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Crosslinked polymers based on polyborosiloxanes: Synthesis and properties

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ABSTRACT

In current work, crosslinked polyborosiloxanes (PBS) were synthesized by the Piers-Rubinsztajn reaction based on polydimethylsiloxanes (PDMS) with terminal dimethylhydrosilyl or distributed methylhydrosilyl groups in the polymer chain and boronic or phenyl boronic acid methyl esters. Depending on the number and location of the methylhydrosilyl groups in the initial PDMS, as well as on the functionality of the boronic component (2 for phenyl boronic and 3 for boronic acid methyl esters), PBS with different macromolecular architecture and crosslinking density were obtained. PBS based on PDMS with terminal dimethylhydrosilyl groups, crosslinked with trimethyl borate, are soluble in common solvents such as THF, toluene and chloroform, whereas PBS based on PDMS with distributed methylhydrosilyl groups are non-soluble. Investigations in an environmental chamber showed hydrolytic stability of the PBS samples under experimental conditions, which was confirmed by gel permeation chromatography (GPC) and infrared spectroscopy (FTIR). In the investigations of thermal stability of obtained PBS, 5% weight loss was observed at 380–430 °C. Differential scanning calorimetry (DSC) experiments showed differences in phase behavior of PBS with different boronic crosslinks.

1. Introduction

Polyborosiloxanes (PBS) are broad class of organoelement compounds, which contain the Si-O and B-O fragments in their structure. Due to the high stability of the B-O and Si-O bonds, PBS and other substances based on them are stable to further oxidative processes. Such derivatives can be used as fire-retardant coatings [1–3] or as precursors for high temperature-resistant ceramic (SIBCO or SIBOC) as new functional materials, stable at ultra-high temperatures for long-life applications [4–6]. Another prospective application of PBS is precursors of ceramic matrices for the protection of carbon fibers in ceramic matrix composites [7,8]. Recently, interest in PBS has increased in terms of their use as new functional materials. Specifically, cheap and non-toxic PBS sols are used as p-emitter for fabrication of n-type silicon wafers [9] or as proton conductive electrolyte [10]. PBS as monomers or oligomers can be used to improve the mechanical properties of polymers and their heat resistance [11]. Being added to PBS, graphene changes its electromechanical properties. Such nanocomposites can be used for fabrication of extremely sensitive electromechanical sensors, which will be used in a number of modern devices [12]. Moreover, it was shown, that some structural types of PBS demonstrated antimicrobial activity [13,14]. Due to high adhesion to various types of surfaces, PBS can be used as adhesives [15,16]. Investigations of the rheological properties of PBS are of great academic interest. It is known that PBS can form weak intermolecular interactions between the free pair of electrons of the oxygen atom and the vacant 2-p orbitals of the boron atom [17]. The formation of an intermolecular physical network often explains the gelation, observed in the case of PBS, which is reversible when heated or under the action of a mechanical load [18]. PBS often behave like a Newtonian fluid and at the same time like an elastic Hooke body. Based on this phenomenon Dow Corning developed popular “jumping putty” or Silly Putty - elastic materials that can slowly flow after some time. As a practical application, Silly Putty was used to increase the stability of extrusion in the production of low density polyethylene, which made it possible to increase the rate of extrusion more than 25–35 times [19]. Currently PBS-based nanocomposites, filled with

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polyvinyl alcohol, polyacetate, polyurethane, silica, and other compounds are used for shockproof and bulletproof materials. Prototypes of the protective suits for footballers [20] and motorcycle racers [21] were developed by Dow Corning. J-Foam recently has released protective suits for skiers [22]. Thus, the growing demand for PBS requires improvement and simplifying of synthetic methods for producing materials based on them. Despite the simplicity of the synthesis using both sol-gel methods [23–27] and catalytic systems [28], PBS, obtained by these methods, undergo hydrolysis [29], which inhibits their widespread use as functional materials and composites. Recently, the new methodology of siloxanes bond formation from precursors, containing both hydrosilane group and alkoxysilane or silanol group by using tris(pentafluorophenyl)boron as catalyst has been developed [30–33]. Its peculiar features are absence of water during the reaction and formation of only gaseous by-products (hydrogen or alkanes). These factor shift the reaction equilibrium to the direction of product formation.

In this research, the opportunity of using Piers- Rubinsztajn reaction for synthesis of PBS based on PDMS with terminal or distributed methylhydrosilyl groups in the polymer chain and boronic or phenyl boronic acid methyl esters was estimated. Besides investigations on the influence of the PBS structure on the physical characteristics, the most important part of current research is to study the hydrolytic degradation rate of the PBS against atmospheric moisture.

2. Experimental section

Gel Permeation Chromatography (GPC) analysis was performed on a Shimadzu LC-10A series chromatograph (Japan) equipped with an RID-10A refractometer and SPD-M10A diode matrix detectors. For analytical separation Phenomenex column (USA) with a size of 7.8 mm × 300 mm filled with the Phenogel sorbent with a pour size of 15–500 Å. ^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded using a Bruker WP-250 SY spectrometer with working frequency of 250.13 MHz. For internal standard signal was used $CDCl_3$ with chemical shift $\delta = 7.25$ ppm. Trimethylborate, phenylboronic acid was purchased in Sigma-Aldrich, tris(pentafluorophenyl)boron (ABCR Gmbh) as 10% solution in dry toluene was prepared in glow-box as stored in it. Dry solvents: toluene, ethanol, methanol, was prepared as follows: after refluxing during 3–5 h over calcium hydride, solvent was distilled under argon and after that, stored for 1 day over molecular sieves 3 Å. Dry chloroform was prepared as mentioned above; instead of calcium hydride, phosphorus pentoxide was used as dehydrator agent. Residual content of water was measured using Karl Fischer coulometric titrator system Metrohm 831 KF (Switzerland).

3. Experimental section

Gel Permeation Chromatography (GPC) analysis was performed on a Shimadzu LC-10A series chromatograph (Japan) equipped with an RID-10A refractometer and SPD-M10A diode matrix detectors. For analytical separation Phenomenex column (USA) with a size of 7.8 mm × 300 mm filled with the Phenogel sorbent with a pour size of 15–500 Å. ^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded using a Bruker WP-250 SY spectrometer with working frequency of 250.13 MHz. For internal standard signal was used $CDCl_3$ with chemical shift $\delta = 7.25$ ppm. DSC was performed by a differential scanning calorimeter DSC-822e (Mettler-Toledo, Switzerland) at a heating rate 10 °C/min in argon. TGA was done on a Derivatograph-C (MOM, Hungary) at a heating rate 10 °C/min in argon. Trimethylborate, phenylboronic acid was purchased in Sigma-Aldrich, tris(pentafluorophenyl)boron (ABCR Gmbh) as 10% solution in dry toluene was prepared in glow-box as stored in it. Dry solvents: toluene, ethanol, methanol, was prepared as follows: after refluxing during 3–5 h over calcium hydride, solvent was distilled under argon and after that, stored for 1 day over molecular sieves 3 Å.. Residual content of water was measured using Karl Fischer coulometric titrator system Metrohm 831 KF (Switzerland).

3.1. Phenylboronic diethyl ester

6.02 g (0.05 mol) phenylboronic acid in 120 ml dry $CHCl_3$ and 65 ml dry ethanol was heated to reflux in round-bottom flask equipped with Soxlet's extractor with molecular sieves 3 Å, which were previously activated in vacuum. After 12 h, reaction mixture allow to cool down and solvents were vaporized using rotary evaporator. Obtained residue was distilled in vacuum to afford 7.35 g of transparent liquid. Yield of the product was 86%. B.p. = 110 °C (26 mbar). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (s, 2H), 7.39 (s, 3H), 4.11 (q, J = 6.8 Hz, 4H), 1.32 (t, J = 6.6 Hz, 6H);

3.2. General procedure of preparation polydimethylsiloxanes with telehelic hydrosilanes

Octamethylcyclotetrasiloxane (19.57 g, 66.1 mmol), 1,1,3,3-tetramethyldisiloxane (0.43 g, 3.22 mmol), and a Purolite CT-175 sulfonic acid resin (0.98 g) were loaded in a 50 mL one necked flask equipped with a reflux condenser. The reaction mixture was stirred for 8–10 h at 70 °C, dissolved, in hexane, and filtered to remove the sulfonic acid resin. The solution was evaporated on a rotary evaporator and cyclic products were distilled off in vacuo for 6 h at 80 °C (1 Torr) to yield 18.5 g (92.5%) of α,ω-dihydrooligodimethylsiloxane with $M_n = 6300$, $M_w/M_n = 1.84$. ^{1}H NMR ($CDCl_3$), δ: 0.08 (s, 510H, Si($C\underline{H}_3$)$_2$); 4.71 (m, 2H, Si-$\underline{H}$).

3.3. General procedure of preparation polydimethylsiloxanes with side functional hydrosilanes

A 250 mL one-necked flask equipped with a reflux condenser was charged with octamethylcyclotetrasiloxane (50 g, 0.1689 mol), BS-94 polymethylhydrosiloxane (1.7652 g, 0.0005 mol), 1,1,1,3,3,3-hexamethyldisiloxane (0.38 g, 0.0023 mol), and a Purolite CT-175 sulfonic acid resin (1.56 g). The reaction mixture was stirred for 8–10 h at 70 °C, dissolved in hexane, and filtered to remove the sulfonic acid resin. The solution was evaporated on a rotary evaporator and cyclic products were distilled off for 20 h at 120 °C (1 Torr) to yield 39.11 g (75%) of the product with $M_n = 14100$, $M_w/M_n = 1.9$. ^{1}H NMR ($CDCl_3$), δ: 0.08 (s, 3 H, Me (PMDS)); 4.71 (m, 1 H, H—Si). Content (Si-H) 3,6% mol. Synthesis is based on the method described in Ref. [34].

General procedure of Piers-Rubinsztajn reaction (without solvent).

Source PDMS was vacuumized previously for 10–15 min in round-bottom flask and filled with argon. After that, appropriate quantity of alkoxyborate was added and reaction mixture was vigorously stirred for a some time. Next, 10 μL 10% solution of tris(pentafluorophenyl)boron in toluene was added by syringe. After some time (30 min–5 h), viscous reaction mixture turned to elastic gel and further stirring become impossible. Tracers of solvent and unreacted alkoxy borates were removed in vacuum (0.5 mbar).

General procedure of Piers-Rubinsztajn reaction (with solvent).

Source PDMS was vacuumized previously for 10–15 min in round-bottom flask and filled with argon. Dry toluene and appropriate quantity of alkoxyborate was added by syringe and reaction mixture was vigorously stirred for a some time. Next, 10 μL 10% solution of tris(pentafluorophenyl)boron in toluene was added by

syringe. The reaction mixture was stirred at room temperature during 6 h. After that, additional portion of the catalyst was added. If no bubbles were detected to release, solvent and unreacted alkoxy borates were vaporized to afford desired product. If reaction has not been finished (bubbles was still released), stirring was continuous for another 6 h and the procedure was repeated.

4. Results and discussion

It is well-known, that rigidity and length of polymer chains, frequency and chemical nature of crosslinks strongly influence the physical properties of polymer network structures [35]. In the case of PBS, another additional factor, which affects the final properties of material, is the presence of donor-acceptor interactions between PBS fragments [36]. To assess the influence of these factors on the physical characteristics of the final crosslinked material, PBS of various structures were synthesized via the Piers–Rubinsztajn reaction, as it was described earlier [37] (Fig. 1).

From PDMS with terminal dimethylhydrosilyl groups ($M_n = 6300$ and 22600) and trimethylborate were obtained crosslinked polymers (type A), which differ from each other only in the size of the crosslinked cells. Two other types of PBS were synthesized from PDMS with distributed methylhydrosilyl groups in the chain. Highly crosslinked PBS (type B) was obtained using trimethylborate as a crosslinking agent. The third type of PBS polymer (type C) was a PDMS with distributed methylhydrosilyl groups, crosslinked with difunctional phenylboronic acid dimethyl ester. After isolation of the solvent, all PBS were transparent elastic materials that looked like rubber.

Despite the presence of crosslinks in their structures, the samples of the obtained PBS type A were soluble in common organic solvents such as chloroform, toluene and THF. Taken into consideration repeated solubility, and also accepting the fact that, in a bulk PBS type A samples exhibit typical rubber behavior - reversibly stretched and compressed, it can be assumed that the elastic properties of rubber in this case are associated with formation of physical networks due to donor-acceptor interchain interactions, disappearing after dissolving. In other words, PBS intermolecular crosslinks in these materials are due to non-covalent donor-acceptor interactions, while in other types of network polymers, the character of intermolecular crosslinks is covalent. Molecular mass characteristics of soluble PBS type A were investigated by gel permeation chromatography (GPC) using polystyrene standards. Surprisingly, the number-average molecular weights (M_n) in the obtained PBS type A increased only by more than 2 times as compared with the initial polydimethylsiloxanes in both cases. This fact, together with the above mentioned assumptions, may be an evidence of the presence of PBS dimers in the solution, which reversibly form a network structure upon removing the solvent. Such behavior is typical for derivatives of boronic acids [38,39].

The molecular masses of PBS type B and type C could not be measured using GPC due to their complete insolubility in organic solvents. During continuous storage, the obtained PBS did not lose their transparency and uniformity of the composition and did not become cloudy during long-term exposure to air, which indicates their stability relative to the effects of atmospheric moisture. The hydrolytic stability against moisture was estimated by treating of small pieces of each PBS in environmental chamber over period 3, 6 and 10 days. After that, every specimen was dried from traces of water and analyzed with IR ATR spectroscopy and GPC (only soluble PBS). Results are summarized on Fig. 2.

According to the acquired IR data, the following main bands can be characterized: νB–O in the range 1500–1300 cm^{-1}, sSi–CH_3 in the 1264–1250 cm^{-1}, νSi–CH_3 at 794 cm^{-1}, νSi–O at 1089-1079 cm^{-1}. Moreover, the band at 870 cm^{-1} and 705-698 cm^{-1} is the fingerprint of the polyborosiloxane fragments in the molecule. Upon processing in environmental chamber, intensity of the bands 1079-1080 cm^{-1}, associated with vibration νSi–O–Si mode, increased for samples PBS type A and B, (Fig. 2 a, b, c), whereas other peaks did not change. It can be explained by conformational changes of PBS's chains during moisture impact. For PBS type C IR ATR spectra were significantly different (Fig. 2d). Upon processing in environmental chamber, intensity of the bands 1079-1080 cm^{-1} also increased, band at 1011 cm^{-1} became significantly lower. More importantly, that intensity of the peaks at 866 and 696 cm^{-1}, which correspond to Si-O-B bands, decreased. Based on these data, we suggest, that PBS type A and B are the most stable against influence of moisture, whereas structure of PBS type C is significantly changed after processing in environmental chamber.

Samples of PBS type A with different molecular weights after

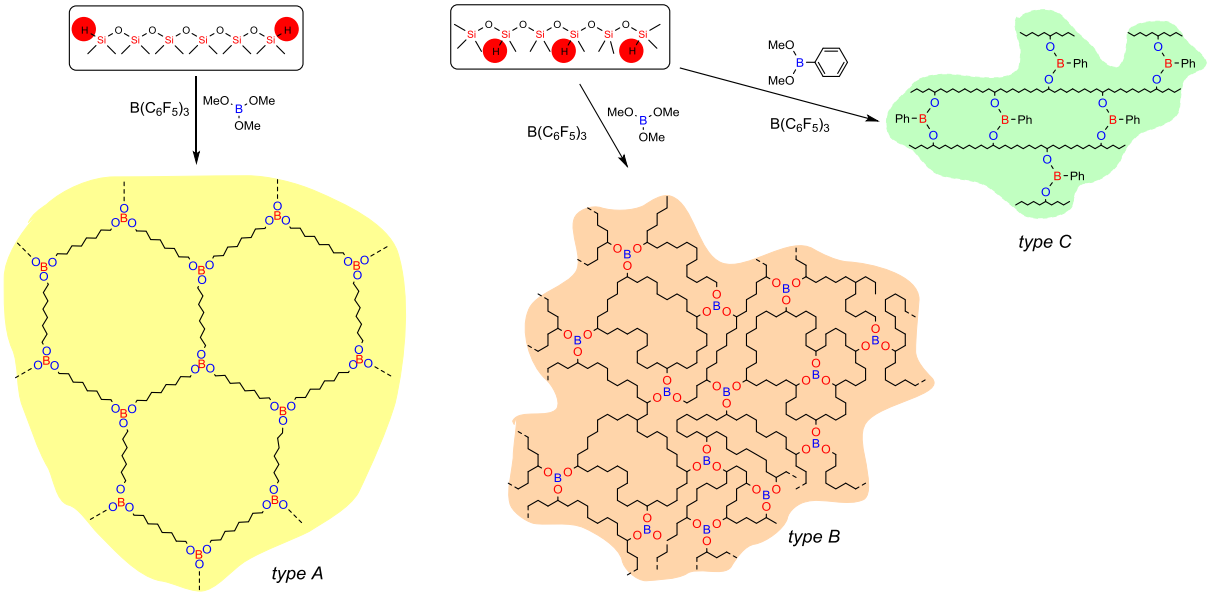

Fig. 1. Scheme of synthesis and structures of crosslinked (type A), highly (type B) and average (type C) crosslinked PBS using Piers-Rubinsztajn reaction.

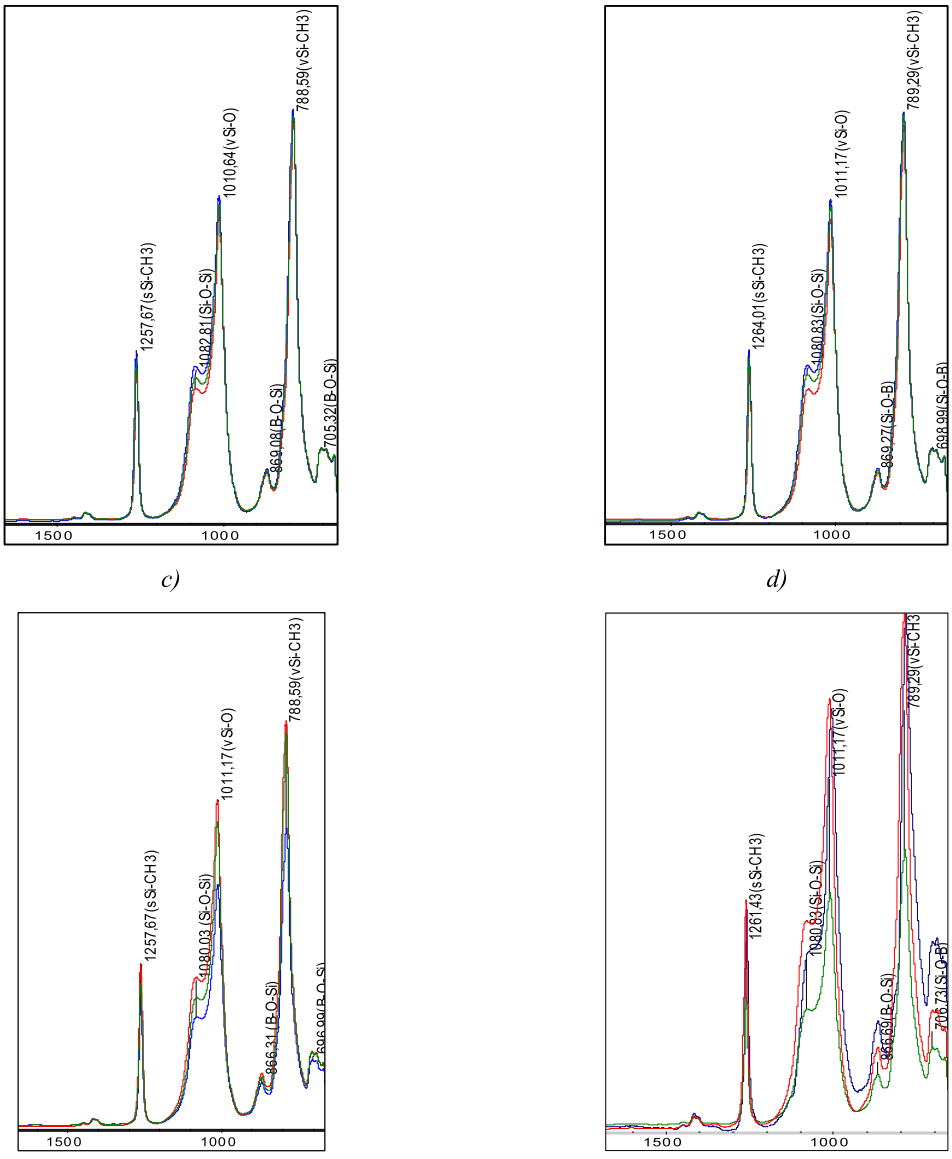

Fig. 2. IR ATR spectroscopy data of all intact PBS and after processing in climatic chamber during 3, 6, 10 days.

processing in the environmental chamber were examined by GPC and compared with control intact sample (Fig. 3). The obtained GPC curves of the samples after 3, 6, and 10 days coincided with the initial GPC data, which also indicates a high hydrolytic stability of the obtained rubbers.

The thermal stability and phase behavior of the obtained PBS were investigated by TGA and DSC methods. According to the DSC data, thermal behavior of PBS type A with different molecular weights (Fig. 4, curves 1 and 2) on the first heating is the same.

On DSC traces there is a jump in the heat capacity at $T_g = -125\,^{\circ}C$, an exothermic peak of cold crystallization at $-93\,^{\circ}C$, and an endothermic melting peak of the PDMS crystalline phase ($-40\,^{\circ}C$). At higher temperatures, a broad weak endothermic peak with a maximum in the region of 100 °C and a heat of transition ~1 J/g is recorded on the DSC curves for both samples (Fig. 4, on the sidebar). At second heating on the DSC curve for sample type A1, all the transitions observed at the first in the region of negative temperatures are repeated, but the jump in the specific heat during devitrification decreases noticeably, as does the exothermic effect corresponding to the cold crystallization (Fig. 4, curve 3). At second heating of sample PBS type A2 ($M_n = 51100$) only the endothermic melting peak of the PDMS crystalline phase ($-40\,^{\circ}C$) is present on the DSC curve (Fig. 4, curve 4). The high-temperature endotherm, which is characteristic of both samples at first heating, disappears. It can be assumed that heating of the samples to the temperature of the end of the high-temperature peak leads to additional thermal polymerization processes, as indicated by the endothermic nature of these transformations. Accordingly, the molecular weight of the oligomers should increase, which is well correlated with a change in the character of the thermal behavior upon reheating, taking into account the difference in the MM of the both original samples PBS type A.

On the DSC curves of PBS type B and C (Fig. 4, curves 5 and 6), there are no thermal effects other than a jump in the specific heat at T_g. The glass transition temperature is the same and equal to $-123\,^{\circ}C$, and the introduction of phenyl groups in the chemical structure does not affect its value. Thus, it can be concluded that the thermal behavior of such cross-linked systems is determined by the

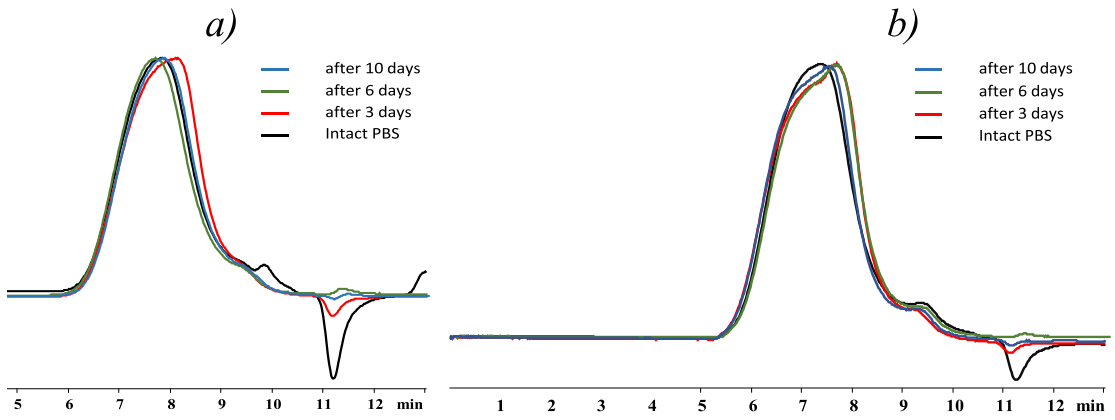

Fig. 3. GPC curves of intact PBS and after processing in environmental chamber during 3, 6, 10 days for samples of PBS type A with Mn = 15140 (a) and Mn = 51100 (b).

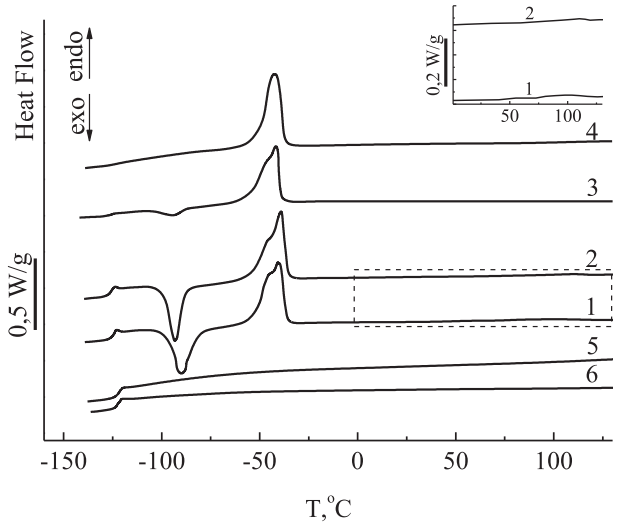

Fig. 4. DSC traces for type A1 (1, 3), type A2 (2,4), type B (5) and type C (6) at first (1, 2, 5, 6) and second (3, 4) heating scans at a heating rate 10 °C/min in argon.

Table 1
Molecular-weight characteristics of precursors and obtained products.

PBS	$[SiMe_2O]/[SiMe(H)O]$	Mn of PDMS	Mn of PBS	Crosslinking agent
Type A	85:2	6300	15140	$B(OMe)_3$
Type A	305:2	22600	51100	$B(OMe)_3$
Type B	240:10	14150	–	$B(OMe)_3$
Type C	240:10	14150	–	$PhB(OMe)_2$

length of the dimethylsiloxane fragments, which are the same for both samples.

The decomposition temperatures for PBS type A are the same and substantially higher than observed for polymers PBS type B and C (Table 2, Fig. 5). Obviously, in the case of PBS type B and C, the lower temperatures of the onset of destructive processes are associated with the low molecular weights of initial PDMS used to synthesize them (14,600). Also, the effects of interchain boron-containing crosslinking agents cannot be excluded (see Table 1).

Effects of phenyl groups on the destruction onset temperature, as well as on the glass transition temperature, were not detected. It should be noted that the higher starting temperatures for decomposition of boron-siloxanes PBS type A indirectly confirm the secondary thermal polymerization in these polymers taking into account that the MM for low weight PBS type A is equal to 15,000, which is close to the MM of PDMS, which was used for crosslinked boron-siloxanes PBS type B and C. It corresponds to the observation that the temperature of the onset of thermal degradation of PDMS increases with increasing its MM [40].

5. Conclusions

In current work, PBS with different architectures of polydimethylsiloxane chains and borate crosslinks were obtained. It is assumed that the character of interchain crosslinks in PBS based on PDMS with terminal dimethylhydrosilyl groups, crosslinked with trimethylborate, is non-covalent, in contrast to PBS based on PDMS with distributed hydrides. Differences in phase behavior also appeared on DSC thermograms, which is obviously due to the different nature of interchain crosslinks in all cases. All the obtained PBS are transparent rubber-like materials with elastic properties. Hydrolytic and high thermo-oxidative stability of crosslinked PBS

Table 2
Thermal characteristics of obtained PBS.

	Crosslinking agent	T_g,[a] °C	T_{cc},[a,b] °C	T_m,[a] °C	High temperature endotherm		$T_d^{5\%}$ °C
					T,[a] °C	ΔH,[a] J/g	
Type A *Mn = 15140*	$B(OMe)_3$	−125 −125	−90 −95	−41 −40	97 –	−1.3 –	430
Type A *Mn = 51100*	$B(OMe)_3$	−125 −125	−93 –	−40 −39	−106 –	−0.8 –	430
Type B	$B(OMe)_3$	− 123	–	–	–	–	380
Type C	$PhB(OMe)_2$	− 123	–	–	–	–	380

[a] The numerator shows the values for measured temperature at the first heating, and the denominator - for the second.
[b] T_{cc} means temperature of cold crystallization.

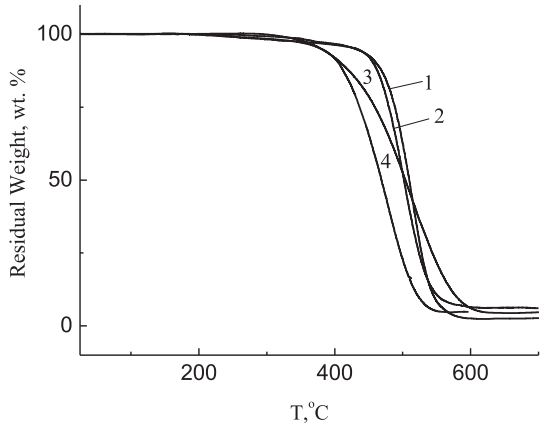

Fig. 5. TGA curves for PBS type A with Mn = 15140 (1) and Mn = 51100 (2), type B (3) and type C (4) at first and second heating at a heating rate 10 °C/min in argon.

was demonstrated. Obtained results confirm the prospects of the further study of these compounds both for academic research and applied material science.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.04.016.

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