DTA data, melts in the temperature interval of 163–165°C, and cures at 230°C (an exothermic peak). This oligomer is soluble in polar amide solvents, DMSO, HCOOH, acetone, and low-polar CHCl$_3$.

According to the ^{1}H-NMR spectroscopy, Oligomer-1 is equivalent to blend of 2 mol of N,N′-hexamethylene-bismaleinimide with 1 mol of the product of the addition (**Compound V**) of 2 mol of N,N′-hexamethylene-bismaleinimide to 1 mol of bis(1H-benzotriazol-5-yl)oxide. This conclusion is confirmed by the ratio of integral intensity of the maleinimide protons (6.99 ppm, s, 32H) to one of the α-protons of a hexamethylene group (3.40 ppm, t, 22H) which is 0.70. The theoretical value of this quantity is 0.75. Moreover, in the ^{1}H-NMR spectrum, there are the resonances at δ 1.44 ppm (d, 35H) and 1.20 ppm (s, 34H) for the β- and γ-protons of the hexamethylene group, respectively. There is a weak multiplet for the aromatic protons at δ 7.10–8.30 ppm also. No a broad resonance for a N—H proton of bis(1H-benzotriazol-5-yl)oxide at δ 15.60 ppm is present, evidencing complete interaction of this bisbenzotriazole.

In ^{13}C-NMR spectrum of Oligomer-1 (Fig. 4), there are the intensive resonances of α-, β- and γ-protons for the hexamethylene group at δ 36.81, 27.60, and 25.43 ppm, respectively. For terminal maleinimide cycles, olefinic and, carbonyl carbons resonate at δ 134.23 and 170.84 ppm, respectively. The low-intensity peaks at δ 172.26 and 173.39 ppm are due to the carbonyl carbons of 1-benzotriazolylcyccinimide cycles, and peak at δ 34.95 ppm is due to the methylene carbons of these cycles.

Basing on NMR spectroscopy data, the following scheme for the synthesis of Oligomer-1 can be depicted (Scheme 2).

The thermogravimetric analysis of Oligomer-1 in air is represented in Figure 5. As seen from Figure 5, the intensive thermal destruction, in spite of the presence of aliphatic chains, begins with about
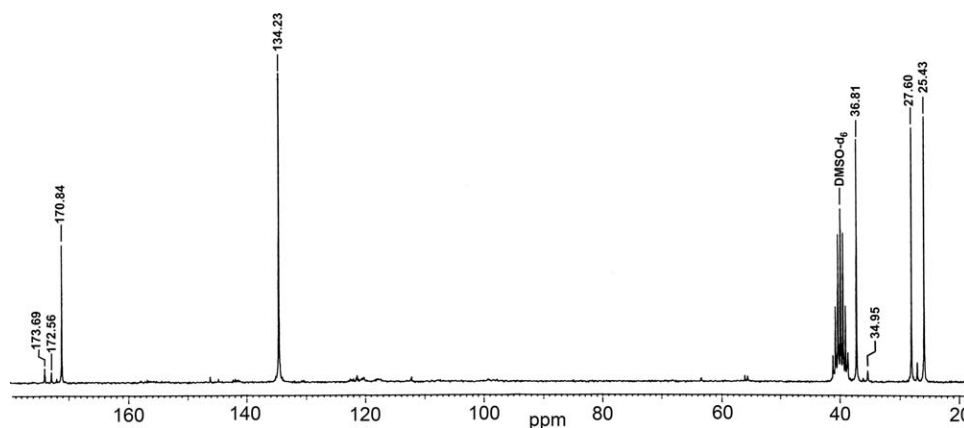
**Figure 4** ^{13}C-NMR spectrum of Oligomer-1 in DMSO-d$_6$.

400–410°C. This fact is due to the formation of a crosslinked polymer under heating. Thermal destruction stopped at about 550–560°C, with the weight loss being about 60% from an initial weight of a sample.

Additionally, oligomers on base of: bis(1H-benzotriazol-5-yl)oxide and N,N′-hexamethylene-bismaleinimide (the molar ratio is 1:3) (**Oligomer-2**), bis(1H-benzotriazol-5-yl)methane and 4,4′-diphenylmethane-bismaleinimide (the molar ratio is 1 : 2) (**Oligomer-3**), bis(1H-benzotriazol-5-yl)methane and 4,4′-diphenylmethane-bismaleinimide (the molar ratio is 1 : 4) (**Oligomer-4**), bis(1H-benzotriazol-5-yl)methane and 4,4′-bis(maleimido)-diphenyl ether (the molar ratio is 1 : 4) (**Oligomer-5**) were synthesized. These oligomers are the yellow amorphous products which are soluble at room temperature in polar amide solvents, DMSO, and HCOOH. Oligomer-2 is soluble in acetone and CHCl$_3$ also. According to DTA, all oligomers fuse at 125–145°C, that is, before processes of thermal crosslinking (at 180–250°C) and destructing (at 360–420°C). These properties of Oligomers 1–5 favor a manufacture of different composites with the good working characteristics.

Using Oligomers 3–5 as binders, the laminate plastics reinforced with a glass-fiber cloth were made. The properties of these plastics are summarized in

Table II. It is seen from Table II that all the plastics possess the high values of the mechanical characteristics. For comparison, the values of flexural strength of ∼ 50 and ∼ 70 MPa for cured blend composites on base of 4,4′-diphenylmethane-bismaleinimide/N-allyl-N′-phenylmaleindiamide (50 mol %) and 4,4′-bis(maleimido)-diphenyl ether/N-allyl-N′-phenylmaleindiamide (50 mol %), respectively, were given as the example in work.[20] The more high values of the mechanical characteristics of our plastics than ones of the cured blend composites[20] may be explained by the reinforced effect of the filler along with possibility of a formation of covalent bonds on the glass-fiber surface via the addition of the maleinimide cycle to the ≡Si—OH surface groups across the olefinic bond. Perhaps, ≡Si—O$^-$Kat$^+$ (where Kat$^+$ is an alkali metal cation) groups on the glass fiber surface influence on this process as the catalyst. Those groups seem to promote curing process of oligomer.

It is known that one of main components of the medium temperature fuel cells is a proton-conducting polymer membrane. As the fuel cells mentioned operate under conditions of elevated temperatures and hostile environments, the exacting requirements, such as high proton conductivity, mechanical
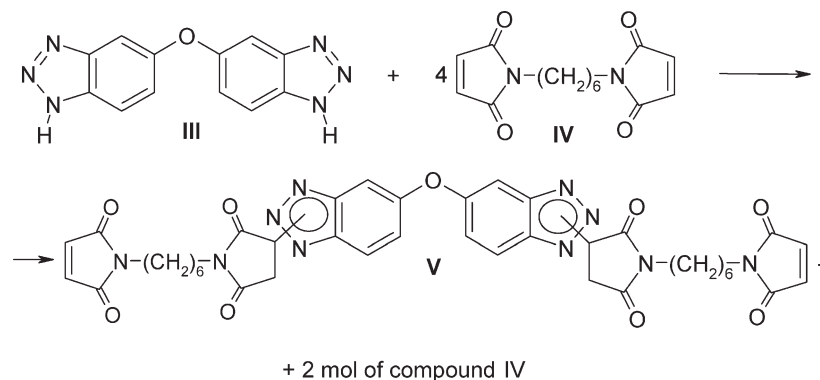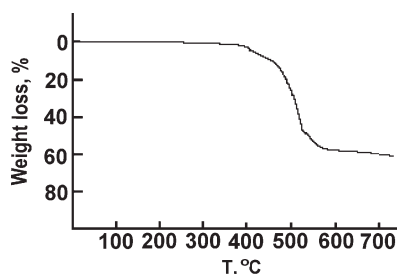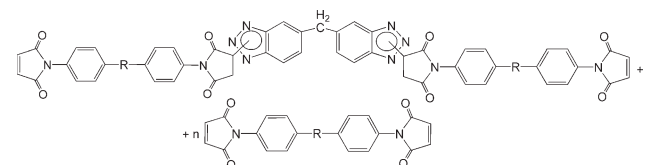

Scheme 2

Figure 5 Thermogravimetric analysis of Oligomer-1 (in air, 10 grad min^{-1}).

strength, chemical resistivity, low permeability to a fuel and an oxidizer, etc. are established for the proton-conducting membranes.[24] It is known also that linear polybenzimidazoles (PBIs) doped by H_3PO_4 are suitable materials for the fuel cells membranes.[22,24–28] The advantages of the use of PBI/H_3PO_4 complex are following: H_3PO_4 possesses good conductivity even if water molecules are absent; PBIs is known to have prominent thermal stability, chemical, and heat resistivity; PBIs hold molecules of H_3PO_4 quite strongly owing to a basic capacity of benzimidazole cycles. The main disadvantage of those membranes is a deterioration of their performances under elevated temperatures and at high doping levels.

To now, the interesting tendency of obtaining crosslinked PBIs to solve those problems is watched. In the literature, there are the scientific works concerning both ionic and covalently crosslinked PBI membranes.[24–28] Such tendency is explained by that the membranes on base of crosslinked PBIs possess the best work characteristics in comparison with the membranes from linear PBIs.

In work,[28] hyperbranched PBIs which can be cured further in process of making the membranes have been offered as one of variants to solve the problem of the deterioration of the membrane performances. Such PBIs have been obtained via polycondensation of 3,3′-diaminobenzidine with aromatic di- and tricarboxylic acids in polyphosphoric acid medium at high temperatures. Ethylene glycol diglycidyl ether and terephthaldehyde have been utilized as the crosslinking agents. That offer has been explained by advanced solubility of hyperbranched polyheteroarylenes and by the well-known property of three-dimensional polymers to adsorb a large quantity of solvent molecules without solubilization.

We offer another way to obtain the covalently crosslinking membranes. This way is that linear PBIs synthesized by the melt/solid-phase method are used as the polymer matrix, and thermosetting benzotriazolylimide oligomers are utilized as the crosslinkers. In this case, the universal abilities of maleimides to react with the N—H bonds of benzimidazole heterocycles[23] and to polymerize across the olefin bond are exploited. An interaction of linear PBIs with maleimide-terminated benzotriazolylimide oligomers along with homopolymerization of the latter should result in three-dimensional networks.

To design the membrane, we have used PBI following structure:
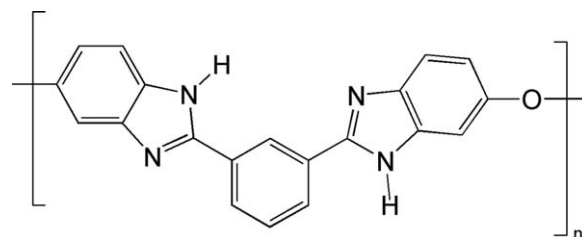
as the basic polymer matrix and Oligomer-2 as the crosslinking agent. This PBI can be readily prepared via the melt/solid-phase synthesis from available monomers,[21] and it is soluble good in common organic polar solvents due to the presence of the ether oxygen bridge. The choice of Oligomer-2 was grounded on the suggestion that the hexamethylene groups of this oligomer would favor flexibility of a final crosslinked film and the ability of this kind of films to adsorb a large quantity of H_3PO_4 molecules without any by-processes.

A doping level and a proton conductivity of the membranes were investigated. Measurements were carried out under normal conditions and dry argon flow. Data are summarized in Table III. It is seen from Table III that both the doping level and the conductivity increase remarkably after H_3PO_4 concentrations of 9–11M. This phenomenon appears to occur due to a free volume expands sharply owing to the intermolecular interactions between the segments of PBI are sufficiently weakened at the high doping levels. The dramatic increase in conductivity may be explained in terms of the change of the nature of this phenomenon.

TABLE II
**Mechanical Properties of Glass-Fiber Cloth Laminate Plastics with Benzotriazolylimide Thermosetting Binders**

No.	Thermosetting binder	Impact resistance (kJ/m^2)	Bending strength (MPa)
1.	Oligomer-3 (R=CH$_2$, $n = 0$)	12.3–16.1	207–218
2.	Oligomer-4 (R=CH$_2$, $n = 2$)	12.0–15.8	195–210
3.	Oligomer-5 (R=O, $n = 2$)	11.4–13.8	189–205

TABLE III
Properties of Membranes Made by Doping of Films in Water Solutions of H_3PO_4 with Different Molar Concentrations

Components of films	Mechanical properties[a]				Doping level (mol %)				Conductivity[a], $\sigma \times 10^{-5}$ (S·sm^{-1})			
	Initial films		Membranes[b]									
	Tensile strength (MPa)	Elongation at break (%)	Tensile strength (MPa)	Elongation at break (%)	7M	9M	11M	13M	7M	9M	11M	13M
PBI	65–72	5–8	6–12	2.5–4.0	356	403	648	864	1.3	14.5	490.0	830.0
PBI + Oligomer-2[c]	110–120	4–6	50	5–6	287	405	597	1290	2.0	3.4	31.0	340
PBI + Oligomer-6[c]	80–120	1.5–2.0	0.07	78.8	294	490	783	—	5.0	6.0	820.0	—

[a] Under normal conditions.
[b] Doped by 9M H_3PO_4.
[c] Thermally crosslinked films.

Also, we were investigated proton conductivity of the membrane doped by 9M H_3PO_4 within temperature range of 51–191°C. Before measurements, the membrane was conditioned at 21.3°C under moist argon flow for about 2 h. When conditioned, conductivity of the membrane was increasing from 4.7 $\times 10^{-5}$ S sm^{-1} to 3.2 $\times 10^{-3}$ S sm^{-1}. This was due to the membrane was absorbing water vapors during this process. Then a measuring cell was heated up to 51°C, and conductivity of the membrane at this temperature was 3.6 $\times 10^{-2}$ S sm^{-1}. Data of following measurements are represented in Figure 6 as the plot. As seen from Figure 6, the dependence within the temperature range of 51–120°C has the extreme character. Extreme conductivity is approximately (1.10–1.15) $\times 10^{-1}$ S sm^{-1} at 75–80°C. Then the value of this parameter decrease rapidly, perhaps, due to evaporation of water from the membrane. In the range of 120–191°C, conductivity does not exchange practically and is (4.5–4.9) $\times 10^{-3}$ S sm^{-1}. Hence, this membrane possesses the acceptable proton conductivity at elevated temperatures although the doping level is low. After the measure of conductivity, the membrane did not break. On the contrary, this membrane became more strength, but no brittle. This proves the operational capability of such type membranes at elevated temperatures. It is necessary to mention that this extreme character of temperature conductivity described above is peculiar to the membranes on base of sulfonated polymers hydrated,[24] but not peculiar to the PBI/H_3PO_4-based membranes.[22,25,28] Hence, this anomalous behavior of the membrane which has been investigated in our work should be comprehensively studied in future.

Additionally, the mechanical properties of the membrane on base of the crosslinked film doped by 9M H_3PO_4 were investigated under normal conditions (Table III). It is seen from Table III that the tensile strength of the membrane decreases from 115 MPa to 50 MPa, when doped by 9M H_3PO_4 (4.03

H_3PO_4 molecules per PBI unit), and the elongation at break does not exchange practically. Hence, this membrane possesses the good mechanical strengths in spite of proton conductivity is low. It is necessary to remark that the membranes with the more high doping levels did not break even if the level of doping reached as high as 1290 mol %. The comparable values of the tensile strength of 54 MPa and the elongation at break of 3.3% for the hyperbranched PBI membrane crosslinked with ethylene glycol diglycidyl ether (3.8 H_3PO_4 molecules per PBI unit) were reported in work.[28]

The crosslinked thermally film on base of PBI and industrial oligomer on base of 4,4′-diphenylmethane-bismaleinimide and 4,4′-diaminodiphenylmethane (**Oligomer-6**) was used as the example for a comparison. The methods of preparing and doping this film were similar to ones for the film on base of PBI and Oligomer-2. Data are summarized in Table III. It is seen from Table III that though the membrane on base of PBI and Oligomer-2 possesses lower conductivity than the membrane on base of PBI and Oligomer-6, the mechanical properties of the latter is
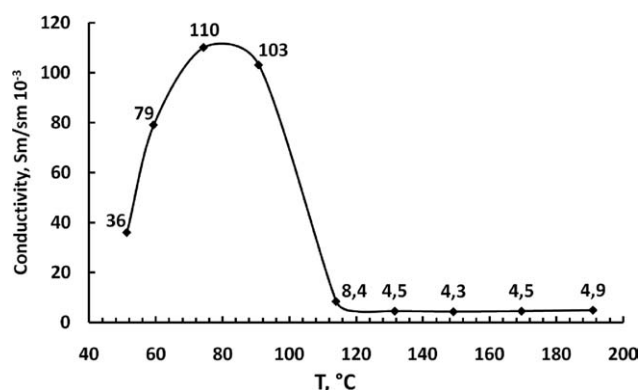

Figure 6 Conductivity of the membrane doped by 9M H_3PO_4 as a function of temperature.

even worse than the analogous properties of pristine PBI.

Hence, the crosslinked films on base of PBIs and thermosetting benzotriazolylimides which, in turn, are prepared from bisbenzotriazoles, and an excess of aliphatic bismaleinimides are the perspective materials for the design of the proton-conducting membranes possessing the good mechanical properties.

CONCLUSIONS

It has been established for the first time that benzotriazoles interact easily with maleinimides in melt at elevated temperatures to afford benzotriazolylsuccinimides. Using NMR spectroscopy data, it has been evidenced that these benzotriazolylsuccinimides contain both major (benzotriazol-1-yl)-succinimide and minor (benzotriazol-2-yl)-succinimide fragments. Moreover, the synthetic procedure elaborated by us can be adopted for preparing other benzotriazolyl-succinimides also.

It has been proved that bisbenzotriazoles interact with an excess of bismaleinimides in melt to afford oligomers. Oligomers, according to ^{13}C-NMR, contain both benzotriazolylsuccinimide and reactive maleinimide terminal groups. They are soluble in common organic solvents, and fuse before the processes of crosslinking and thermal destructing, according to DTA. After crosslinking, oligomers possess the good thermal stability in air up to 410°C.

It has been proved also that the press materials and the crosslinked films which have been made with using benzotriazolylsuccinimide oligomers possess the high mechanical characteristics. Hence, these oligomers are suitable as the thermosetting binders for the filled press-materials and as the crosslinkers for basic linear polymers to make the crosslinked films. These films have been established to be the advanced materials to design the phosphoric acid electrolyte membranes for the medium temperature fuel cells.

References

1. Sroog, C. E. Prog Polym Sci 1991, 16, 561.
2. Chin, J. W.; Wightman, J. P. Compos A: Appl Sci Manufact 1996, 27, 419.
3. Crivello, J. V. (General Electric Co.) U.S. Patent 3,738,967, June 12, 1973.
4. Iha, R. K.; Wooley, K. L.; Nyström, A. M.; Burke, D. J.; Kade, M. J.; Hawker, C. J. Chem Rev 2009, 109, 5620.
5. Kloxin, C. J.; Scott, T. F.; Adzima, B. J.; Bowman, C. N. Macromolecules 2010, 43, 2643.
6. Ouchi, M.; Terashima, T.; Sawamoto, M. Chem Rev 2009, 109, 4963.
7. Rivas, K.; Vargas, F.; Aguiar, G.; Torrealba, A.; Machado, R. J Photochem Photobiol 1997, 104, 53.
8. Hamerton, I.; Barton, J. M.; Chaplin, A.; Howlin, B. J.; Shaw, S. J. Polymer 2001, 42, 2307.
9. Fan, S.; Boey, F. Y. C.; Abadie, M. J. M. Eur Polym Mater 2008, 44, 2123.
10. Allen, N. S. Photochemistry 2005, 35, 206.
11. Lin, R.-H.; Liu, Y.-H.; Chen, Y.-H.; Lee, A.-C.; Ho, T.-H. Eur Polym Mater 2007, 43, 4197.
12. Srikanth, A. P.; Sunitha, T. G.; Nanjundan, S.; Rajendran, N. Prog Org Coat 2006, 56, 120.
13. Wanga, R.-M.; Chaia, C.-P.; Hea, Y.-F.; Wanga, Y.-P.; Li, S.-B. Eur Polym Mater 1999, 35 2051.
14. Gall, W. G. (du Pont de Nemours and Co.). U.S. Patent 3,376,233, April 2, 1968.
15. Katritzky, A. R. J Heterocycl Chem 1999, 36, 1501.
16. Rachwal, S.; Katritzky, A. R. Comprehensive Heterocyclic Chemistry III; Elsevier, 2008, Chapter 5.01, pp. 1–158.
17. Abramov, I. G.; Smirnov, A. V.; Abramova, M. V.; Ivanovskii, S. A.; Plakhtinskii, V. V. Chem Heterocycl Compd 2000, 36, 1062.
18. Hopewell, J. L.; Hill, D. J. T.; Pomery, P. J. Polymer 1998, 39, 5601.
19. Bekker, H.; Domschke, G.; Fanghenel, E.; Organikum. Organisch-chemisches Gründpraktikum; Veb Deutscher Verlag der Wissenschaften: Berlin, 1990.
20. Lin, K.-F.; Lin, J.-S., Cheng, Ch.-H. Polymer 1996, 37, 4729.
21. Vogel, H.; Marvel, C. S. J; Polymer Sci A: Polymer Chem 1963, 1, 1531.
22. Li, Q.; Hjuler, H. A.; Bjerrum, N. J J Appl Electrochem 2001, 31, 773.
23. Batotsyrenova, A. I., Radnaeva, L. D., Mognonov, D. M., Izyneev, A. A., Erzh, B. V.; Yunnikov, V. V. Polym Sci USSR: Ser A 1990, 32, 375.
24. Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J Chem Mater 2003, 15, 4896 and references therein.
25. Li, Q.; Jensen, J. O.; Savinell, R. F.; Bjerrum, N. J Progr Polym Sci 2009, 34, 449 and references therein.
26. Li, Q.; Pan, C.; Jensen, J. O.; Noyé, P.; Bjerrum, N. J Chem Mater 2007, 19, 350 and references therein.
27. Noyé, P.; Li, Q.; Pan, C.; Bjerrum, N. J Polym Advan Technol 2008, 19, 1270.
28. Xu, H. J.; Chen K. C.; Guo, X. X.; Fang, J. H.; Yin, J. J Membr Sci 2007, 288, 255.