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Abstract

4-(2-(4-((β-Methallyl)oxy)phenyl)propan-2-yl)phenol was prepared *via* the reaction of methallyl chloride with bisphenol A and used for the synthesis of hexakis-4-(2-(4-((β-methallyl)oxy)phenyl)propan-2-yl)phenoxycyclotriphosphazene. It was revealed that the latter undergoes the Claisen rearrangement and can be also epoxidized by 3-chloroperbenzoic acid. The obtained epoxide was cured by a treatment with isophorone diamine. The decomposition and glass transition temperatures of cured resin were also estimated (275 and 130 °C, respectively) by DSC and TGA methods.

Keywords: phosphazene, bisphenol A, epoxidation, epoxi resin, thermostability.

Introduction

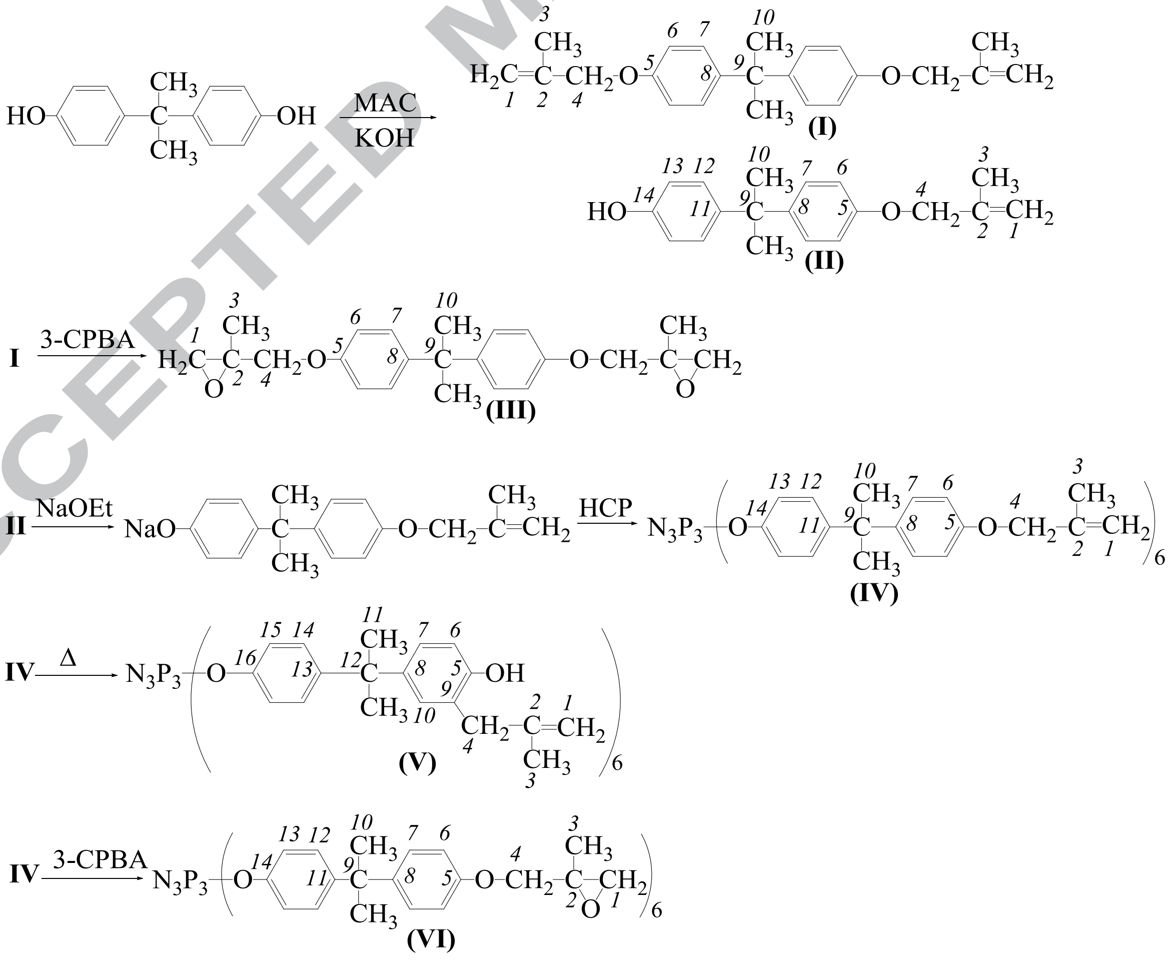
Phosphazenes have proved themselves to be beneficial modifiers of various polymeric materials, improving their performance properties. An introduction of various functional phosphazenes into polyurethanes allows one to improve their fire resistance [1], thermal stability, coke content in the residue [2], tensile strength [3], and hardness and hydrophobicity of coatings containing them [4]. Modification of methyl methacrylate by propyl ester of phosphazene significantly elevates its initial decomposition temperature [5]. Self cross-linked acrylic latex, which was obtained *via* an emulsion polymerization of 2,2,2-trifluoroethyl methacrylate, methyl methacrylate, butyl acrylate, methacrylic acid, and hexakisallylaminocyclotriphosphazene, exhibited excellent physico-chemical and electrochemical properties, and also became more stable due to the incorporated phosphazene [6]. Propyl ester of phosphazene has also demonstrated a positive effect on polystyrene properties, *i.e.*, the destruction temperature and residual yield of coke are increasing along with the phosphazene content in a polymer [7]. The fire resistance properties of phosphazenes are especially appropriate for a cotton modification [8], since they can also improve the abrasion hardness of cotton cloth and its water resistance [9]. An addition of phosphazene-triazine to the polylactide provided the composition possessing the high value of oxygen limit index (34.3%), which have successfully passed a test for vertical combustion (the flammability category of material was V-0) [10]. Hexakis(4-nitrophenoxy)cyclotriphosphazene was added to polycarbonate, which resulted in the oxygen limit index of polymer increased by 1.68 times as compared to the pure polycarbonate [11]. It was possible to increase the modulus of elasticity in flexure and impact resistance of carbon fiber based on polyamide 6 *via* its doping with hexaphenoxycyclotriphosphazene [12]. Moreover, the value of oxygen limit index of that fiber was 38.4%, which allows one to utilize it in the aerospace industry. Epoxy resins obtained from phosphazenes are especially important since they can be applied in many areas of science and technology. Materials based on phosphazene-containing epoxy resins can be utilized in electronics, space technology, military and civil aviation due to their fireproof properties, hydrophobicity, thermostability, and nontoxicity [13-22], as well as promising dielectric and mechanical properties [23].

To employ phosphazenes as the most efficient modifiers of epoxy resins, their compatibility with resin has to be achieved in order to obtain homogeneous polymer matrix. This could be implemented *via* the introduction of epoxy groups into phosphazene. A treatment of various functional phosphazenes with substances containing epoxy groups is one among the common synthetic approaches to such compounds [17,22,24]. However, this method may be accompanied by various side reactions, *e.g.*, cross-linking. This can usually be avoided by taking the epoxy-containing reagent in excess to phosphazene, but in such case, the problem of product purification arises.

Another way to prepare epoxy phosphazenes is the epoxidation of phosphazenes containing double bonds by peracids [25,26]. This method allows avoiding intermolecular cross-links, but it has been reported that in the case of allyloxy groups, the epoxidation of double bonds does not proceed completely.[26] It was suggested that it is caused by the –I effect of oxygen atom, which reduces the electron density of double bond of the allyl group. The present work was aimed on the verification of this hypothesis in addition to the increasing degree of epoxidation of allyl-containing phosphazenes. A replacement of allyloxy groups by β-methallyloxy ones bearing methyl groups, which cause an +I effect on the double bonds, was the major approach proposed herein.

Results and discussion

Since the methyl group of 2-methallyloxy moiety can provide steric hindrances during epoxidation, we have initially decided to carry out a model reaction between bis-β-methallyl ether of bisphenol A (Scheme 1, compound **I**) and 3-CPBA, which resulted in the formation of compound **III** (see Scheme 1).



Scheme 1. The shown numbering of carbon atoms corresponds to that used in the description of chemical shifts in ^{13}C NMR (see experimental section).

The comparison of ^{1}H NMR spectra of compound **I** (Fig. 1,*a*) and **III** (Fig. 1,*b*) allowed us to conclude that the epoxidation of double bonds proceeded completely. Thus, the next steps were to obtain hexakis-4-(2-(4-((β-methallyl)oxy)phenyl)propan-2-yl)phenoxycyclotriphosphazene (compound **IV**) and to perform its epoxidation, which required to synthesize the monofunctional derivative of 4-(2-(4-((β-methallyl)oxy)phenyl)propan-2-yl)phenol (compound **II**). However, the problem occurred during the preparation of compound **II**: since bisphenol A is the bifunctional compound, an attempt to alkylate only one hydroxyl group always resulted in a mixture of compounds (bisphenol A, compounds **I** and **II**). To separate this mixture, the special procedure given in experimental section was developed. Thus, compound **II** was successfully isolated, and its ^{1}H NMR spectrum is shown in Fig 1,*c*.

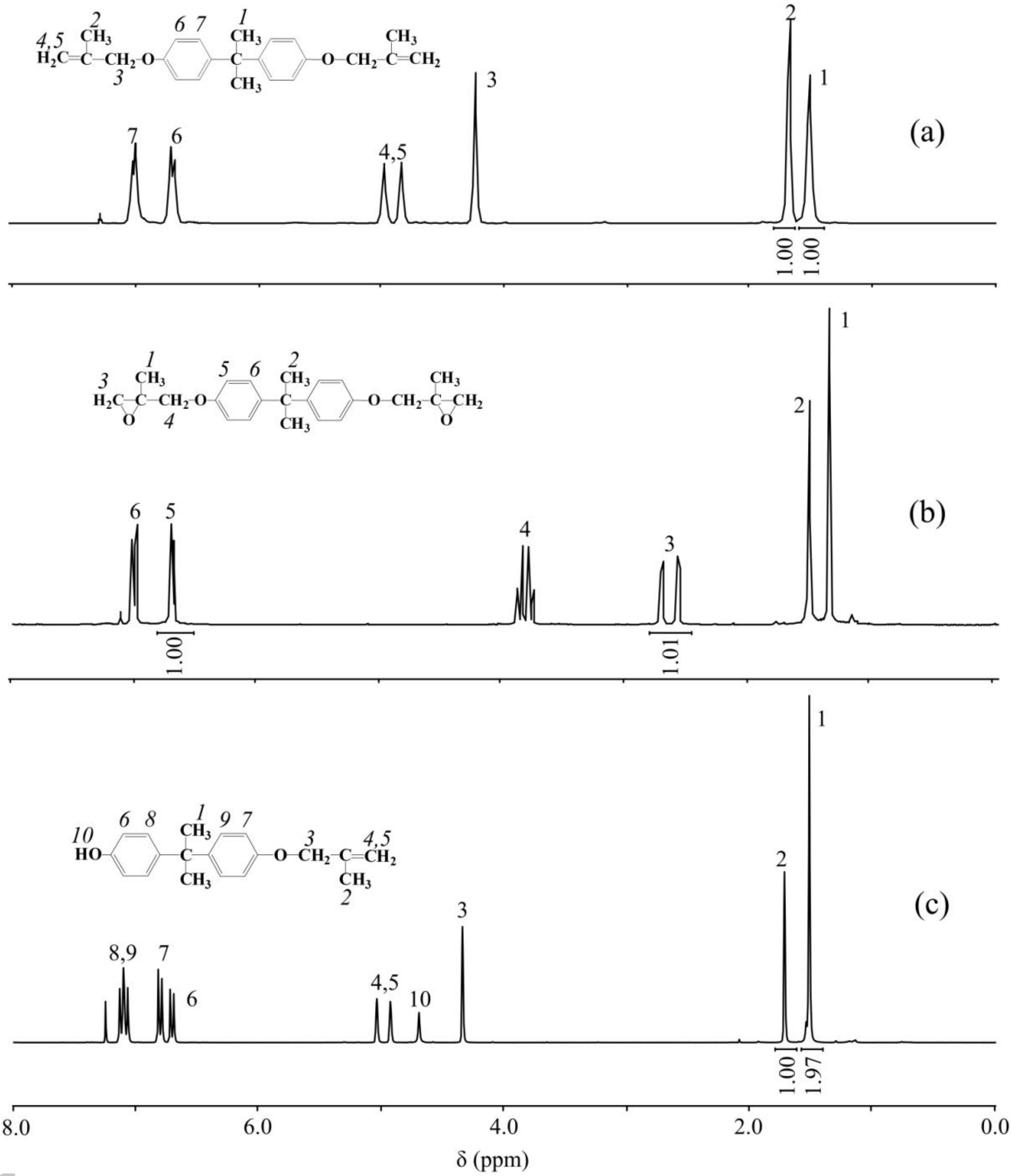


Fig. 1. ^{1}H NMR spectra of compounds (*a*) **I**, (*c*) **II**, and (*b*) *III*. The numbers indicate the hydrogen atoms in the compounds and the signals corresponding to them.

Compound **IV** was synthesized according to the phenolate method in two steps. The phenolate was initially prepared by the treatment of compound **II** with sodium ethoxide. The reaction of HCP with excess of obtained phenolate was carried out in diglyme at 120°C, since this was the only way to completely substitute the chlorine atoms in HCP, which was confirmed by singlet peak in the ^{31}P NMR spectrum of obtained product (Fig. 2,*a*).

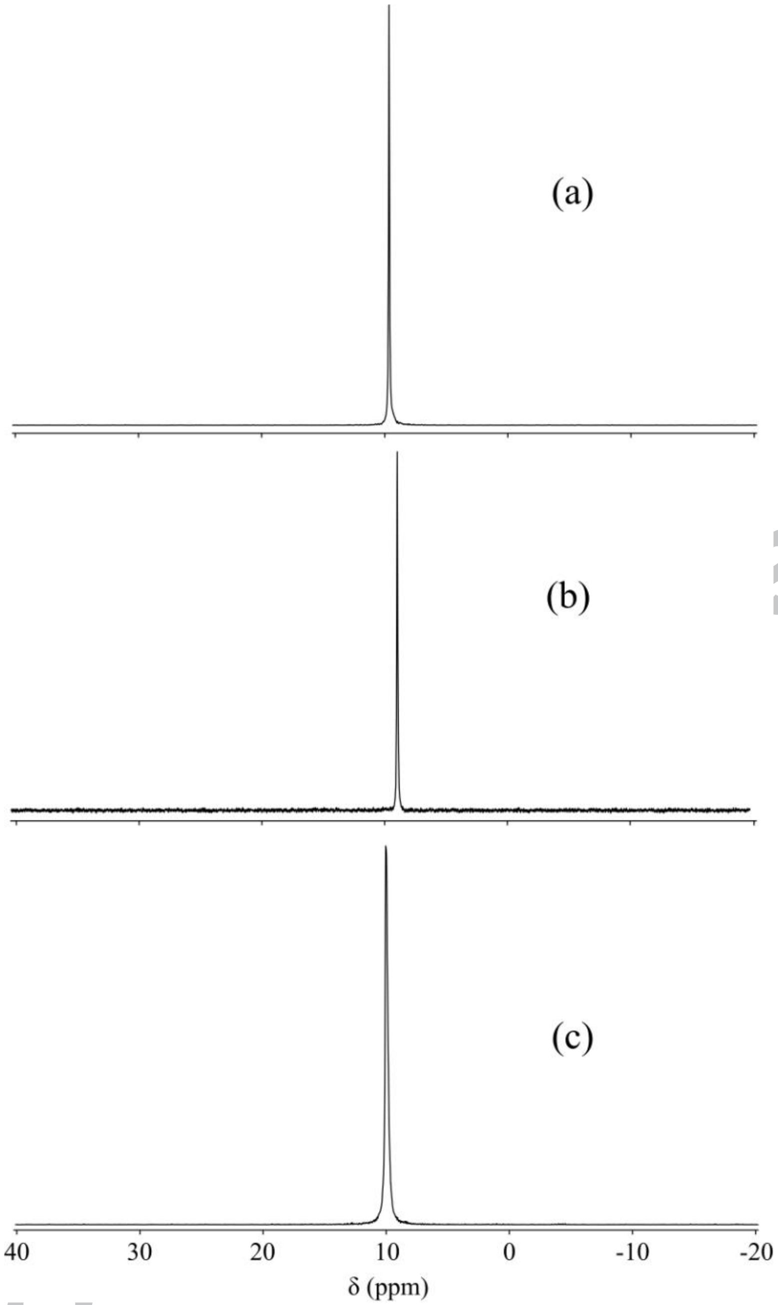


Fig. 2. ^{31}P NMR spectra of compounds (*a*) **IV**, (*b*) **V**, and (*c*) **III**.

Compound **IV** was initially isolated as a viscous yellow mass. However, this substance became glassy at room temperature after its reprecipitation from ethanol. It can be explained by the removal of traces of compound **II** from the product. DSC data allowed us to determine the glass transition temperature of compound **IV**, which is 30°C (Fig. 3).

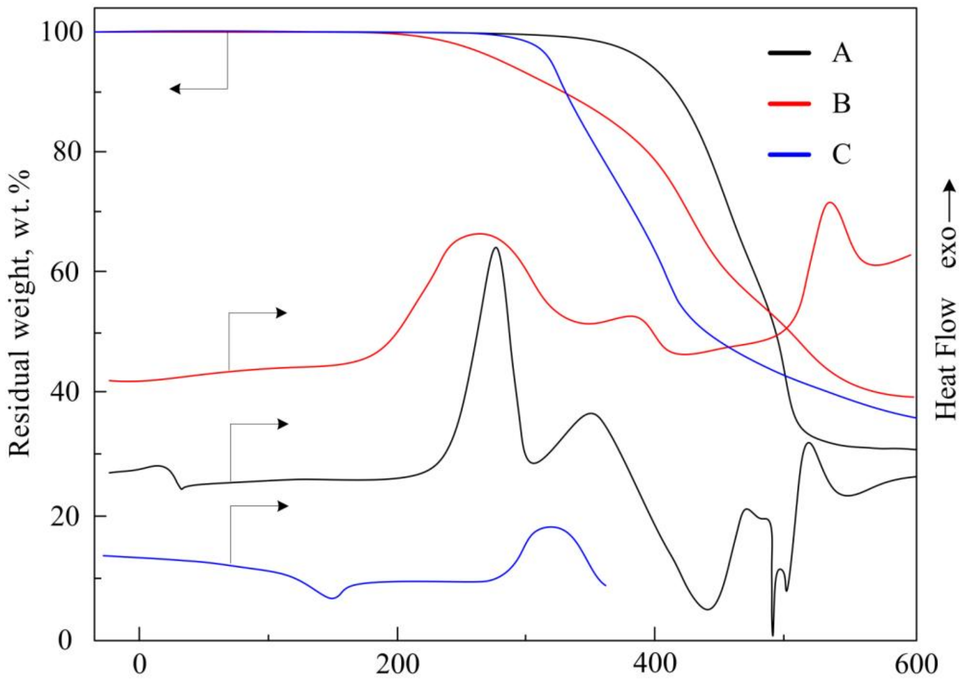


Fig. 3. TGA and DSC curves of compounds (*A*) **IV** and (*B*) **VI**, and (*C*) those of compound **VI** cured with isophorone diamine.

During the further heating, there were no thermal effects observed on the DSC curve up to the temperature of 210 °C. Above this temperature, there is an exothermic peak, which could be interpreted as the beginning of destruction. However, there is no mass loss on the TGA curve at this temperature (see Fig. 3). This fact could be explained only by the occurrence of exothermic chemical reaction, *e.g.*, polymerization of double bonds. To reveal the nature of this reaction, compound **IV** was heated in a sealed ampoule under inert (Ar) atmosphere up to 300 °C and investigated using NMR spectroscopy. The comparison of ^{1}H NMR spectra of initial (Fig. 4,*a*) and heated (Fig. 4,*b*) samples of compound **IV** can clearly confirm the preservation of double bonds in the heated sample, which consequently excludes any polymerization processes. However, there is a difference in the signals of aromatics protons in the heated sample, in particular, the new singlet appears in the spectrum, which indicates the absence of two adjacent protons presented earlier. Therefore, the reaction proceeds with the participation of an aromatic ring and *via* the substitution of its hydrogen atom. In addition, there is an upfield shift of signal of the methylene group protons. Taking into account these observations, it could be concluded that the reason of exothermic effect was the Claisen rearrangement, which proceeded at the conversion of 88% (based on the comparison of integral ratios of the proton signals of isomerized and nonisomerized groups). Thus, compound **V** was formed in this reaction (see Scheme 1 for its structure). It should be noted that the phosphazene cycle was preserved during the rearrangement, which was confirmed by the singlet peak in the ^{31}P NMR spectrum (see Fig. 2,*b*).

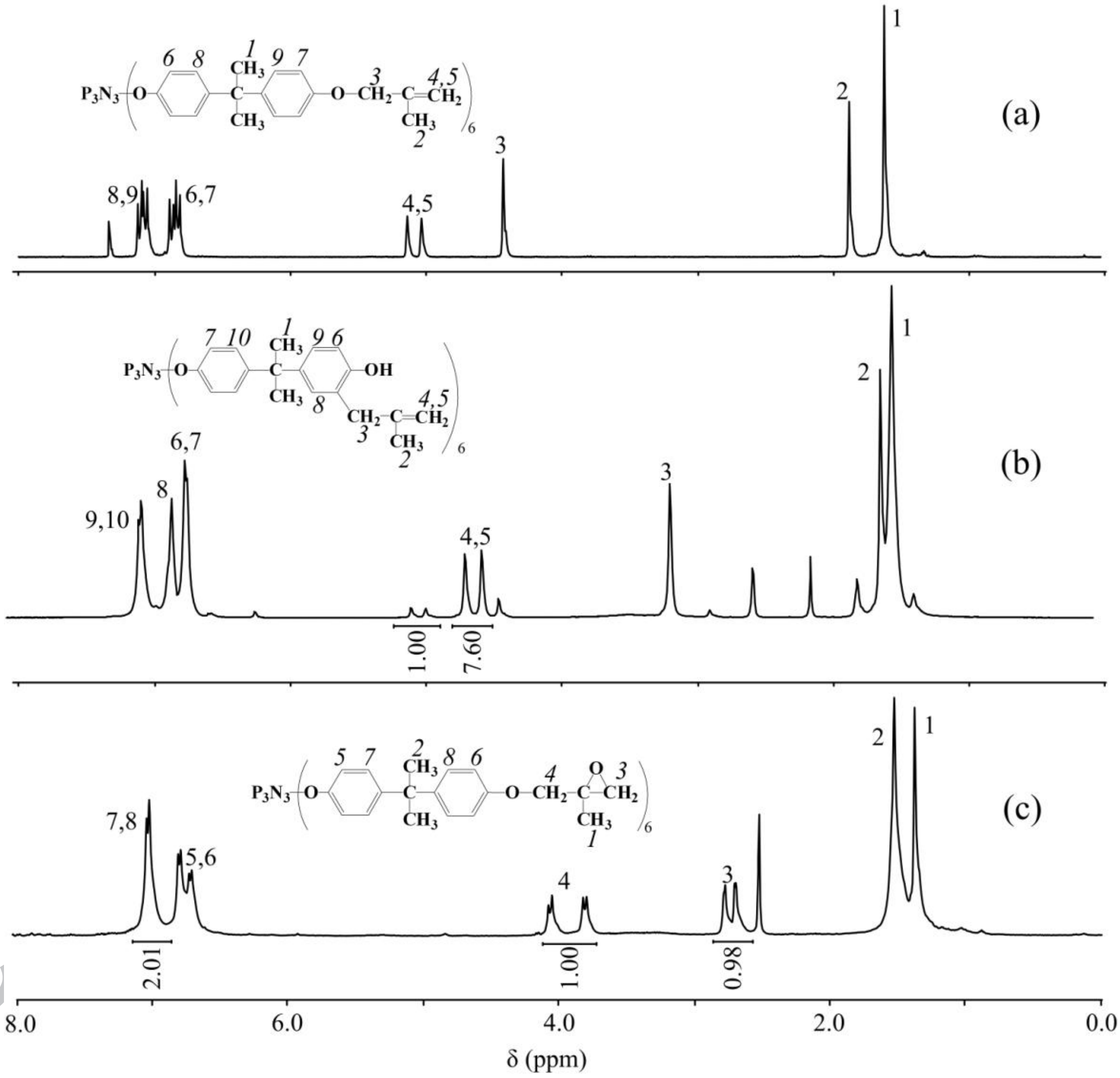


Fig. 4. ^{1}H NMR spectra of compounds (*a*) **IV**, (*b*) **V**, and (*c*) **VI**. The numbers indicate the hydrogen atoms in the compounds and the peaks corresponding to them.

Similarly to the case of model compound **I**, the epoxidation of allyl groups in compound **IV** have proceeded completely, which was confirmed by ^{1}H NMR of obtained compound **VI**. It should be noted that the full epoxidation of compound **I** takes 48 h, while that of compound **IV** completes within 72 h. This was probably caused by the steric hindrances due to a large size of molecule of compound **IV**. The epoxidation reaction proceeds without any participation of phosphazene ring, since the ^{31}P NMR spectrum of epoxidation product contain only the singlet peak as was in starting compound IV (see Fig. 2,*c*).

Compound **VI** is a white brittle amorphous (according to the Smallangle X-ray Scattering data) substance. There is no any kind of thermal effects on the DSC curve up to the temperature of ~180 °C (see Fig. 3). After reaching this temperature, an exothermic process was observed, which can be explained by the destruction of substance, since the TGA curve confirmed the loss of mass at this temperature.

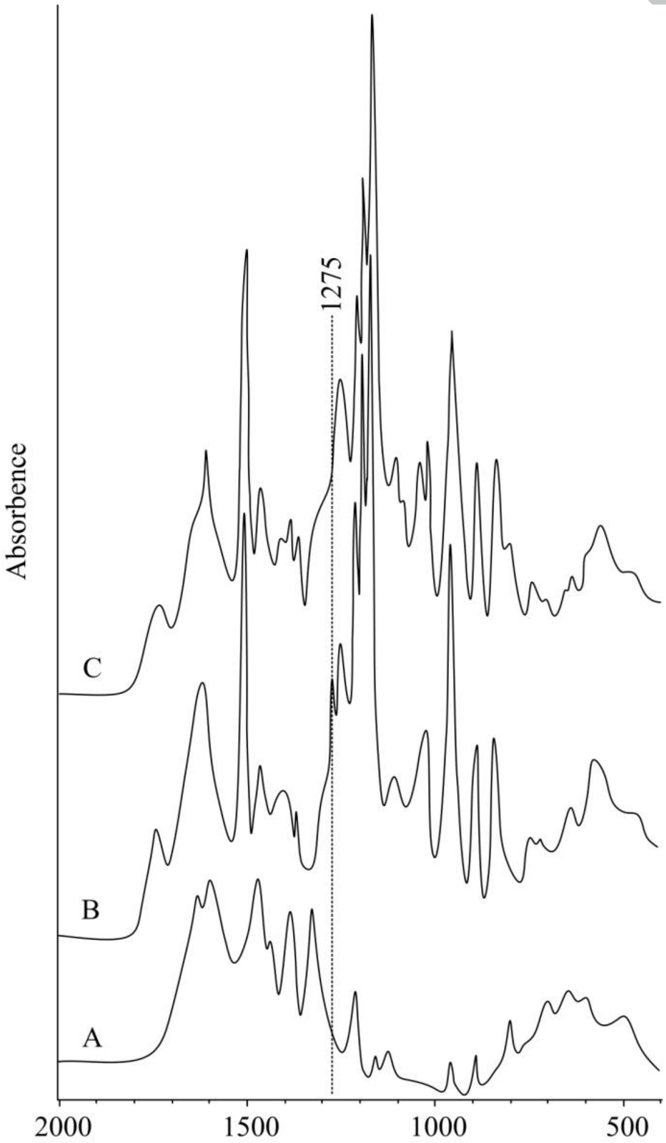


Fig. 5. IR spectra of isophorone (*A*) diamine, (*B*) compound **VI**, and (*C*) the resin based on them.

To evaluate the properties of compound **VI** as the epoxide resin, it was cured by the treatment with isophorone diamine. Since compound **VI** was not softened upon heating, it was impossible to prepare a composition *via* its direct mixing with the curing agent. Thus, we decided to obtain the composition by mixing all the components in a solution with the consequent evaporation of solvent. Thus, a brown colored substance was obtained. The comparison of IR spectra of initial components and obtained resin revealed the absence of peak at 1275 cm^{-1} in the spectrum of resin, which was present in the case of compound **VI** (Fig. 5). This peak is responsible for the symmetrical stretch vibrations of epoxy group.

This observation allowed us to conclude that all the epoxy groups were involved in the reaction with diamine. In addition, the complete conversion was also confirmed by a high content of gel-fraction (98%).

The obtained resin possess the glass transition temperature of 130 °C (see Fig. 3) and the decomposition temperature of 275 °C, which makes it promising for practical applications.

Conclusions

This work have clearly demonstrated that the methallyl moiety can be epoxidized more efficiently due to the electron-donor effect of methyl group. The reaction between HCP and phenolate of 4-(2-(4-((β-methallyl)oxy)phenyl)propan-2-yl)phenol can completely proceed only in high boiling solvents, which can well solvates cations. It was also revealed that the Claisen rearrangement occurred at the high temperature, and the complete epoxidation of double bonds in hexakis-4-(2-(4-((β-methallyl)oxy)phenyl)propan-2-yl)phenoxycyclotriphosphazene procceds within 72 h. The resin based on the synthesized epoxide demonstrated promising thermal characteristics, which allows it to be utilized in glue compositions.

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Highlights

- Mono-β-methallyl ester of bisphenole A was synthesized.
- The reaction between mono-β-methallyl ester of bisphenole A and hexachlorocyclotriphosphazene was provided.
- The double bonds in obtained aryloxyphosphazene was epoxidized with 3-chloroperbenzoic acid.
- The epoxidized aryloxyphosphazene was cured with isophorone diamine.