Synthesis of curing agent for epoxy resin based on halogenophosphazene

Lucie Zarybnicka,[1] Radka Bacovska,[2] Miroslav Vecera,[1] Jaromir Snuparek,[1] Milan Alberti,[2,3] Jozef Rychly,[4] Petr Kalenda[1]

[1]Faculty of Chemical Technology, Institute of Chemistry and Technology of Macromolecular Materials, University of Pardubice, Studentska 573, Pardubice 532 10, Czech Republic
[2]Department of Chemistry Faculty of Science, Masaryk University, Kamenice 5, 625 00, Brno, Czech Republic
[3]Department of Physical Electronics Faculty of Science, Masaryk University, Kotlarska 2, 611 37, Brno, Czech Republic
[4]Polymer Institute, Slovak Republic, Slovak Academy of Sciences, Dubravska Cesta 9, Bratislava 45, 845 41, Czech Republic
Correspondence to: L. Zarybnicka (E-mail: Zarybnicka.L@email.cz)

ABSTRACT: Epoxy resins are, due to their excellent properties (such as chemical resistance, dimensional stability, and heat resistence), widely used in practice. The basic principle of curing epoxy resins with a hardener containing multiple amino groups is the crosslinking reaction between active hydrogen atoms in the hardener and the oxirane groups in the epoxy resin. This study deals with the synthesis and characterization of hexachloro-*cyclo*-triphosphazene derivative and its subsequent use for curing epoxy resins. The new hardener was prepared from hexachloro-*cyclo*-triphosphazene by nucleophilic substitution with isophorone diamine and its curing capability was compared with original isophorone diamine. The prepared derivative hexaisophorone diamino-*cyclo*-triphosphazene (HICTP) provided advantages over conventional curing system, as it improved mechanical properties as well as the flame resistance. Testing of the cured epoxy resin during burning was carried out using dual cone calorimeter, which enables more extensive monitoring of parameters in comparison with testing using oxygen index that has been used in many publications. The epoxy resin cured with the prepared phosphorus containing HICTP exhibits lower values for total heat release, amount of smoke released and oxygen consumed, which may cause a slower flame spread. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42917.

INTRODUCTION

The most significant cyclo halogenophosphazenes include hexachloro-*cyclo*-triphosphazene which was first synthesized by J. von Liebig in 1834. It was prepared by reaction between phosphorus pentachloride and ammonia. The phosphate NPNH was detected as a minor amount of a substance which in their findings belonged empirical formula $N_3P_3C_{l5}$ or NP_2C_{l3}, respectively. C. Gerhardt[1,2] and C. Laurent[3] identified the melting point of this material (114°C) and the empirical formula $NPCl_2$. Stokes and Schlenck with Röme[4,5] continued in this work. J.H. Gladstone, D. Holmes,[6,7] and H. Wichelhaus[8] found by measuring the vapor pressure that the substance was a trimer $(NPCl_2)_3$.

The typical reaction of hexahalogeno-*cyclo*-triphosphazene is a nucleophilic substitution where the nucleophile is able to pass its free electron towards attacking electrophilic phosphorus atoms. Amines, alcoholates, alcohols, or thiols are among the most common compounds used in the nucleophilic substitution. Phosphazene derivatives which contain in their structure active hydrogen atoms, can be used as hardeners for epoxy resins.

Hexahalogeno-*cyclo*-triphosphazene contains alternating phosphorus and nitrogen atoms in the cycle with two substituents attached to the phosphorus atoms. This compound exhibits unusual thermal properties, such as flame retardancy and self-extinguish ability.[9,10] The reason is that the thermal decomposition of the phosphazene-based polymers is an endothermic process. Phosphate, metaphosphate, polyphosphate generated in the thermal decomposition form a nonvolatile protective film on the surface of the polymer to isolate it from the air. This film can cut off the supply of oxygen so as to achieve the synergistic flame retardancy.[11,12]

Epoxy resins belong to the category of thermosets, a group of compounds which, after curing, exhibit excellent properties,
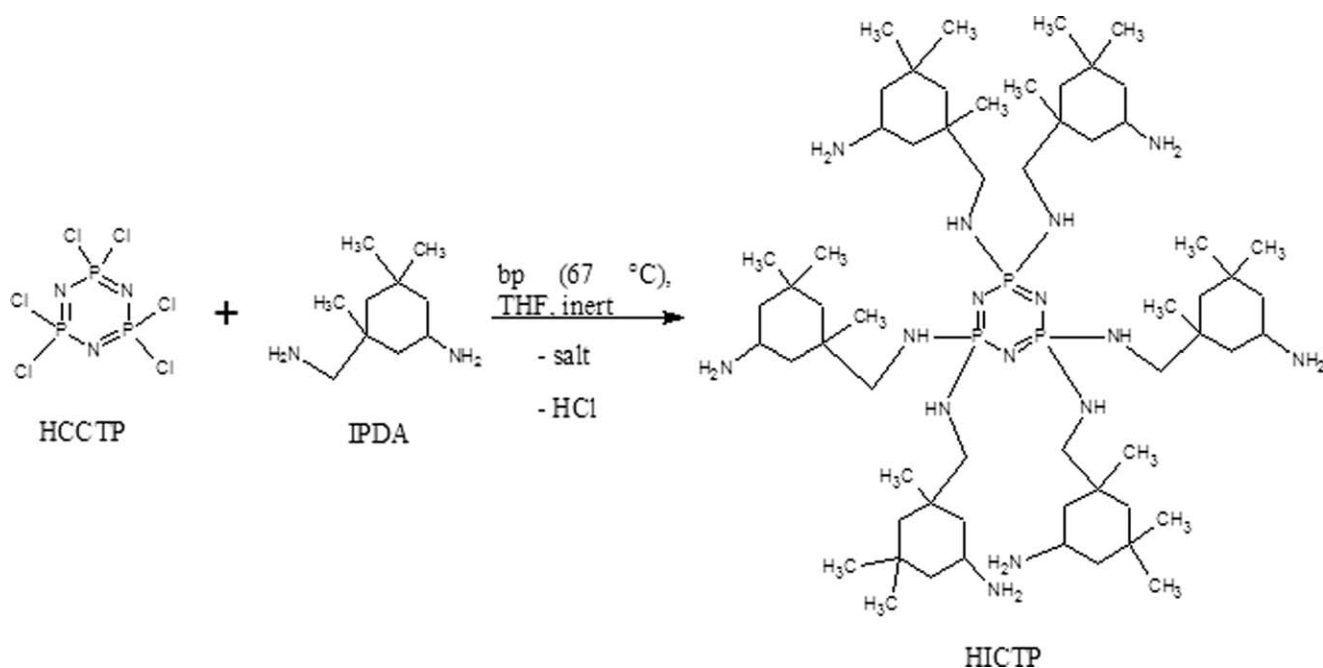
Figure 1. Schematic representation of the synthesis reaction of HICTP.

such as chemical resistance, excellent adhesion, and electrical properties.[13] Some derivatives of hexachloro-*cyclo*-triphosphazene found their use as flame retardants and antioxidants in polymers. Several derivatives of hexachloro-*cyclo*-triphosphazene have already been synthesized and used as hardeners for epoxy resins.[14–20] They can be used directly as hardeners or as additives with the ability of flame retardancy such as phenoxy-phosphazene.[22] The derivative containing *n*-propanol and ammonia[21] was also used for curing epoxy resins.[22] Diaminotetrabromophenoxy-*cyclo*-triphosphazene derivative was prepared to improve flame retarding properties.[23] It was found that cured resins also exhibit a high temperature resistance. Another fully substituted derivative was hexachloro-*cyclo*-triphosphazene substituted with glycidol. It was mixed with diglycidyl ether of bisphenol A and cured with 4,4'-methylene dianiline as co-hardener.[24]

This paper deals with synthesis of hexaisophorone diamino-*cyclo*-triphosphazene (HICTP) and its subsequent use for curing epoxy resins. Properties of the cured epoxy resin using HICTP were compared with the cured epoxy resin using isophorone diamine. In view of the fact that phosphazenes are used as flame retardants. HICTP was used as a hardener with respect to reach an improved flame resistance.

EXPERIMENTAL

Materials
Isophorone diamine (IPDA) (Vestamin IPD, Evonik, purity 99,7%), tetrahydrofuran (THF) (Penta Chemicals, Czech Republic, purity 99.8%), hexachloro-*cyclo*-triphosphazene (HCCTP) (Sigma-Aldrich, purity 99.0%) were used in the synthesis. Tetrahydrofuran was stored under anhydrous conditions using activated molecular sieves. Epoxy resin labelled CHS-EPOXY 520 (EE kg^{-1} = 5.266) was supplied by Spolchemie, Czech Republic.

Instruments
The products of synthesis were analyzed by elemental analysis, ^{31}P NMR, Fourier transform infrared (FT-IR) spectroscopy, and mass spectrometry (MS). The cured epoxy resin was characterized by FT-IR spectroscopy, reacted epoxide groups were determined by titration according to Jay,[25] by differential scanning calorimetry (DSC), thermogravimetry (TGA), dynamic mechanical analysis (DMA), and Brinell hardness test method. The testing of materials against burning was carried out in the dual cone calorimeter.

The elemental analysis was performed on a FLASH Organic 2000 Elemental Analyzer (ThermoFisher Scientific), which can detect carbon, hydrogen, nitrogen, and sulfur. Determination of chlorine was carried out by burning in oxygen atmosphere flowed by titration with sulfuric acid according to Schöniger.[26] The method was tested on *o*-chlorobenzoic acid standard containing chlorine 21.915%.

^{31}P NMR spectra (δ, ppm; J, Hz) were recorded using a BRUKE AVANCE DRX 300 instrument at the frequency of [31]P: 202.46 MHz and 85% H_3PO_4 (as the external standard). The samples were sealed in Simax tubes (diameter 4 mm), inserted in NMR cuvettes (diameter 5 mm) filled with D_2O (external lock). The spectra were measured in the coaxial NMR cuvette system.

The FT-IR spectroscopy of the samples was performed on a Nicolet IS50 with integrated diamond ATR FT-Raman module. The FT-IR spectrometer with an integrated module and ATR fully reflective optics has a broadband DLaTGS detector to make measurements in the area 5000–100 cm^{-1}. The spectral resolution of the device is 0.09 cm^{-1}.

MS was performed on an Agilent Technologies instrument (MSD Model 5975B) with a probe for direct entry. Mass selective detector operated in electron impact ionization mode (i.e.,

**Table I.** Results of Elemental Analysis

Element	Theory (%)	Experiment (%)
C	62.63	62.63 ± 0.02
H	11.04	11.06 ± 0.02
N	18.26	18.27 ± 0.02
P	8.08	8.04 ± 0.02
Cl	–	–

EI ionization) with an ionization energy of 70 eV. The samples were prepared 0.01% in methanol for analysis.

DSC analysis was performed according to ISO 11357-2 using a Perkin-Elmer DSC with a control and evaluation software Universal Analysis 2000 QSeries. Measurements were performed in a nitrogen atmosphere at a heating rate of 20°C min^{-1} with a temperature range of 25–400°C. The sample weight ranged from 1 to 5 mg.

TGA was performed on the device consisting of the computer, oven and Sartorius balance BP210E S. It was measured in a quartz ampoule in the temperature range of 25–950°C at a heating rate of 5°C min^{-1} under air.

DMA was performed according to DIN EN ISO 6721-7, in the temperature range of 23–250°C, heating rate of 3°C min^{-1}, a frequency of 1 Hz. ARES device for measuring geometries was chosen for torsional terminals. Measurements were conducted in an air atmosphere and the obtained data were processed in Rheometric Scientific program.
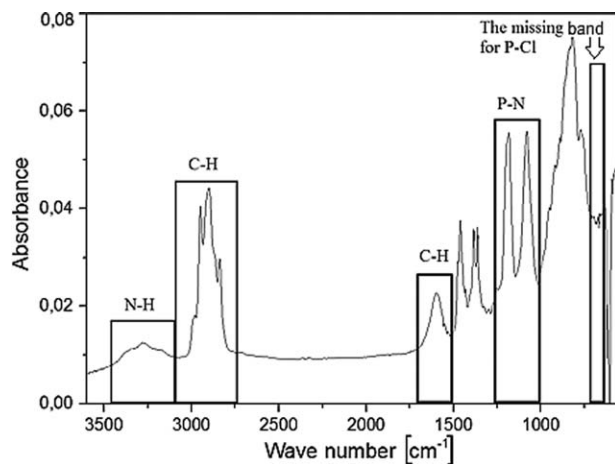
Figure 3. FT-IR spectrum of the product HICTP.

Brinell Hardness Test Method

Test specimens were prepared with a thickness of 4 mm. Measurement was carried out according to standard EN ISO 6506-1. Value was determined for hardness HB/15.6/10 and HB/15.6/60 using instrument HP 250 VEB Leipzig, Germany.

Testing of materials (7 × 7 × 5 cm) against burning was carried out in the dual cone calorimeter that was a product of Fire Testing Technology, England. The sample was placed into the adopted sample holder suitable for testing of thermally thin materials. The centre of the samples was situated 6 cm from the
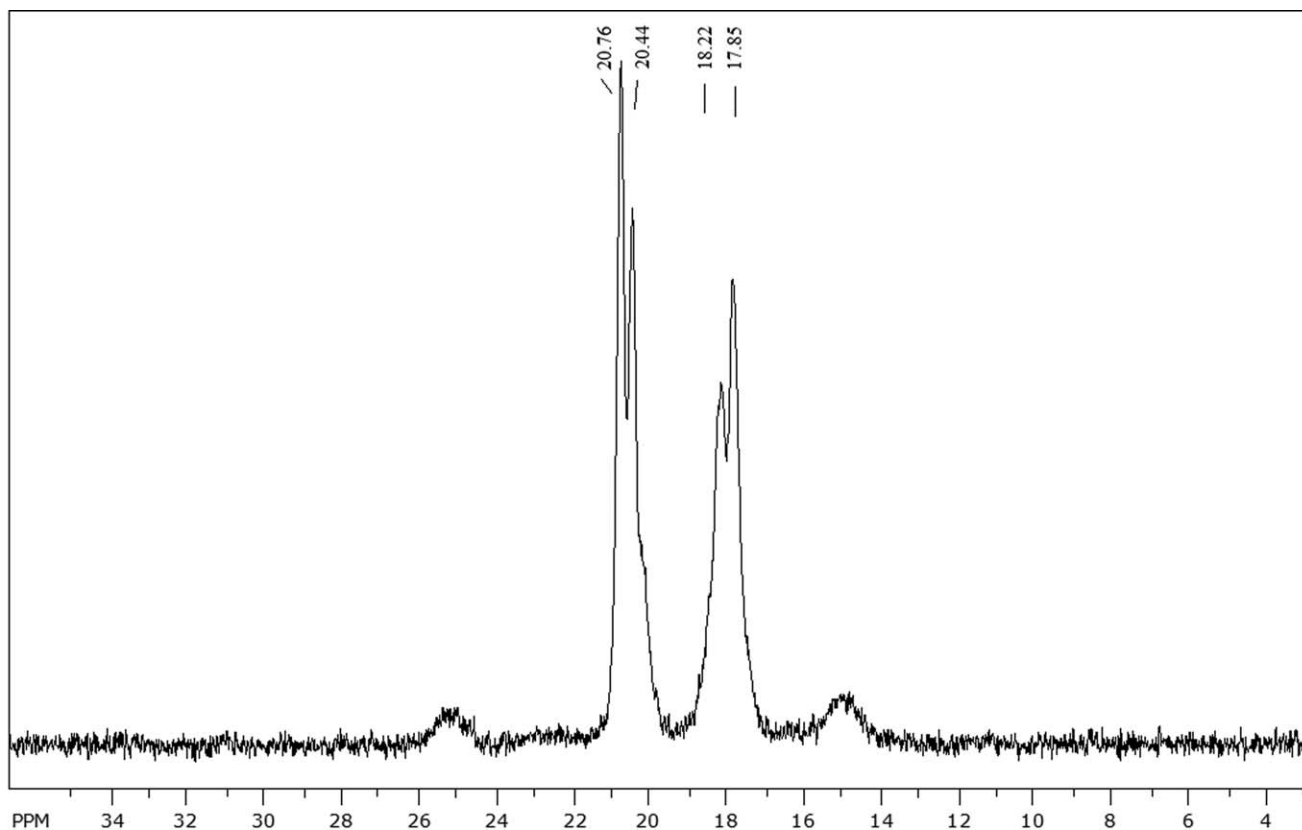
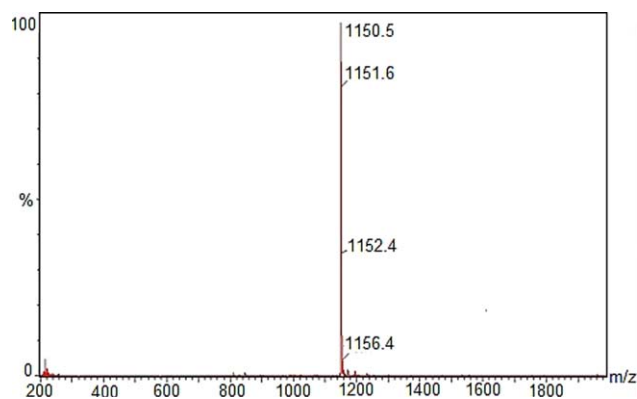**Figure 2.** ^{1}P NMR spectrum of the prepared product HICTP.

Figure 4. MS spectrum of the product HICTP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

lowest part of the cone heater. The heat release rate was calibrated by burning methane. The cone radiancy 25 kWm^{-2} used corresponds to a cone temperature 680°C. It was set from the calibration diagram for a distance of the sample from the cone edge 6 cm.

Synthesis of HICTP

The synthesis reaction of phosphazene derivative is shown in Figure 1. All syntheses were performed under anhydrous conditions in an inert argon atmosphere using Schlenk containers. A Schlenk flask was filled in with 0.753 mol of isophorone diamine and 50 mL of THF under an inert atmosphere. 0.037 mol of hexachloro-*cyclo*-triphosphazene dissolved in tetrahydrofuran was slowly added dropwise into the stirred reaction mixture at boiling point of tetrahydrofuran. The reaction was terminated after 24 h followed by filtration resulting salts, three times washing with THF was followed by vacuum distillation to remove THF from the product. The preparation was monitored during synthesis by means of thin layer chromatography and the identity of the prepared derivative was confirmed also by measuring refractive index value. The final product HICTP was characterized by ^{31}P NMR, elemental analysis, mass spectroscopy, and FT-IR spectroscopy.
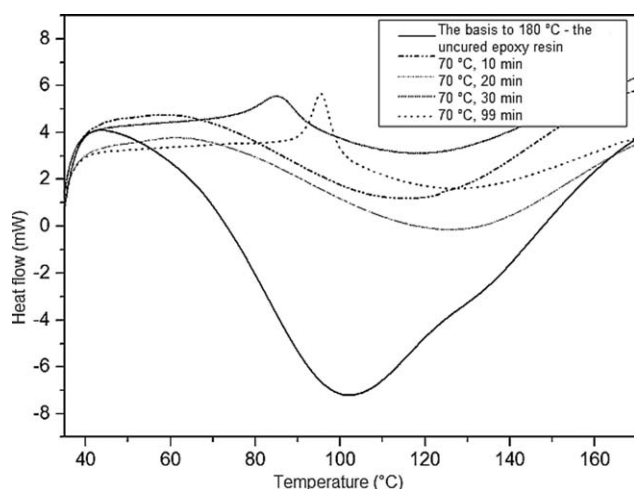
Table II. Value of Enthalpy in Monitoring the Curing Kinetics for Epoxy Resin CHS-EPOXY E520

Temperature program	Enthalpy evolution at 70°C (J g^{-1})	Conversion of curing epoxy resin (%)
The basis to 180°C— the uncured epoxy resin	−288	0
70°C, 10 min	−102	64.58
70°C, 20 min	−89,9	68.78
70°C, 30 min	−26,5	90.70
70°C, 99 min	−19,1	93.36

Curing of Epoxy Resin

The prepared product HICTP was mixed with the commercially available CHS-EPOXY E520 epoxy resin (epoxy equivalent EE kg^{-1} = 5.266 and the average molecular weight below 700 g mol^{-1}). It is a low molecular weight liquid epoxy resin based on bisphenol A designated mainly for embedding electronic and electrical components and also in construction.[27]

Curing of epoxy resin was conducted as follows. The product HICTP having the value of hydrogen equivalent H_{ekv} = 64.1 g mol^{-1} and the epoxy resin were mixed with 1% excess of HICTP relative to the epoxy equivalent (1.1 in the formula). The amount of curing agent was calculated according to the formula (1):

$$\frac{\text{g of the curing agent}}{\text{kg of the epoxy resin}} = \frac{EE}{kg} \cdot Hekv..11 \qquad (1)$$

The mixture was after 3 min stirring centrifuged in order to remove air bubbles from the sample. First, the mixture was cured at room temperature for 4 h followed by curing at 110°C for additional 4 h. The cured epoxy resin was further characterized by Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetry (TGA), and dynamic mechanical analysis (DMA), Brinell hardness test method, and the flame resistance was tested. The number of reacted epoxy groups in the cured epoxy resin was determined by titration. The epoxy groups determination were performed as follows: an 0.5 g sample of the cured epoxy resin in the form of sawdust was put into the
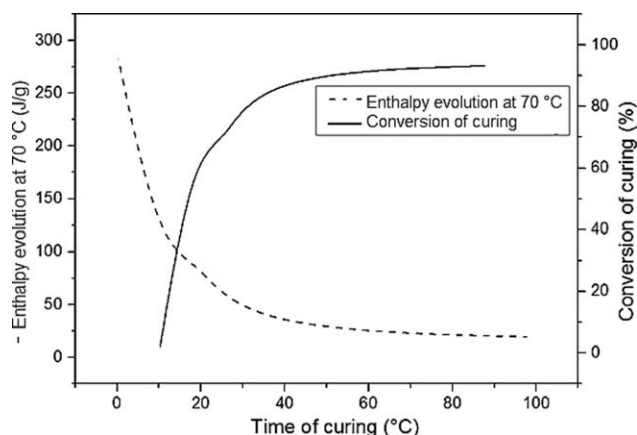

Figure 5. DSC, the record of kinetics of curing CHS-EPOXY E520 epoxy resin.

Figure 6. Graphic illustration of the conversion of curing and enthalpy evolution at 70°C with time.
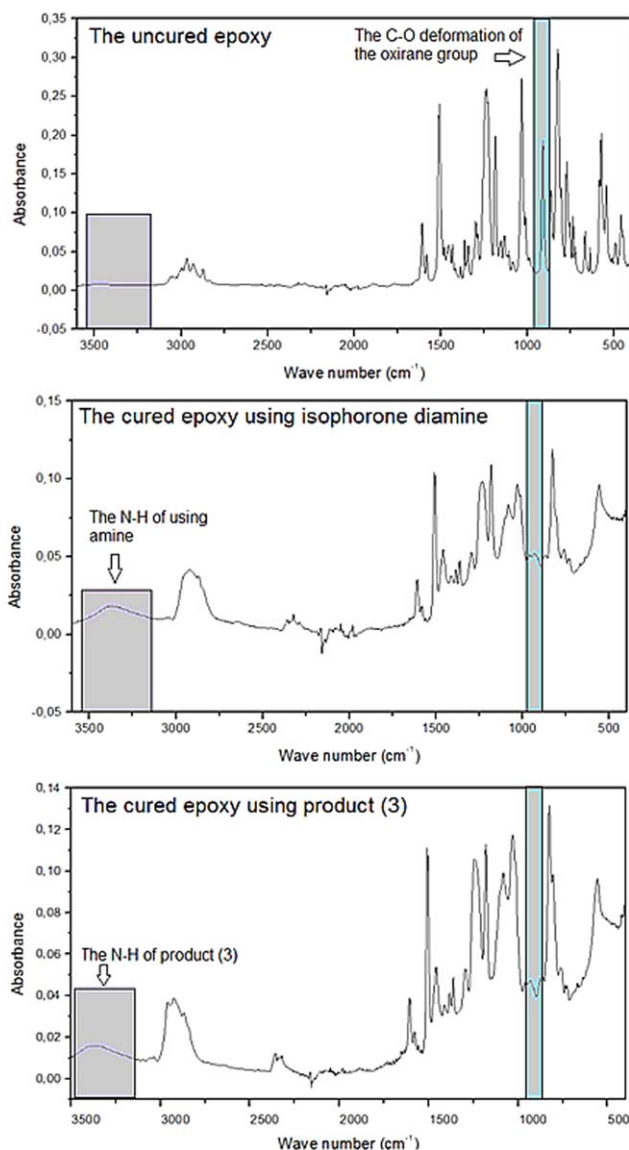
Figure 7. FT-IR spectra of the cured CHS-EPOXY 520 epoxy resin. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]

Erlenmeyer flask and then 50 mL of chloroform was added. The resulting mixture was placed in a shaker for 20 min. The epoxy groups present in the extracted material was determined by titration with $HClO_4$ according to Jay.[25] The epoxy groups of the epoxy resin was calculated using the formula (2):

$$\frac{EE}{kg} = \frac{(A - B) \cdot f \cdot 0{,}1}{n} \qquad (2)$$

where: A consumption $0.1M$ $HClO_4$ of sample (mL), B consumption of $0.1M$ $HClO_4$ of blank test (mL), f factor of $0.1M$ $HClO_4$, n sample weight (g).

Reacted epoxy groups was calculated using the formula (3):

$$\text{Reacted epoxy groups } (\%) = \frac{EE/kg1}{EE/kg2} \cdot 100 \qquad (3)$$

where EE $kg1^{-1}$, epoxy equivalent of the cured epoxy resin; EE $kg2^{-1}$, epoxy equivalent of uncured epoxy resin.

The reaction kinetics of curing of a low molecular epoxy resin with HICTP as a hardener was investigated by DSC. The procedure was as follows: the samples of epoxy resin with hardener were heated to 70°C for different hold periods 10, 20, 30, and 99 min, then cooled to the room temperature. Immediately after that a DSC measurement was carried out in the range 35–180°C. During the measurement the partially cured sample was heated up to 180°C and the rest of curing reaction proceeded.

RESULTS AND DISCUSSION

Characterisation of Synthesized Phosphazene Derivative

The prepared hexaisophorone diamino-*cyclo*-triphosphazene was characterized by elemental analysis, the elements C, H, N, P present in the compound were determined using elemental analyzer. The determination of chlorine was made by burning in an oxygen atmosphere to verify the full substitution. Obtained data are listed in Table I. The results of elemental analysis did confirm the theoretical structure of the prepared derivative. Theoretical results for contents of individual elements C, H, N, P, Cl in the product HICTP are consistent with the obtained experimental results as it is obvious from Table I.

Isophorone diamine exists in two different conformations, namely *cis* and *trans*. *Trans* isomerism is thermodynamically preferable and more stable. Thus, the prepared derivative HICTP also exhibits two conformations (*cis* and *trans*), which correspond to the ^{31}P NMR spectrum with two singlets at a chemical shift δ $(S) = 20.76$ and 20.44 ppm and 18.22 and 17.85 ppm, respectively, as is shown in Figure 2. Isophorone diamine contains amino group on the aliphatic chain and the amino group on the cycloaliphatic ring, the amino groups on the aliphatic chain are more reactive.[28] Based on the theoretical assumptions singlet with chemical shift δ $(S) = 20.76$ and 20.44 ppm can be assigned to a *trans* isomer of IPDA substituent while the singlet with chemical shift δ $(S) = 18.22$ and 17.85 ppm to a *cis* isomer of IPDA substituent in HICTP.

The synthesized HICTP was also characterized by FT-IR spectroscopy. FT-IR spectrum is shown in the Figure 3. The P–N cycle vibration is located at 1213 and 1190 cm^{-1}, the vibration for the N—H bond correspond to 3273 and 1607 cm^{-1}. Valence

Table III. Results of DMA for the Cured Epoxy Resin

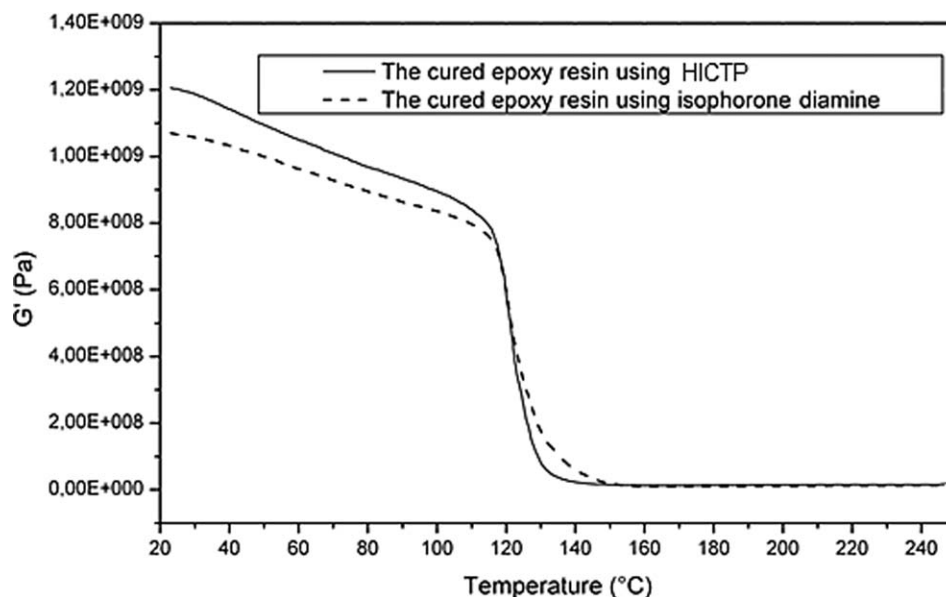| Sample	DMA		DSC	Brinell hardness test	
	G′ (23°C) (MPa)	Tg (tanδ) (°C)	Tg (°C)	HB/15.6/10	HB/15.6/60
Epoxy resin curing using HICTP	1206	135	134.1	305.47	271.65
Epoxy resin curing using IPDA	1070	147	143.6	291.83	268.10

Figure 8. Dependence of the elastic modulus (G') on a temperature of the cured epoxy resins.

vibrations (v_{as} and v_s) of C—H$_x$ groups ($x = 1$–3) were found between 2849 and 2932 cm^{-1}. Bands of deformation vibrations δ_{as} of C—H$_x$ groups ($x = 1$–3) occurred in region 1508 to 1553 cm^{-1}. Vibrations (v_{as}) at 551 cm^{-1} correspond to P—Cl groups. This band in the spectrum is missing, which confirms the full nucleophilic substitution of HCCTP as it obvious from Figure 3.

The theoretical molecular mass of HICTP is 1150.66 g mol^{-1}. Practically identical value was found using mass spectrometry analysis, as it is demonstrated in Figure 4. Results of mass spectrometry 1150.5 g mol^{-1} correspond to fully substituted derivative and confirm the successfulness of the synthesis.

Characterization of Epoxy Resin Curing with HICTP
The reaction kinetics of curing of a low molecular epoxy resin with HICTP as a hardener was investigated. The record of kinetics of CHS-EPOXY E520 curing is shown in Figure 5.

Results of enthalpy measurements indicated that with the increasing curing time at 70°C, the values of enthalpy decreased, accordingly with the extent of epoxy resin curing reaction. Calculated conversions were summarized in Table II and Figure 6. After a period of 4 h at 70°C the crosslinking reaction was completed.

Characterization of Epoxy Resin Cured with HICTP and Epoxy Resin Cured with IPDA
The portion of reacted epoxy groups in the epoxy resin cured with HICTP was 93.7%. In comparison to this experiment, the same reaction was carried out with IPDA, a commonly used amine hardener. In this case, 95.1% of epoxy groups reacted with IPDA.

The epoxy resin cured with HICTP and the epoxy resin cured with IPDA were characterized using ATR–FT–IR spectroscopy with a diamond crystal. For assessing the reaction between epoxy groups and active hydrogens of the hardener, the changes in vibration at 910 cm^{-1} corresponding to epoxy groups were

used.[29] The disappearing of bands at 910 cm^{-1} after curing can be observed in Figure 7. This confirmed practically total consumption of epoxy groups during curing with both hardeners.

Some properties of the epoxy resin cured with HICTP and IPDA hardeners were compared. Dynamic mechanical analysis was performed according to DIN EN ISO 6721-7. The elastic modulus of the epoxy resin was $G' = 1207$ MPa if cured with HICTP and the resin cured with isophorone diamine exhibited the elastic modulus value of $G' = 1070$ MPa. These values were measured at 23°C and they are together with glass transition temperatures of cured resins shown in Table III. The dependence of elastic modulus of the cured epoxy resins on temperature is shown in Figure 8. The higher value of G' for the epoxy resin cured with HICTP indicates that the use of the product HICTP as a curing agent should increase the hardness of the material in comparison with IPDA cured one. This was confirmed by measurig of Brinell hardnes of cured samples. Brinell hardness test of the epoxy resin cured with HICTP showed higher values of hardness (HB/15.6/10 = 305.47 and HB/15.6/60 = 271.65) than the epoxy resin cured with IPDA (HB/15.6/10 = 291.83 and HB/15.6/60 = 268.1) as it is shown in Table III.
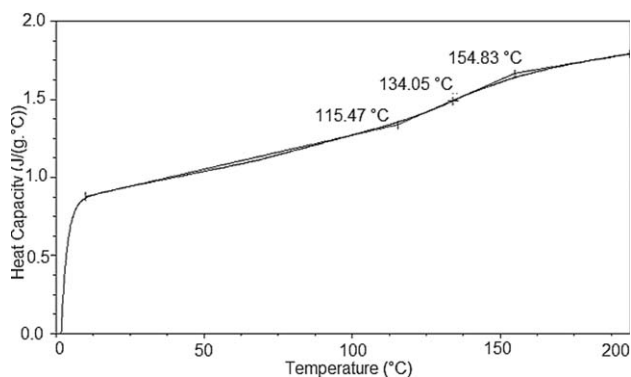

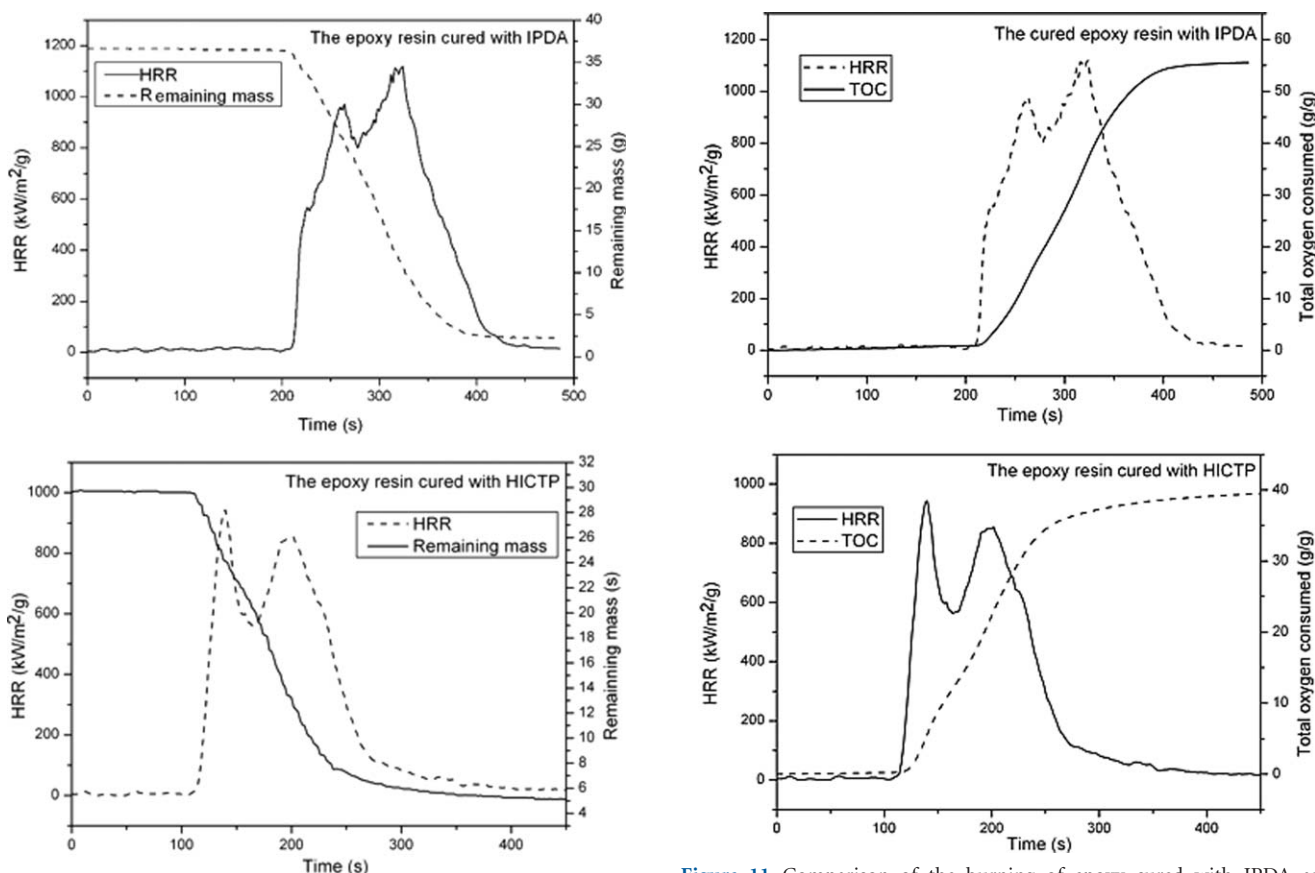**Figure 9.** DSC of CHS-EPOXY E520 epoxy resin cured with HICTP.

Figure 10. Comparison of the burning of epoxy cured with IPDA and epoxy resin cured with HICTP in dual cone calorimeter—HRR and remaining mass with time.

Figure 11. Comparison of the burning of epoxy cured with IPDA and epoxy resin cured with HICTP in dual cone calorimeter—HRR and total oxygen consumed with time.

The glass transition temperatures were also determined by differential scanning calorimetry. It can be observed from Figure 9 that the glass transition temperature of the epoxy resin cured with HICTP was 134.1°C, while the glass transition temperature of the epoxy resin cured with IPDA was 143.6°C. The lower T_g value of the epoxy resin cured with HICTP in comparison with IPDA cured one is probably associated with the structure of HICTP as a result of steric shielding during the curing process. Secondary amine groups of HICTP in comparison with primary amine groups were screened by phosphazene cycles, thus, during curing of the epoxy resin reacted slower and possibly not completely, causing a lower network density. The both found values were about 15°C higher than values commonly obtained with aliphatic amines as dipropylenetriamine, ethylenediamine or triethylenetetramine having T_g in the range of 110–120°C.[30]

The DSC results of T_g values were comparable with those obtained from DMA (using DMA for the epoxy resin cured with HICTP $T_g = 135$ vs. 134.1°C using DSC; using DMA for the epoxy resin cured with IPDA $T_g = 147$ vs. 143,6°C using DSC) as it is summarized in Table III.

The thermogravimetric analysis was used to characterize a thermal stability of cured samples. It is shown in Figure 10 that the material cured with HICTP began to decompose at about 320°C while at 480°C the decomposition reached 70.3%. Measurements of the epoxy resin cured with IPDA were performed at the same conditions. The material began to decompose at about 359°C while at 480°C the decomposition reached 75.3%. It is obvious from Table IV that, despite of initial decomposition at lower temperature, HICTP increases the thermal resistance at higher temperatures. That means, that the material cured with HICTP produced a lower amount of gaseous flammable products of degradation.

Table IV. The Results of TG Analysis

Sample	Tonset (°C)	T_{max} (°C)	Decomposition of material at 480°C (%)
Epoxy resin curing using HICTP	324.6	351.2	70.3%
Epoxy resin curing using IPDA	359.6	386.1	75.3%

Table V. Results for Testing the Cured Epoxy Resins against Burning

Evaluated parameters	Epoxy resin cured with HICTP	Epoxy resin cured with IPDA
Initial mass (g)	29.4 g	36.6 g
Mean HRR (kW m^{-2} g^{-1})	9.7	13.3
Mean EHC (MJ kg^{-1})	25.9	25.8
Total heat release (MJ m^{-2} g^{-1})	3.4	3.8
Total oxygen consumed (g g^{-1})	0.63	0.74
Total smoke release (m^{-2} m^{-2} g^{-1})	98.6	116.1
Carbon residue at flame extinction (%)	17.0	6.2
MARHE	348	344

where HRR, heat release rate, EHC, effective heat of combustion, MARHE, maximum rate of average heat emission.

The cured epoxy resins were tested on burning using a dual cone calorimeter. The results in Figures 11 and 12 and in Table V indicate that epoxide cured with HICTP ignites easier than that cured with IPDA. This may by connected with the shift of nonisothermal thermogravimetric run to lower temperature. On the other hand epoxy resin cured with the prepared derivative HICTP exhibits lower values of total heat release, amount of smoke released and oxygen consumed, which may cause a slower flame spread. Lower total smoke released during buring of sample cured with HICTP may be due to more efficient oxidation of carbon particles in the flame in the presence of the phosphorous compound present regardless that the amount of carbon residue is significantly higher in the case of the epoxy resin cured with HICTP. It is assumed that the phosphorus atom reacted in the gas phase, where the main role was played by PO radical. This effect was confirmed by decreased heat release due to a reduced heat release rate (HRR)/mass loss rate value during burning.[31] The other parameter obtained from dual cone calorimeter measurements was the flammability expressed by MARHE (Maximum Rate of Average Heat Emission). The obtained values of MARHE parameters of samples cured by HICTP as well as by IPDA were similar.

CONCLUSIONS

The derivative of hexachloro-*cyclo*-triphosphazene was prepared by nucleophilic substitution with isophorone diamine using the one-step synthesis. HICTP synthesis was carried out repeatedly with reproducibility better than 98%. The structure of HICTP was verified using elemental analysis, ^{31}P NMR, mass spectrometry, and FT-IR spectroscopy. The prepared derivative was effective as a hardener for the commercially available epoxy resin CHS-EPOXY E520. The glass transition temperature of the epoxy resin cured with HICTP was 134.1°C. The results of G' for the cured epoxy resin has shown that the use of HICTP as a curing agent should increase the hardness of the material in comparison with IPDA cured one. This was confirmed by measurig of Brinell hardnes of cured samples. The cured epoxy resins were tested during burning. The results have proved that the epoxy resin cured with phosphorus containing HICTP exhibits lower total heat release, lower total smoke release as well as lower total smoke production compared to the epoxy resin cured with IPDA. The results of testing during burning of the epoxy resin cured with HICTP proved that the fire should spread more slowly and a lesser production of smoke should be advantageous to the environment polution.

REFERENCES

1. Gerhardt, C. *Ann. Chim. Phys.* **1846**, *18*, 188.
2. Gerhardt, C. *C. R. Acad. Sci.* **1846**, *22*, 858.
3. Laurent, A. *C. R. Acad. Sci.* **1850**, *32*, 356.
4. Kiliç, A. *J. Qafqaz Univ.* **2000**, *3*, 133.
5. Allcock, H. R. Chemistry and Applications of Polyphosphazenes; Wiley-Interscience: Hoboken, **2003**, p 725.
6. Gladstone, J. H.; Holmes, J. D. *J. Chem. Soc.* **1864**, *17*, 225.
7. Gladstone, J. H.; Holmes, J. D. *Ann. Chim. Phys.* **1846**, *3*, 465.
8. Gladstone, J. H.; Holmes, J. D. *Bull. Soc. Chim. France* **1865**, *3*, 113.
9. Krishnamurthy, S. S.; Sau, A. C.; Woods, M. In: Advances in Inorganic Chemistry and Radiochemistry; Academic Press: New York, **1978**, p 41.
10. Allen, C. W. *Chem. Rev.* **1991**, *91*, 119.
11. Levchik, G. F.; Grigoriev, Y. V.; Balabanovich, A. I.; Levchik, S. V. *Polym. Int.* **2000**, *49*, 1095.
12. Gu, J. W.; Zhang, G. C.; Dong, S. L.; Zhang, Q. Y.; Kong, J. *Surf. Coat. Technol.* **2007**, *201*, 7835.
13. May, C. Epoxy Resins: Chemistry and Technology; Vol. *2*, CRC Press, Boca Raton, **1987**, p 1288.
14. Gu, X.; Wei, H.; Huang, X.; Tang, X. *J. Macromol. Sci. A: Pure Appl. Chem.* **2010**, *47*, 828.
15. Yamamot, T.; Takahashi, K.; Kon, Y.; Harakawa, K. *Kobunshi Ronbunshu* **1988**, *45*, 851.
16. Sun, J.; Wang, X.; Wu, D. *ACS Appl. Mater. Interfaces* **2012**, *4*, 4047.
17. You, G.; Cheng, Z.; Hao, P.; He, H. *Chin. J. Appl. Chem.* **2014**, *31*, 993.
18. He, Y.; Su, S. *PCT Int. Appl.* **2014**, WO 2014089934 A1 20140619.
19. He, Y.; Su, S. Flame Retardant Resin Composition without Halogen and Its Application, Faming Zhuanli Shenqing, **2013**, CN 103013046 A 20130403.
20. Ru, J.; Liu, S.; Wu, H. Flame Retardant Adhesive with Low Halogen Content, and Flexible Copper Clad Laminate Therewith, Faming Zhuanli Shenqing, **2010**, CN 101892027 A 20101124.
21. Lee, C. Y.; Chiu, Y. S. Process for Preparing a Mixture of Amino-Containing Phosphazenes from Chlorophosphazenes, *n*-propanol and Ammonia by a Water-Free Process, **2001**, US 6265599 B1 20010724.

22. Yoon, H. *J. Korean Fiber Soc.* **1999**, *36*, 572.

23. Yoon, H. S.; Choi, K. S.; Takahashi, K. *Han'guk Somyu Konghakhoechi* **1996**, *33*, 610.

24. Gouri, M.; El, B.; El, A.; Hegazi, S. E.; Ziraqui, R.; Rafik, M.; El Harfi, A. *J. Mater. Environ. Sci.* **2011**, *2*, 319.

25. Jay, R. R. *Anal. Chem.* **1964**, *36*, 667.

26. Francis, H. J., Jr.; Liteanu, C.; Růzicka, J. *Talanta* **1971**, *18*, i. doi: 10.1016/0039-9140(71)80164-9.

27. Datasheets from suppliers, downloaded on March 21, **2015** from http://www.spolchemie.cz.

28. Dodiuk, H., Goodman, S. H. Handbook of Thermoset Plastics, 3rd edition; William Andrew, **2013**, p 800.

29. González, M. G.; Cabanelas, J. G; Baselga, J. "Applications of FTIR on Epoxy Resins-identification, Monitoring the Curing Process, Phase Separation and Water Uptake," in Infrared Spectroscopy-Materials Science, Engineering and Technology, T. Theophanides, Ed., Intech, **2012**, pp. 261–284.

30. Nikolic, G.; Zlatkovic, S.; Cakic, M.; Cakic, S. *Sensors* **2010**, *10*, 684.

31. Schartel, S. *Materials* **2010**, *3*, 4710.