ACS OMEGA

Article

Solid-State Nuclear Magnetic Resonance as a Versatile Tool To Identify the Main Chemical Components of Epoxy-Based Thermosets

Timmy Schäfer, Gerd Buntkowsky,* and Torsten Gutmann*

Read Online

ACCESS | Metrics & More | Article Recommendations | SI Supporting Information

ABSTRACT: Cross-linked thermosets are investigated by ^{13}C solid-state nuclear magnetic resonance (NMR) spectroscopy to determine their structure and to distinguish important epoxy resins and hardening agents. In addition to the epoxy resin and hardening agent, the identification of phosphorus-containing flame retardants is demonstrated by ^{31}P solid-state NMR. These studies provide a spectral database for routine use, which is finally applied to analyze commercial products containing an unknown multicomponent system.
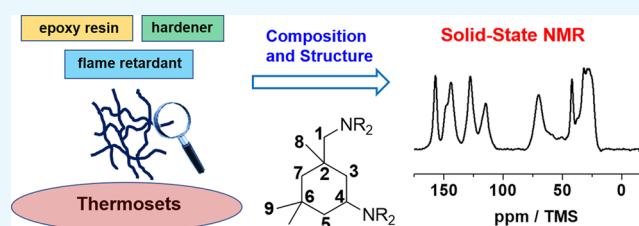
1. INTRODUCTION

The outstanding physical−chemical properties of epoxy-based thermosets make these materials very interesting for industry applications in, for example, automotive or aerospace technology.[1] These properties include a high resistance against chemicals and corrosion, low cure shrinkage, excellent electrical insulation behavior, and high thermal stability. Moreover, these materials have a good compatibility with a large number of materials and no volatiles are formed during curing processes.[1,2] Although thermosets have a widespread use in our daily life, detailed knowledge on their complex composition and structure is limited up to now. This knowledge is however of importance to optimize them for specific applications and to understand their long-time stability. An uncured formulation consists of at least two components, namely, (i) the epoxy resin that typically contains reactive epoxy groups and (ii) a hardening agent that contains different functional groups enabling a curing process with the epoxy resin. Such hardening agents can be, for example, aliphatic, cycloaliphatic, or aromatic amines. To form a highly cross-linked network, commercial epoxy resins usually contain two or more epoxy groups and the hardening agents two or four reactive groups per molecule.[3] In addition to the selected epoxy resin and hardening agents, different additives (modifiers) and flame retardants may be mixed to change the properties of the thermoset.[1,3] In that way, thermosets can be designed to be rigid, filled or foamed, fire-retardant, and resistant to heat and chemicals.[1]

To ensure an almost complete curing process, epoxy resins and amine-containing hardening agents have to be combined in a defined stoichiometric ratio. For this purpose, the epoxy equivalent weight (EEW)[4] and the amine hydrogen equivalent weight (AHEW)[5] of the components have to be taken into account. During the curing process, a 3D network is formed, which makes the cured epoxy resins insoluble, durable, stable, and not meltable.[2]

Uncured epoxy formulations or partially cross-linked epoxy resins can be characterized by a number of analytical techniques including spectroscopy, thermal analysis, or mass spectrometry. Specifically, for the analysis of elastomers containing partially cross-linked epoxy resins, pyrolysis GC−MS is mainly used to study their chemical composition.[6] Additives in elastomers can be detached by means of Soxhlet extraction. Further separation of individual compounds in the extract by high-performance liquid chromatography (HPLC)[7] enables the identification of each component by techniques, such as MALDI-ToF-MS,[6] nuclear magnetic resonance (NMR), and infrared spectroscopy (FTIR).[8]

Thermosets, however, are usually fully cross-linked. It is therefore not feasible to dissolve the resin or components, which makes their characterization more challenging. Up to now, pyrolysis GC−MS has been used for the damage analysis of thermosets. Puype et al.[9] have demonstrated that pyrolysis GC−MS can be employed to analyze thermosets with respect to contained flame retardants. As a result, the presence of a specific flame retardant in the thermoset has been proven. However, no structural details about the resin and hardening agent in the cross-linked thermoset are available with this characterization technique.

To learn more about the composition and structure of the cured epoxy network, infrared spectroscopy (FTIR)[10−13] and solid-state NMR (ssNMR)[10−12,14−18] have been applied. For example, ssNMR has been successfully used to investigate the nature of chemical reactions during the curing process, including intramolecular processes taking place and the formation of side products,[10,14] or to determine the degradation of epoxy resins under high energy irradiation.[16] Moreover, the kinetics of the curing process has been studied by means of ssNMR.[15]

Although these works addressed the NMR signal assignment, studies that compare different hardening agents and epoxy resins have not been presented, and a spectral database for routine characterization of systems with unknown composition is still missing. Thus, the aim of this work is to investigate various cured epoxy resins with different hardening agents by means of ssNMR to determine the original components. This will be the basis to build a database for routine analysis of thermosets with unknown composition.

To evaluate ssNMR for the characterization of thermosets, model systems containing the epoxy resins bisphenol A diglycidyl ether (DGEBA; Scheme 1 (I)) or bisphenol F

Scheme 1. Structures of DGEBA (I) and DGEBF (II)
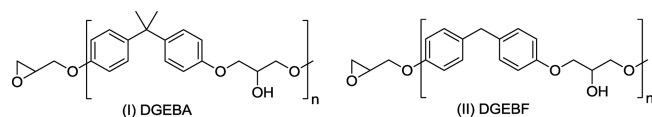
diglycidyl ether (DGEBF; Scheme 1 (II)) and various amine hardening agents are investigated by $^1H \rightarrow {}^{13}C$ cross-polarization magic-angle spinning nuclear magnetic resonance (CP MAS NMR). In a second step, a flame retardant is added to some of the model systems. $^1H \rightarrow {}^{13}C$ and $^1H \rightarrow {}^{31}P$ CP MAS NMR experiments are applied to identify flame retardants in cured epoxy-based thermosets. Finally, two commercial products of unknown composition are investigated to determine the contained epoxy resin, the hardening agent, and flame retardant.

2. EXPERIMENTAL SECTION

2.1. General Methods. Model systems of fully cured epoxy-based thermosets were synthesized and analyzed via ssNMR. For these model systems, the epoxy resins bisphenol A diglycidyl ether (DGEBA; structure in Scheme 1; Sigma-Aldrich) and bisphenol F diglycidyl ether (DGEBF; structure in Scheme 1; Sigma-Aldrich) were cured with different amine-containing hardening agents, namely, triethylenetetramine (TETA; structure in Figure S5; Acros Organics), isophorendiamine (IPDA; structure in Figure S6; Sigma-Aldrich), diethyltoluenediamine (DETDA 80, an isomeric mixture containing 80% of 3,5-diethyl-2,4-diaminotoluene and 20% of 3,5-diethyl-2,6-diaminotoluene; structure in Figure S7; Haihang Industry), 4,4′-methylenebis(2,6-diisopropylaniline) (M-DIPA; structure in Figure S8; abcr), or 4,4′-methylenebis(2,6-diethylaniline) (M-DEA; structure in Figure S9; Sigma-Aldrich). In addition to these components, the phosphorus-containing oligomeric flame retardants for epoxy-based thermosets, which have been given the trade names DOPO (9,10-dihydro-9-oxy-10-phosphaphenanthren-10-oxid; structure in Figure S11a; HARKE Chemicals), DXM (structure in Figure S11b; Metadynea), HFC-X (structure in Figure S11c;

Sigma-Aldrich), and SPB 100 (structure in Figure S11d; Haihang Industry) were added to some of the samples. Finally, to apply our approach, two commercially available adhesives (C01 and C02) with unknown composition and structure were investigated.

2.2. Synthesis of Cured Epoxy-Based Thermosets. To form epoxy-based thermosets, a stoichiometric amount of the appropriate epoxy resin and hardening agent were mixed, homogenized, and cured in an oven with air ventilation. The cured epoxy resins were pulverized by a cryogenic mill or by rasp and separated from possible non-cross-linked components by Soxhlet extraction for 12 h with acetone yielding the epoxy-based thermosets.

The compositions of the epoxy-based thermosets, which are addressed in this work, are listed in Table 1. The epoxy resin

Table 1. Sample Compositions

used epoxy resin	used hardening agent	used flame retardant
DGEBA	TETA	
DGEBA	IPDA	
DGEBA	DETDA 80	
DGEBA	M-DIPA	
DGEBA	M-DEA	
DGEBF	TETA	
DGEBF	IPDA	
DGEBF	DETDA 80	
DGEBF	M-DIPA	
DGEBF	M-DEA	
DGEBA	IPDA	DOPO
DGEBF	IPDA	DOPO
DGEBA	IPDA	DXM
DGEBF	IPDA	DXM
DGEBA	IPDA	HFC-X
DGEBF	IPDA	HFC-X
DGEBA	IPDA	SPB 100
DGEBF	IPDA	SPB 100

and amine-containing hardening agent have to be mixed in a stoichiometric ratio to reach an almost complete curing of the samples. For this purpose, the epoxy equivalent weight (EEW) and the hydrogen equivalent weight (HEW) of the respective components, which are listed in Table 2, were taken into account.

Assuming that about 3 g of each sample has to be produced, specific amounts of the epoxy resin and hardening agent

Table 2. Weighed Substance Amounts with Respect to the EEW and HEW Values

epoxy resin	EEW (g/mol)	mass (g)	hardening agent	HEW (g/mol)	mass (g)
DGEBA	178.7	2.411	DETDA 80	44.58	0.599
DGEBA	178.7	2.649	TETA	24.33	0.358
DGEBA	178.7	2.088	M-DEA	77.61	0.910
DGEBA	178.7	1.990	M-DIPA	91.65	1.010
DGEBA	178.7	2.429	IPDA	42.58	0.575
DGEBF	178.7	2.392	DETDA 80	44.58	0.611
DGEBF	178.7	2.641	TETA	24.33	0.365
DGEBF	178.7	2.082	M-DEA	77.61	0.923
DGEBF	178.7	1.965	M-DIPA	91.65	1.033
DGEBF	178.7	2.422	IPDA	42.58	0.585

according to the EEW and HEW values were weighed (Table 2) and mixed.

Next to these epoxy-based thermosets, additional ones were synthesized containing various phosphorus-containing flame retardants. The compositions of these samples are listed in Table 3.

Table 3. Weighed Substance Amounts of the Epoxy Component, the Hardening Agent, and the Used Flame Retardant

epoxy resin	mass (g)	hardening agent	mass (g)	flame retardant	mass (g)
DGEBA	2.181	IPDA	0.520	SPB100	0.301
DGEBA	2.174	IPDA	0.524	HFC-X	0.307
DGEBA	2.182	IPDA	0.529	DOPO	0.311
DGEBA	2.190	IPDA	0.522	DXM	0.293
DGEBF	2.180	IPDA	0.527	SPB100	0.299
DGEBF	2.164	IPDA	0.526	HFC-X	0.296
DGEBF	2.161	IPDA	0.512	DOPO	0.291
DGEBF	2.173	IPDA	0.523	DXM	0.308

For the curing process, each sample was transferred into a small aluminum tray and cured in a convection oven (Binder) employing the curing programs listed in Table 4. The temperature was continuously increased at 1 °C/min between each step in the curing program.

Table 4. Overview on Curing Programs

hardening agent	curing program		
	step 1	step 2	step 3
DETDA 80	60 min, 90 °C	120 min, 180 °C	
TETA	15 min, 70 °C	60 min, 80 °C	120 min, 120 °C
M-DEA	60 min, 90 °C	120 min, 180 °C	
M-DIPA			
IPDA	30 min, 80 °C	30 min, 120 °C	60 min, 160 °C

2.3. Characterization by Solid-State NMR. Approximately 50 mg of each pulverized thermoset sample was filled in a 4 mm ZrO_2 rotor for ssNMR analytics. All ssNMR measurements were performed on a Bruker Avance III HD 300 spectrometer (Rheinstetten, Germany) employing a 4 mm broad band H/X probe. Spectra were recorded at 7 T, corresponding to a frequency of 121.49 MHz for ^{31}P and 75.47 MHz for ^{13}C, at 10 kHz spinning, respectively, at room temperature. Spectra were referenced to phosphoric acid for ^{31}P (0 ppm) and to TMS (0 ppm) for ^{13}C using adamantane (+38.5 ppm) as an external standard. The ramped CP MAS sequence[19] was utilized with a contact time of 3.2 ms for $^1H \rightarrow$ ^{31}P CP MAS and 3.0 ms for $^1H \rightarrow$ ^{13}C CP MAS experiments. The recycle delay was set to 2 s, and tppm decoupling[20] employing a 15° phase jump was applied during data acquisition. The acquisition time for $^1H \rightarrow$ ^{13}C CP MAS was set to 50 ms and that for $^1H \rightarrow$ ^{31}P CP MAS to 25 ms. All spectra were recorded with 2048 scans. The radiofrequency field strengths were 70 kHz for ^1H, 50 kHz for ^{13}C, and 28 kHz for ^{31}P.

In addition to the model systems, spectra of the pure epoxy resins, the hardening agents and the flame retardants were recorded. In cases where these compounds are liquids, ^{13}C NMR spectra under static conditions were acquired employing

single pulse excitation. An excitation pulse length of 3.5 μs was used, and the spectra were recorded with 1024 scans and a recycle delay of 2 s. The acquisition time for the single pulse experiments was set to 30 ms.

3. RESULTS AND DISCUSSION

3.1. Epoxy Component and Amine Containing Hardening Agent. Various samples were prepared from different combinations of epoxy resin and amine-containing hardening agent and were investigated by means of $^1H \rightarrow$ ^{13}C CP MAS NMR spectroscopy to analyze the resulting thermosets with respect to their components and structure. The ^{13}C resonances marked in Figure 1a with a plus sign (+) are visible in all
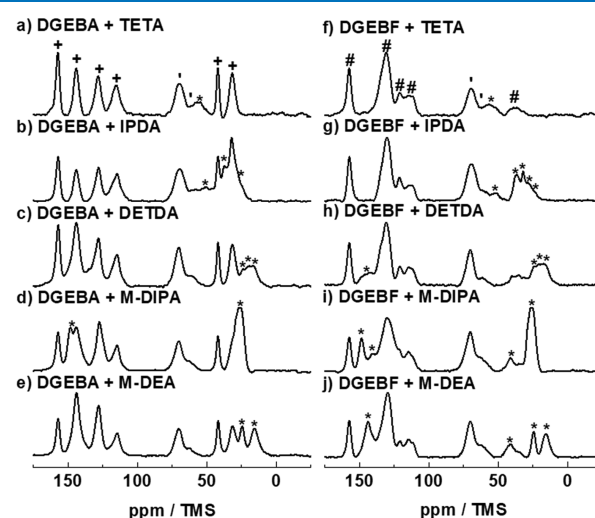

Figure 1. $^1H \rightarrow$ ^{13}C CP MAS NMR spectra of the samples a−j. On the left side, the specific signals of DGEBA (a−e) are marked with a plus sign (+). On the right side, the specific signals of DGEBF (f−j) are marked with a number sign (#). Signals marked with a prime (′) are signals that appear for every epoxy resin. Specific signals of the appropriate hardening agent are marked with asterisks.

spectra shown in Figure 1a−e. They are attributed to the ^{13}C nuclei of cross-linked DGEBA according to the literature.[16] Similarly, the ^{13}C resonances marked with a number sign (#) in Figure 1f are visible in all spectra shown in Figure 1f−j. They are assigned to ^{13}C nuclei of cross-linked DGEBF according to the literature.[17] Details on the chemical shifts of these resonances and their assignments to structural groups of the epoxy resins are given in Table S1, and the spectra of pure DGEBA and DGEBF are shown in Figures S3 and S4 in the Supporting Information. The signals at 70.4 and 61.8 ppm marked with a prime (′) appear for every amine-cured epoxy resin. The underlying structural elements formed in each amine-cured epoxy resin from the reaction of an epoxide with an amine are shown in Scheme 2. Details on the chemical shifts and their assignments to structural elements are listed in Table 5.

Typically, three signals are expected for this structure. However, the calculated difference in the chemical shift between the carbon atom **1** and the carbon atom **2** is only 2 ppm. Since the line width of the signal at 70.4 ppm is about 560 Hz the individual signals are not resolved and thus only one signal is observed for the carbons **1** and **2**.

By comparing the spectra of samples containing different epoxy resins and equal amine-containing hardening agent (e.g.,

Scheme 2. Common Structural Element of a Thermoset Formed by the Reaction of an Epoxy Resin with an Amine-Containing Hardening Agent[a]

[a]R′ represents aromatic groups, and R″ represents aliphatic or aromatic groups.

Table 5. ^{13}C Chemical Shifts of the Specific Signals of Structural Elements Formed in Each Amine-Cured Epoxy Resin

chemical shift	structure
1: 70.4 ppm (-CH-CH$_2$-OR')	
2: 70.4 ppm (-CH$_2$-CH-OH)	R' = aromatic structure of the epoxy resin
3: 61.8 ppm (R''N-CH$_2$-CH-OH)	R'' = aliphatic or aromatic structure of the hardening agent

Figure 1a compared with Figure 1f), specific signals of the hardening agent can be identified, which are independent of the epoxy resin. These signals are marked throughout the spectra with an asterisk. Details on the chemical shifts and their assignments to structural groups of the hardening agents are listed in Table 6. For comparison, the spectra of the pure hardening agents are shown in Supporting Information, Figures S5–S9. Note that only a few signals of the hardening agents are visible in the spectra since the remaining signals are overlapped by signals of the epoxy resins. In case signals of

Table 6. ^{13}C Chemical Shifts and Corresponding Structural Groups of the Specific Signals of the Amine-Containing Hardening Agents of Figure 1

curing agent	chemical shift	structure
TETA a) + f)	**1**: 56.7 ppm (-CH$_2$-CH$_2$-NR$_2$) **2, 3**: overlaid by other signals	 R = Epoxy resin
IPDA b) + g)	**1**: 51.1 ppm (-C$_q$-CH$_2$-NR$_2$-) **2**: 36.9 ppm (CH$_3$-C$_q$-CH$_2$-NR$_2$,) **3**: 36.9 ppm (CH$_3$-C$_q$-CH$_2$-CH-) **5**: 36.9 ppm ((CH$_3$)$_2$-C$_q$-CH$_2$-CH-) **6**: 32.0 ppm (-C$_q$-(CH$_3$)$_2$) **9**: 28.3 ppm (-C$_q$-(CH$_3$)$_2$) **8**: 24.9 ppm (-C$_q$-CH$_3$) **4, 7**: overlaid by other signals	 R = Epoxy resin
DETDA c) + h)	**2, 9**: 142.5 ppm (-C$_q$(arom.)-NR$_2$) **5, 14, 16**: 23.9 ppm (-C$_q$(arom.)-CH$_2$-CH$_3$) **6, 15, 17**: 19.0 ppm (-CH$_2$-CH$_3$) **7, 18**: 16.8 ppm (-C$_q$(arom.)-CH$_3$) **1, 3, 4, 8, 10, 11, 12, 13**: overlaid by other signals	 R = Epoxy resin
M-DIPA d) + i)	**4**: 148.4 ppm (-C$_q$(arom.)-CH-(CH$_3$)$_2$) **5**: 140.2 ppm (-C$_q$(arom.)-NR$_2$) **1**: 41.1 ppm (-C$_q$-CH$_2$-C$_q$-) **6**: 26.9 ppm (-CH-(CH$_3$)$_2$) **7**: 25.5 ppm (-CH-(CH$_3$)$_2$) **2, 3**: overlaid by other signals	 R = Epoxy resin
M-DEA e) + j)	**5**: 143.8 ppm (-C$_q$(arom.)-NR$_2$) **1**: 40.9 ppm (-C$_q$-CH$_2$-C$_q$-) **6**: 24.5 ppm (-CH$_2$-CH$_3$) **7**: 15.6 ppm (-CH$_2$-CH$_3$) **2, 3, 4**: overlaid by other signals	 R = Epoxy resin

structural groups of the hardening agents cannot be clearly identified in the spectra due to such an overlay, it is indicated in Table 6. Spinning sidebands are not expected for these samples as demonstrated exemplary for DGEBA + DETDA 80 (for details see Supporting Information, Figure S10).

The amine containing hardening agents TETA (spectra a and f in Figure 1) and IPDA (spectra b and g in Figure 1) are distinguishable by additional signals in the aliphatic region. While TETA shows only one additional signal in the aliphatic region at 56.7 ppm, IPDA shows five signals at 51.1, 36.9, 32.0, 28.3, and 24.9 ppm. By using the DGEBA resin, the signals at 32.0 and 28.3 ppm of IDPA are overlapped by a signal of the resin. The spectra of cured epoxy resins containing aromatic amine hardening agents (spectra c−e and h−j in Figure 1) should be recognizable by differences in the aromatic region. Due to an overlay of the four signals of DGEBA in the aromatic region with potential signals of the hardening agents (spectra c−e in Figure 1), only for M-DIPA (spectra d in Figure 1), an additional signal in the aromatic region is obtained at 148.4 ppm. This additional signal in the aromatic region is assigned to the quaternary carbon of the $-C_q(arom.)-CH-(CH_3)_2$ moiety.

Luckily, all used aromatic hardening agents contain additional aliphatic substituents and thus show signals also in the aliphatic region. These signals can be used as a fingerprint to distinguish between different hardening agents. Comparing spectra c and h in Figure 1, there are three signals at 23.9, 19.0, and 16.8 ppm, which are representative for DETDA 80. For M-DIPA (spectra d and i in Figure 1), a broad signal is observed, which is split into two signals at 26.9 and 25.5 ppm. Finally, for M-DEA (spectra e and j in Figure 1), there are two specific signals in the aliphatic region at 24.5 and 15.6 ppm.

Using DGEBF as a resin, an additional signal in the aromatic region at 142.5 ppm (spectrum h in Figure 1) is observed for DETDA 80. For the hardening agent M-DIPA (spectrum i in Figure 1), an additional signal at 140.2 ppm is found, which is overlapped by signals of the resin when using DGEBA (spectrum d in Figure 1). By using the hardening agent M-DEA (spectrum j in Figure 1), an additional signal at 143.8 ppm is observed. These additional signals ease the distinguishing of DETDA 80, M-DIPA, and M-DEA in case DGEBF is employed as a resin.

3.2. Phosphorus-Containing Flame Retardants. Next to thermosets containing only epoxy resins and amine hardening agents, flame retardants are often added, which have to be also addressed by ssNMR. As typical model systems, we studied the phosphorus-containing flame retardants DOPO, DXM, HFC-X, and SPB 100. First, ^{1}H → ^{13}C CP MAS spectra of the pure flame retardants were recorded (see Supporting Information, Figure S11), and the observed signals were assigned to the structural motifs of the flame retardants. These spectra can serve as a reference for the identification of flame retardants in epoxy resins. Following the analysis of the pure flame retardants, thermosets consisting of the epoxy components DGEBA or DGEBF, the amine curing agent IPDA and the respective flame retardant were investigated by ^{1}H → ^{13}C CP MAS NMR. By comparing the ^{1}H → ^{13}C CP MAS spectra of the thermosets with those of the pure flame retardant, characteristic signals of the flame retardant have to be identifiable. Such a comparison is shown in Figure 2 for the flame retardant HFC- X.

As seen in the spectra, many signals of the flame retardant are overlaid by signals of the epoxy resin or the hardening
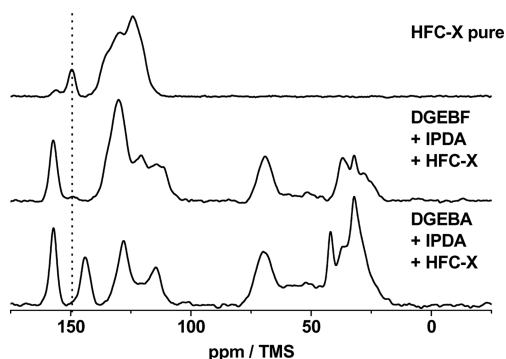
Figure 2. $^1H \rightarrow {}^{13}C$ CP MAS spectrum of pure HFC-X and spectra of samples containing ca. 10 wt % of the flame retardant HFC-X, the hardening agent IPDA, and the epoxy resin DGEBA or DGEBF.

agent. The signal at 149.3 ppm of the flame retardant can also be concealed by other signals and is observed only in the spectrum of the model system containing DGEBF. Because of the low amount of the flame retardant (ca. 10 wt %) in the model samples, the intensity of the signal at 149.3 ppm in the model systems is low. This makes it difficult to unambiguously identify the retardant by means of ^{13}C ssNMR.

Since many flame retardants are derivates of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and thus contain phosphor, ^{31}P ssNMR studies are employed to identify them and to shed more light on their structures. Figure 3 shows the $^1H \rightarrow {}^{31}P$ CP MAS spectra of the pure flame retardants DOPO, DXM, HFC-X, and SPB 100 and the assignment of the ^{31}P signals to different structural motifs, which allows us to distinguish them.

For DOPO (Figure 3a), besides the main signal at 10.4 ppm (−O—P═O, **1**), two signals with a lower intensity are observed at 13.5 and 23.2 ppm. The additional signal at 13.5 ppm most probably refers to the phosphorous nucleus **1'** in 6-hydroxy-(6H)-dibenzo[1,2]oxaphosphorine (DOPO-OH) since DOPO-OH is present in tautomeric equilibrium with DOPO.[21] The signal at 23.2 ppm is attributed to the phosphorous nucleus **2'** of 2'-hydroxydiphenyl-2-phosphinic acid, which is formed by the reaction of DOPO with water.[22] In the $^1H \rightarrow {}^{31}P$ CP MAS NMR spectrum of the flame retardant DXM (Figure 3b), the main signal is obtained at 5.6 ppm, which is assigned to the phosphorous nucleus **1** in DXM. In addition to this signal, a shoulder is visible at 2.5 ppm. This signal probably refers to the phosphorous nucleus **1'** of (DOP)$_3$Mel, which is the precursor for DXM.[23]

The $^1H \rightarrow {}^{31}P$ CP MAS NMR spectrum of HFC-X (Figure 3c) shows two specific signals at 31.1 and 3.9 ppm, which can be assigned to the two different phosphorous nuclei **1** and **2** in HFC-X.

In the $^1H \rightarrow {}^{31}P$ CP MAS NMR spectrum of the flame retardant SPB 100 (Figure 3d), several ^{31}P signals are observed, although only one phosphorus species is expected for this flame retardant. In addition to the main signal at 8.8 ppm, signals in the high field range from −10.5 to −23.0 ppm appear. While the main signal at 8.8 ppm is attributed to the phosphorous nuclei **1** in SPB 100, the additional signals ranging from −10.5 to −23.0 ppm may refer to phosphorous (**1'−5'**) present in impurities of the precursors of SPB 100.[24]

Figure 4 compares the $^1H \rightarrow {}^{31}P$ CP MAS NMR spectra of pure HFC-X and the model systems DGEBA + IPDA + HFC-X and DGEBF + IPDA + HFC-X. According to the structural assignment of ^{31}P signals of different flame retardants in the
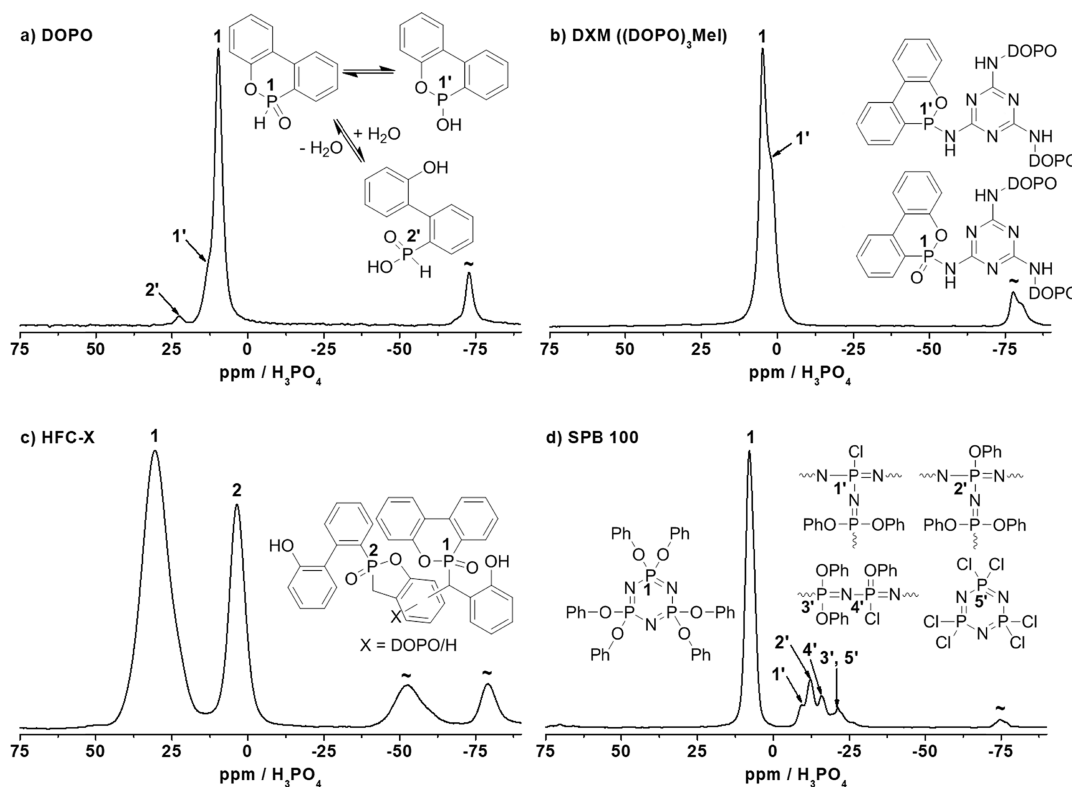

Figure 3. $^1H \rightarrow {}^{31}P$ CP MAS NMR spectra of the phosphorus-containing flame retardants (a) DOPO, (b) DXM, (c) HFC-X, and (d) SPB 100. Signals marked with tilde (∼) are spinning sidebands.
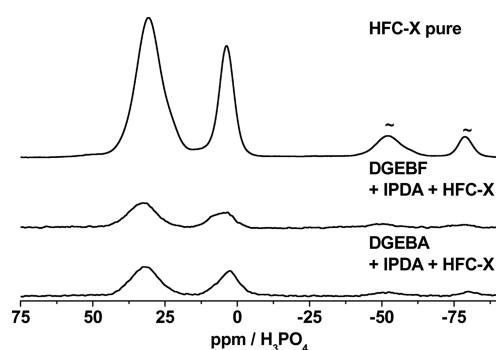
Figure 4. $^{1}H \rightarrow {}^{31}P$ CP MAS NMR spectrum of pure HFC-X and spectra of samples containing 10 wt % of the flame retardant HFC-X, the hardening agent IPDA, and the epoxy resin DGEBA or DGEBF. Signals marked with tilde ($\sim$) are spinning sidebands.

previous paragraph, the signals at 31.1 and 4.0 ppm clearly identify the flame retardant HFC-X in the model systems. Such additional $^{1}H \rightarrow {}^{31}P$ CP MAS NMR studies are especially important in cases where only small amounts of flame retardant (e.g., 1 wt %) are present in a sample and the sensitivity of $^{1}H \rightarrow {}^{13}C$ CP MAS NMR experiments is too low to detect a signal of the retardant or the signal is concealed by other signals of the system.

This is illustrated in the Supporting Information, Figure S12 where $^{1}H \rightarrow {}^{13}C$ CP MAS NMR spectra of model systems containing DGEBA, IPDA, and different amounts of the flame retardant HFC-X are shown. No additional signal is obtained for the sample containing 1 wt % of the flame retardant HFC-X compared to the sample containing no flame retardant. Using 10 wt % of the flame retardant, an additional signal at 149.3 ppm appears. Because of the concealing of this signal by other signals (see Figure 2), this signal at 149.3 ppm is however not specific enough to clearly identify the flame retardant. Thus, it is necessary to measure $^{1}H \rightarrow {}^{31}P$ CP MAS NMR spectra for identification.

Two signals at 31.3 and 4.2 ppm are obtained in the $^{1}H \rightarrow {}^{31}P$ CP MAS NMR spectra (Figure 5) of the samples containing 10 and 1 wt % of the flame retardant, respectively. According to the interpretation of the spectra in Figures 3 and 4, these signals confirm the presence of the retardant HFC-X in both these samples.
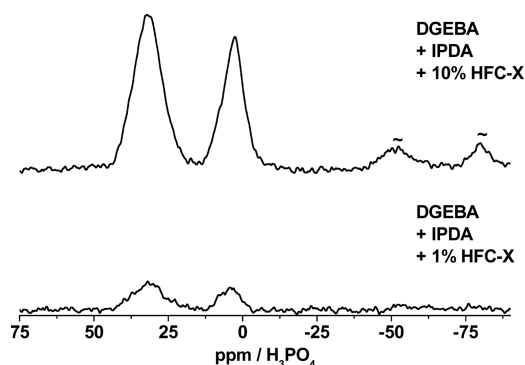

Figure 5. $^{1}H \rightarrow {}^{31}P$ CP MAS NMR spectra of samples containing different amounts of the flame retardant HFC-X, the hardening agent IPDA, and the epoxy resin DGEBA. Signals marked with tilde ($\sim$) are spinning sidebands.

3.3. Systems Containing Several Hardening Agents. Since thermosets can contain several hardening agents, it is also important to analyze the ability of our ssNMR approach for such systems. For this purpose, the multicomponent model systems DGEBA + M-DIPA + M-DEA and DGEBA + M-DIPA + DETDA 80 were synthesized and analyzed by ssNMR.

Comparison of the signals of the three-component thermoset DGEBA + M-DIPA + M-DEA on the left side in Figure 6 with the specific signals of the thermosets containing only the hardening agents M-DIPA or M-DEA (Figure 1d and Figure 1e), it is obtained that specific signals of both hardening agents are present in the multicomponent system. The observed specific signals of M-DIPA are marked with blue bars, and the specific signals of M-DEA are marked with red bars. Especially, the signals of M-DIPA at 148.4 and 26.9 ppm and the signal of M-DEA at 15.6 ppm are characteristic for this mixture and can be used as probes to distinguish between the two hardening agents. On the other hand, the signals at 24.5 and 26.9 ppm are too close to each other and thus are insufficient for the differentiation.

In the second sample, M-DEA was replaced by DETDA 80 (right side in Figure 6). The specific signals of the hardening agents are obtainable for this sample similar to the previous sample. The observed specific signals of M-DIPA are marked with blue bars, and the specific signals of DETDA 80 are marked with red bars. According to our interpretation of Figure 6, the signals at 148.4 and 26.9 ppm are characteristic for M-DIPA. In addition to this, two signals at 19.0 and 16.8 ppm are obtained in the spectrum of the three-component system (right side in Figure 6), which are attributed to DETDA 80. This clearly demonstrates the feasibility to distinguish M-DIPA and DETDA 80 in a three-component system by means of ^{13}C ssNMR.

3.4. Characterization of a Two-Component Commercial Product. The previous analyses have been performed on model systems with defined composition. To demonstrate that this type of analysis is also applicable to "real-world" systems, we carried out the analysis on a commercial two-component adhesive as a proof of concept. In the first step, the epoxy component of the adhesive has to be identified. For this, the $^{1}H \rightarrow {}^{13}C$ CP MAS NMR spectrum of the commercial product is compared with the spectra of samples containing the typically employed epoxy resins DGEBA or DGEBF and the common hardening agent TETA (Figure 7). For this comparison, it is necessary to know the chemical shift values of all specific signals of the epoxy resins, which are collected in the Supporting Information, Table S1. The corresponding spectra are shown in Figure S1 for DGEBA and in Figure S2 for DGEBF in the Supporting Information.

By comparing the $^{1}H \rightarrow {}^{13}C$ CP MAS NMR spectrum of the commercial product with the spectra of the model systems, it is indicated that DGEBA was used as an epoxy resin in the commercial product (C01). This is demonstrated by the fact that the $^{1}H \rightarrow {}^{13}C$ CP MAS NMR spectrum of the commercial product shows signals with specific chemical shifts at 157.1, 144.0, 128.2, 117.7, 41.9, and 31.6 ppm (dotted lines) that are attributed to DGEBA.

After the successful determination of the resin, the used amine containing hardening agent has to be identified. The comparison of the $^{1}H \rightarrow {}^{13}C$ CP MAS NMR spectrum of the commercial product with reference spectra of samples containing the epoxy resin DGEBA and different amine-containing hardening agents is shown in Figure 8.
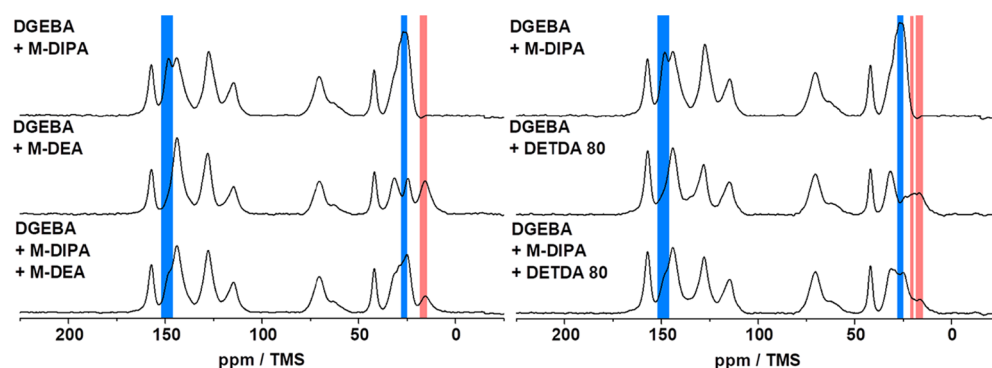
Figure 6. $^1H \rightarrow {}^{13}C$ CP MAS NMR spectra of different three-component systems and spectra of the corresponding two-component systems.
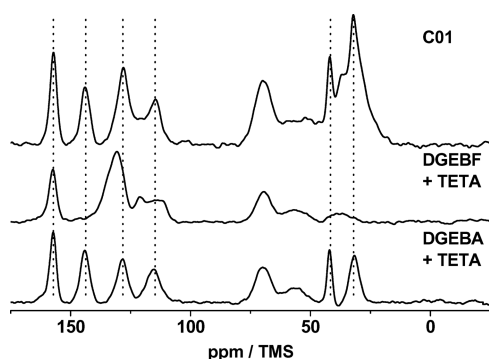

Figure 7. $^1H \rightarrow {}^{13}C$ CP MAS NMR spectra of samples containing the hardening agent TETA and the epoxy resin DGEBA or DGEBF compared with the spectrum of a commercial product.
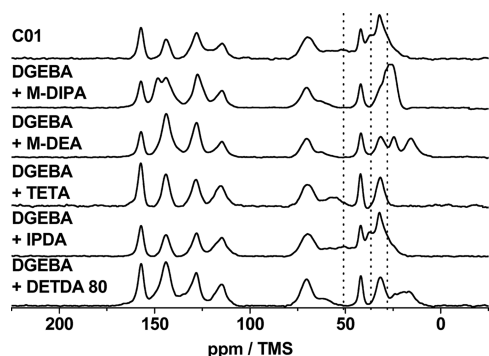

Figure 8. $^1H \rightarrow {}^{13}C$ CP MAS NMR spectra of samples containing the epoxy resin DGEBA and different amine-containing hardening agents compared with the spectrum of a commercial product.

From Figure 8, it is clearly seen that the spectrum of the commercial product (C01) shows additional signals at 51.1, 36.9, and 28.3 ppm besides the signals of DGEBA. These signals indicate the presence of the amine-containing hardening agent IPDA (dotted lines). From this analysis, we can conclude that the commercial product mainly contains the epoxy resin DGEBA and the hardening agent IPDA. A quantification of the two components would require the use of time-consuming direct excitation ^{13}C MAS NMR experiments. Alternatively, a semiquantitative analysis may be performed, which requires the measurement of $^1H \rightarrow {}^{13}C$ CP MAS spectra with different contact times and their analysis to understand the cross-polarization process[25] in the system. Both are beyond the scope of the present work.

3.5. Characterization of a Multicomponent Commercial Product Containing an Additional Retardant.

In a similar fashion, we analyzed a second commercial product of unknown composition (C02). Again, the epoxy component was determined by comparing the $^1H \rightarrow {}^{13}C$ CP MAS spectrum of sample C02 with the spectra of model systems containing TETA and the epoxy component DGEBA or DGEBF.

The $^1H \rightarrow {}^{13}C$ CP MAS NMR spectra in Figure 9 demonstrate that the commercial product C02 contains

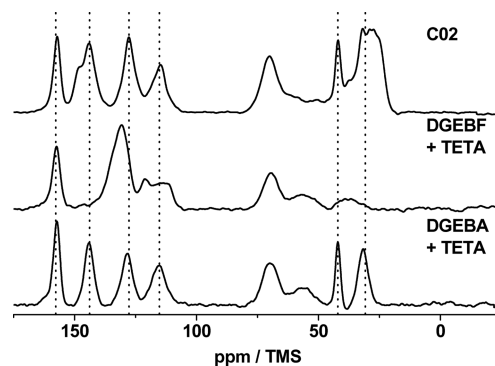**Figure 9.** $^1H \rightarrow {}^{13}C$ CP MAS NMR spectra of samples containing the hardening agent TETA and the epoxy resin DGEBA or DGEBF compared with the spectrum of an unknown sample C02.

specific signals of the epoxy resin DGEBA (dotted lines). Thus, the epoxy component in the unknown sample is identified as DGEBA. Similar to the previous analysis on C01, the used amine-containing hardening agent is determined by comparing the $^1H \rightarrow {}^{13}C$ CP MAS NMR spectrum of sample C02 with reference spectra of samples containing the epoxy resin DGEBA and different amine-containing hardening agents as shown in Figure 10.

From Figure 10, it is clearly visible that the spectrum of sample C02 does not match completely to one of the reference spectra. This let us assume that a third component is present in this sample. Detailed analysis of the spectra shows that the specific signals of the amine-containing hardening agents M-DIPA at 148.4 and 25.8 ppm (blue bars) and IPDA at 51.1 and 36.9 ppm (red bars) match to the signals of sample C02, which implies that C02 contains both M-DIPA and IPDA. Since, in addition to the epoxy component and the amine-containing hardening agent, also flame retardants may be present in the sample, the $^1H \rightarrow {}^{31}P$ CP MAS spectrum of C02 was recorded

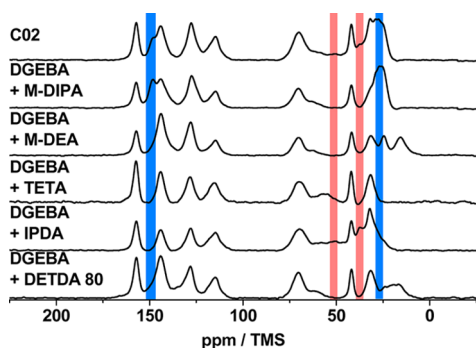**Figure 10.** $^1H \rightarrow {}^{13}C$ CP MAS NMR spectra of samples containing the epoxy resin DGEBA and different amine-containing hardening agents compared with the spectrum of sample C02.

and compared with the spectra of different pure flame retardants.

As shown in Figure 11, the ^{31}P chemical shift of the signal in the spectrum of C02 (10.5 ppm) matches with the signal
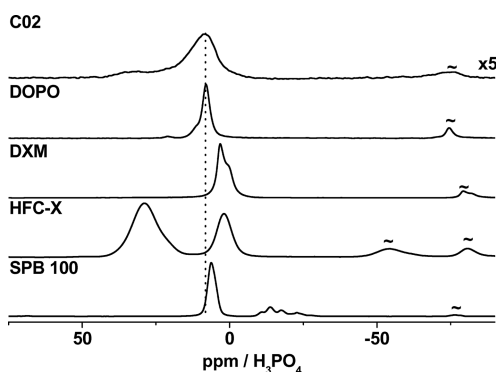

Figure 11. $^1H \rightarrow {}^{31}P$ CP MAS NMR spectra of different pure flame retardants compared with the spectrum of sample C02.

obtained for the flame retardant DOPO (10.4 ppm). This is a strong indication of the presence of DOPO in the sample C02. These results clearly demonstrate that the composition of the commercial product can be analyzed by a combination of ^{13}C and ^{31}P ssNMR.

4. CONCLUSIONS

The present study examines the application potential of ssNMR spectroscopy for the characterization of thermosets with regard to their original components and structure. The evaluation was carried out on defined model systems of epoxy resins and various amine-containing hardening agents. Specific signals in the ssNMR spectra of each epoxy resin, each phosphorus-containing flame retardant, and each used amine-containing hardening agent tested here were identified. To show that the presented analysis method is not only limited to model systems but can also be applied to commercial products, the composition of two commercial products was determined by our approach. The results showed that, also for multi-component samples of unknown composition, the identification of the single components is feasible via specific signals within the sensitivity of solid-state NMR. By combination of solid-state NMR with dynamic nuclear polarization, sensitivity issues may be overcome in the future.

ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04482.

Chemical structures of cross-linked epoxy resins and ^{13}C NMR spectra of epoxy resins, hardening agents, and flame retardants and chemical shift assignments (PDF)

AUTHOR INFORMATION

Corresponding Authors

Gerd Buntkowsky − *Eduard-Zintl-Institute for Inorganic Chemistry and Physical Chemistry, Technical University Darmstadt, 64287 Darmstadt, Germany;* orcid.org/0000-0003-1304-9762; Email: gerd.buntkowsky@chemie.tu-darmstadt.de

Torsten Gutmann − *Eduard-Zintl-Institute for Inorganic Chemistry and Physical Chemistry, Technical University Darmstadt, 64287 Darmstadt, Germany; Institute of Chemistry and Center for Interdisciplinary Nanostructure Science and Technology, University of Kassel, 34132 Kassel, Germany;* orcid.org/0000-0001-6214-2272; Email: gutmann@chemie.tu-darmstadt.de

Author

Timmy Schäfer − *Eduard-Zintl-Institute for Inorganic Chemistry and Physical Chemistry, Technical University Darmstadt, 64287 Darmstadt, Germany*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.9b04482

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Petrie, E. *Epoxy adhesive formulations*; McGraw-Hill: United States of America, 2006.

(2) Ehrenstein, G. W. R. G.; Teawiel, P. Brief characterization of key polymers. In *Thermal Analysis of Plastics*; Carl Hanser Verlag GmbH & Co. KG: 2004.

(3) Ellis, B. *Chemistry and technology of epoxy resins*; New York: Blackie Academic & Professional: London, 1993.

(4) Jay, R. R. Direct titration of epoxy compounds and aziridines. *Anal. Chem.* **1964**, *36*, 667−668.

(5) Garcia, F. G.; da Silva, P. M.; Soares, B. G.; Briones, J. R. Combined analytical techniques for the determination of the amine hydrogen equivalent weight in aliphatic amine epoxide hardeners. *Polym. Test.* **2007**, *26*, 95−101.

(6) Kurr, F. *Praxishandbuch der Qualitäts- und Schadensanalyse für Kunststoffe*; Carl Hanser Verlag: 2014, DOI: 10.3139/9783446437289.

(7) Jue, C.; Juan, L.; Wantai, Y. Curing behavior and thermal properties of trifunctional epoxy resin cured by 4,4'-diaminodiphenyl-methane. *J. Appl. Polym. Sci.* **2009**, *114*, 1976−1983.

(8) Song, T.; Li, Z.; Liu, J.; Yang, S. Synthesis, characterization and properties of novel crystalline epoxy resin with good melt flowability and flame retardancy based on an asymmetrical biphenyl unit. *Polym. Sci., Ser. B* **2013**, *55*, 147−157.

(9) Puype, F.; Samsonek, J. Direkte Identifizierung von Hochleistungspolymeren - Reaktive und konventionelle Pyrolyse-GC-MS. *News Analytik* **2015**, 1−2.

(10) Pfitzmann, A.; Fliedner, E.; Fedtke, M. Curing of epoxy resins with dicyandiamide: NMR and IR investigation of isolated main products. *Polym. Bull.* **1994**, *32*, 311−317.

(11) Mertzel, E.; Koenig, J. L. Application of FT-IR and NMR to epoxy resins. *Adv. Polym. Sci.* **1986**, *75*, 73−112.

(12) Thuillier, F. M.; Jullien, H.; Grenier-Loustalot, M. F. The structure of microwave-cured epoxy resins studied by FT i.r. and ^{13}C NMR CPMAS. *Polym. Commun.* **1986**, *27*, 206−208.

(13) Kisseross, K.; Pasztor, M. IR studies on epoxy-resin systems cross-linked with dicarboxylic-acid anhydride. *Magy. Kem. Foly.* **1987**, *93*, 16−23.

(14) Attias, A. J.; Bloch, B.; Laupretre, F. Chemical-structure of networks resulting from curing of N,N-diglycidylaniline-type resins with aromatic amines. IV. Characterization of TGDDM DDS and TGDDM DDM networks by high-resolution solid-state ^{13}C-NMR. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3445−3466.

(15) Alessi, S.; Caponetti, E.; Güven, O.; Akbulut, M.; Spadaro, G.; Spinella, A. Study of the curing process of DGEBA epoxy resin through structural investigation. *Macromol. Chem. Phys.* **2015**, *216*, 538−546.

(16) Longiéras, N.; Sebban, M.; Palmas, P.; Rivaton, A.; Gardette, J. L. Degradation of epoxy resins under high energy electron beam irradiation: Radio-oxidation. *Polym. Degrad. Stab.* **2007**, *92*, 2190−2197.

(17) Alessi, S.; Spinella, A.; Caponetti, E.; Dispenza, C.; Spadaro, G. Structural investigation of e-beam cured epoxy resins through solid state NMR. *Radiat. Phys. Chem.* **2012**, *81*, 1328−1331.

(18) Grenier-Loustalot, M. F.; Grenier, P. The role of impurities in the mechanisms and kinetics of reactions of epoxy resins and their effects on final resin properties. *Br. Polym. J.* **1990**, *22*, 303−313.

(19) Metz, G.; Wu, X. L.; Smith, S. O. Ramped-amplitude cross polarization in magic-angle-spinning NMR. *J. Magn. Reson., Ser. A* **1994**, *110*, 219−227.

(20) Bennett, A. E.; Rienstra, C. M.; Auger, M.; Lakshmi, K. V.; Griffin, R. G. Heteronuclear decoupling in rotating solids. *J. Chem. Phys.* **1995**, *103*, 6951−6958.

(21) Kleiner, H.-J. Method for preparing 6H-Dibenzo[c,e][1,2]-oxaphosphorin-6-one. US5481017A, 1996.

(22) Rathfelder, P. R. H.; Dietrich, J. Process for the preparation of a DOP-containing mixture. WO/1997/000878, 1997.

(23) Zich, T.; Freidel, F. J.; Mehofer, B.; Döring, M.; Ciesielski, M.; Burk, B. Verfahren zur Herstellung von phosphorhaltigen Flamm-schutzmitteln. WO/2014/032070, 2014.

(24) Zhang, S.; Ali, S.; Ma, H.; Zhang, L.; Wu, Z.; Wu, D.; Hu, T. S. Preparation of poly(bis(phenoxy)phosphazene) and [P-31]P NMR analysis of its structural defects under various synthesis conditions. *J. Phys. Chem. B* **2016**, *120*, 11307−11316.

(25) Stejskal, E. O.; Memory, J. D. *High Resolution NMR in the Solid State Fundamentals of CP-MAS*; Oxford University Press: New York, 1994; p 1−189.