

Characterization of Unsaturated Polyester and Alkyd Resins Using One- and Two-Dimensional NMR Spectroscopy

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ABSTRACT: One- (1D) and two-dimensional (2D) ^1H - and ^{13}C -NMR spectroscopy was used to characterize polyester and alkyd resins used in the coatings industry. The wealth of chemical composition information of the ^1H - and ^{13}C -NMR 1D spectra of the resins is revealed through 2D NMR experiments that spread chemical shifts in two dimensions, thus facilitating the peak assignment of the various components of the resins. It is shown that the types of polyols, acids, and vegetable oils used to modify the resins

can be efficiently traced by NMR spectroscopic techniques. Information on the quantitative composition of the resins and especially the abundance of unsaturated fatty acid double bonds, which influences resin dryability and hardness, can be easily extracted from the ^1H -NMR spectra upon successful assignment. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1881–1888, 2003

Key words: NMR; crosslinking; resins; coatings

INTRODUCTION

Unsaturated polyester and alkyd resins are industrially important network polymers.^{1,2} Alkyd resins are widely used as coatings, paints, adhesives, and additives, whereas unsaturated polyesters are used in combination with glass reinforcement for the preparation of hard polymeric materials for marine applications. Alkyd resins are prepared from polyfunctional monomers, so that crosslinking occurs during the polyesterification reaction. Phthalic anhydride is by far the most common dibasic acid derivative used, whereas glycerol, pentaerythritol (PE), and trimethylolpropane (TMP) are common polyalcohols.^{3,4} Unsaturated polyester resins are crosslinked by a subsequent addition polymerization reaction through reactive double bonds incorporated into the polyester backbone.⁵ Oil-modified alkyds are prepared by transesterification of the polyalcohol with triglycerides (TGs) contained in synthetic or natural oils before polymerization, or by conducting the polymerization in the presence of fatty acids and heating. Addition of a suitable solvent, driers, and pigments leads to alkyd paints that dry in the presence of atmospheric oxygen through a free-radical crosslinking reaction. The rapidity of drying depends on the amount of oil fatty acids incorporated in the alkyd resin and their degree of unsaturation.

This study reports the full characterization of the chemical structure of a series of polyester resins by ^1H - and ^{13}C -NMR spectroscopy. It is well known that polymers in solution produce NMR spectral signals broadened by the effects of conformational heterogeneity and restricted molecular motion.⁶ The NMR spectra of resins are further complicated because of the multitude of functional monomers used in their synthesis and because some of these monomers are mixtures themselves (e.g., natural oils). The assignment of the NMR spectra has been achieved by employing gradient two-dimensional (2D) NMR spectroscopic techniques. 2D NMR is highly suited for the characterization of polymeric materials because of the increased resolution offered by spreading chemical shift information in two spectral dimensions.⁶ Pulse field gradients have been recently^{7,8} exploited in 2D NMR for coherence selection, avoiding time-consuming phase-cycling schemes and improving considerably the resolution of signals in crowded regions.

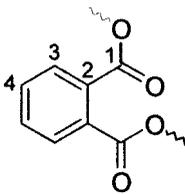
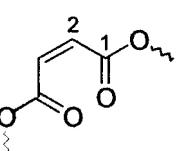
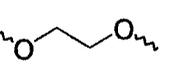
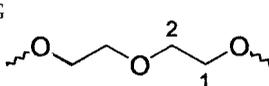
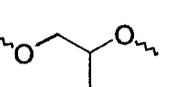
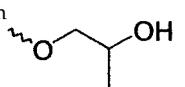
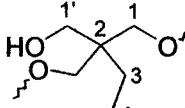
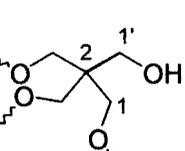
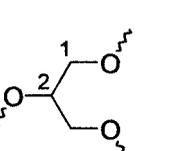
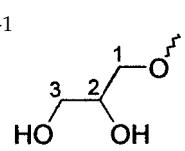
EXPERIMENTAL

Materials

All samples were used as supplied by Interchem Hellas, diluted in white spirit or xylenes. S1 is a long-oil alkyd resin, S2 is a short-oil alkyd resin, S3 and S4 are short-oil polyols, and S5 is an oil-free polyester resin. The available manufacturer information on the resins was reported previously.¹⁴ Table I summarizes the chemical structure of the monomeric units of the resins, and the notation used throughout this report.

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TABLE I
Monomer Units Identified (+) on Resins S1–S5, and Their ¹H- and ¹³C-NMR
Chemical Shifts Measured in Acetone-d₆ Solutions

Monomer unit ^a	NMR chemical shifts [δ]				Resin				
	¹³ C-NMR		¹ H-NMR		S1	S2	S3	S4	S5
PHT 	166.8	C-1			+	+	+	+	+
	132.2	C-2							
	131.0	C-3	7.55	H-3					
	129.0	C-4	7.75	H-4					
MA 	164.1	C-1							+
	133.2	C-2	6.85	H-2					
EG 	62.8	CH ₂	4.6	CH ₂					+
DEG 	64.2	C-1	4.4	H-1					+
	68.6	C-2	3.75	H-2					
PG 	70.1	CH	5.4	CH				+	+
	66.9	CH ₂	4.4	CH ₂					
	15.8	CH ₃	1.4	CH ₃					
PGm 	70.5	CH	4.1	CH				+	+
	66.8	CH ₂	4.4	CH ₂					
	19.1	CH ₃	1.2	CH ₃					
TMP 	66.0	C-1	4.2	H-1			+	+	
	64.2	C-1'	3.6	H-1'					
	41.5/ 42.7	C-2							
	23.5	C-3	1.6	H-3					
	7.5	C-4	1.0	H-4					
PE 	63.2	C-1	4.2	H-1	+		+		
	61.1	C-1'	3.7	H-1'					
	44.4/ 43.0	C-2							
TG 	69.2	C-2	nd ^b	nd	+	+	+		
	62.2	C-1	nd	nd					
MG-1 	63.5	C-3	H-3	3.6		+	+		
	65.2	C-1	H-2	4.2					
	70.5	C-2	H-2	4.0					
Oleic acid					+	+	+		
Linoleic acid					+	+	+		
Linolenic acid					+	+			
Lauric acid					+	+	+	+	
Eleostearic acid						+			
Ricinoleic acid							+		
Abietic acid						+			

^a PHT, phthalate ester; MA, maleate ester; EG, ethylene glycol; DEG, diethylene glycol; PG, propylene glycol; PGm, propylene glycol end group; TMP, trimethylolpropane; PE, pentaerythritol; TG, triglyceride; MG-1, 1-monoglyceride.

^b Not determined.

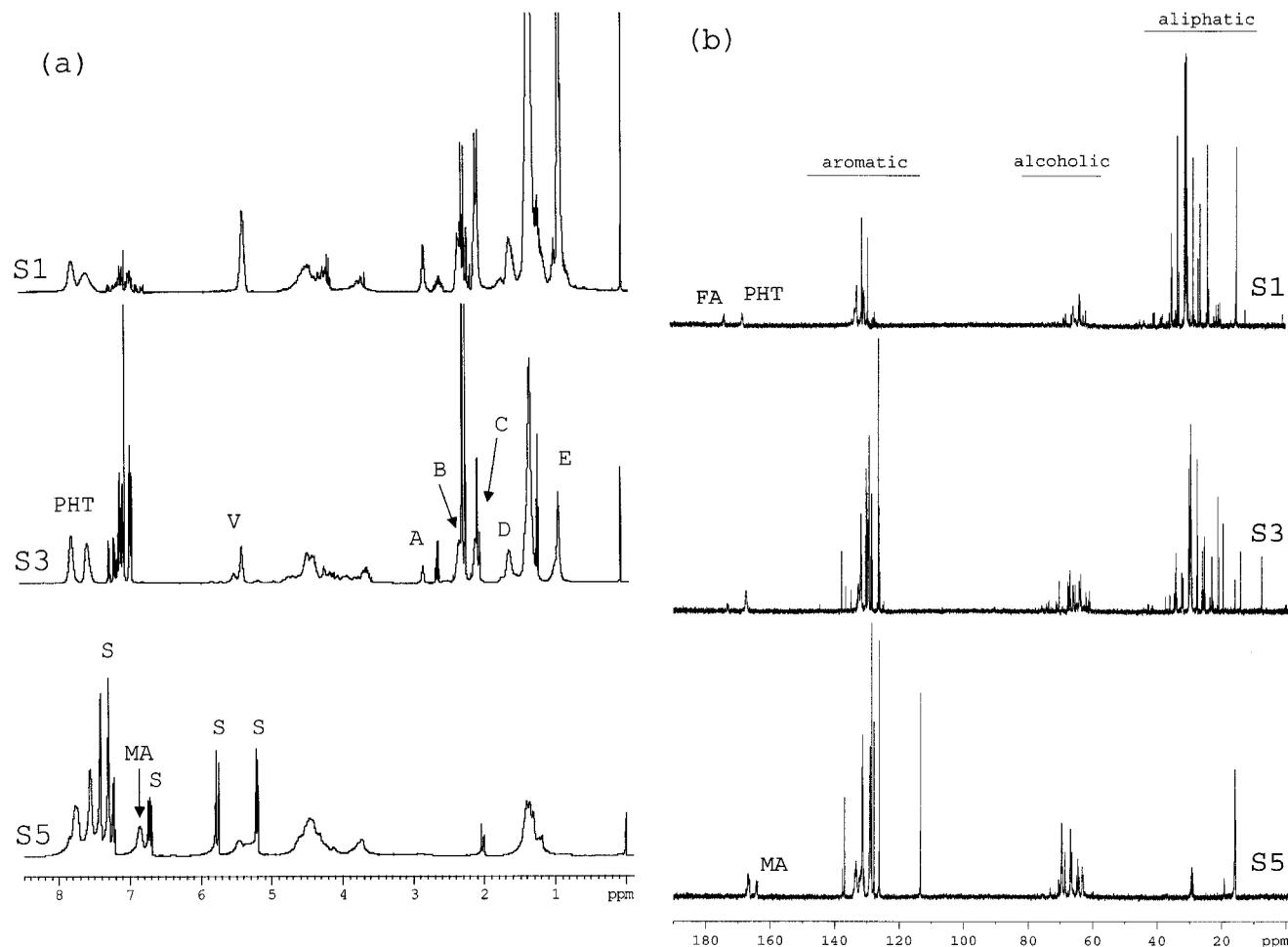


Figure 1 (a) ¹H-NMR spectra of resins S1, S3, and S5 at 500.1 MHz in acetone-*d*₆. S indicates the styrene solvent proton peaks in S5. See text for other labeling. (b) ¹H-decoupled ¹³C-NMR spectra of resins S1, S3, and S5 at 125.4 MHz in acetone-*d*₆. See text for labeling.

NMR spectroscopy

¹H- and ¹³C-NMR spectra were obtained on a Bruker AMX-500 spectrometer (Bruker Instruments, Billerica, MA) operating at 500.1 and 125.4 MHz for the two nuclei, respectively, at a probe temperature of 30°C in (CD₃)₂CO. Chemical shifts are reported relative to internal TMS.

¹H-¹H homonuclear gradient correlated spectroscopy (COSY) 2D NMR spectra⁹ were obtained using 256 increments of 1K data points, 16 scans, and four dummy scans with a recycle delay of 1 s. ¹H-¹³C heteronuclear gradient multiple quantum correlation (HMQC) 2D NMR spectra⁹ were obtained using 128 increments of 1K data points, 16 scans, and four dummy scans with a recycle delay of 1 s. This experiment was optimized for one bond ¹H-¹³C couplings of 140 Hz by setting the evolution delay to 3 ms. Before Fourier transformation all 2D data sets were zero-filled to a 1K × 1K matrix, and a square-sinusoidal window function was used for processing. No phase correction was applied and the 2D spectra are displayed in magnitude mode.

RESULTS AND DISCUSSION

One-dimensional (1D) ¹H-NMR spectra

Figure 1(a) presents the ¹H-NMR spectra of resins S1, S3, and S5 acquired in acetone-*d*₆. The low field region δ 6.5–8.0 contains aromatic protons originating from phthalic (PHT) and maleic (MA) ester fragments of the polyesters. Also in this region appear the aromatic protons of the resin solvents [e.g., white spirit (S1), xylenes (S3), and styrene (S5)]. The middle region of the proton spectra (δ 3.5–6.0) contains peaks from the vinyl protons of the fatty acids (FA) incorporated in the alkyd resins (V, δ 5.3), and from protons neighboring hydroxyl or ester groups. The latter group includes α-hydroxy protons from both alcohols and glycerides incorporated in the polymer network. The peaks in this region are broad and signals from different fragments severely overlap, making their direct assignment impossible. The high field region of the proton spectra (δ 0–3.5) contains mainly methylene and methyl peaks from fatty acid protons, as can be seen in the spectra of S1 and S3 in Figure 1(a). Signals are

observed at the positions expected for $V-CH_2-V$ (A), $-CH_2-COOH$ (B), $-CH_2-V$ (C), $-CH_2-CH_2-COOH$ (D), and $-CH_3$ (E) protons of fatty acids in these spectra.^{11,12} Nevertheless, the 1H -NMR spectrum of S5, the only resin that contains no fatty acids, also shows signal intensity from alcohols in this region. Thus, alcohols and fatty acids give possibly overlapping signals in the 1H -NMR spectra of S1–S4, and therefore make the quantification of proton signals ambiguous.

1D ^{13}C -NMR spectra

Figure 1(b) presents the 1H -decoupled ^{13}C -NMR spectra of polyesters S1, S3, and S5. In the region δ 160–180 the carbonyl groups of phthalic, maleic, and fatty acid esters appear at well-separated chemical shifts, which are summarized in Table I. The aromatic carbon region (δ 125–135) of the NMR spectra contains mainly signals from PHT,¹³ MA,¹³ and from vinyl carbons of unsaturated fatty acids (UFA). The presence of UFA in resins S1, S3, and MA in S5 was verified by signals observed in the carbonyl and aromatic region of the spectra. However, the aromatic spectral region is rather crowded in resins dissolved in xylenes (S2–S4), given that multiple peaks arising from xylene aromatic carbons appear in this region.¹⁰ The region δ 60–75 contains peaks originating from carbon atoms directly bonded to an oxygen atom, so it can provide information regarding the types of alcohols incorporated in the polyester resins. The assignment of peaks in this region, however, cannot be made by simple comparison with the NMR spectra of model free and esterified alcohols.^{10,13} This is because of the structural similarity of the alcohols used as starting materials, and the fact that NMR chemical shifts are frequently shifted with respect to those of model low molecular weight compounds. The high field spectral region (δ 0–50) of the ^{13}C -NMR spectra contains mainly methylene and methyl carbon peaks of fatty acids¹¹ and alcohols^{10,13} present in the resins. Thus it is very useful for the identification of the oils or fatty acids used for the modification of the resins. The full assignment of the ^{13}C - and 1H -NMR spectra of the resins was accomplished using gradient 2D NMR spectroscopy, as described in the following sections.

2D NMR spectra

The spread of chemical shift information in two spectroscopic dimensions greatly enhances the ability to distinguish between multiple components of broad signals in 1D NMR spectra. For all five resins, 1H - 1H gCOSY and 1H - ^{13}C gHMQC 2D NMR spectra were acquired for the same samples used to obtain the 1D NMR spectra. The 1H - 1H gCOSY spectra reveal connectivities between neighboring protons in the polymer chains, whereas the 1H - ^{13}C gHMQC spectra cor-

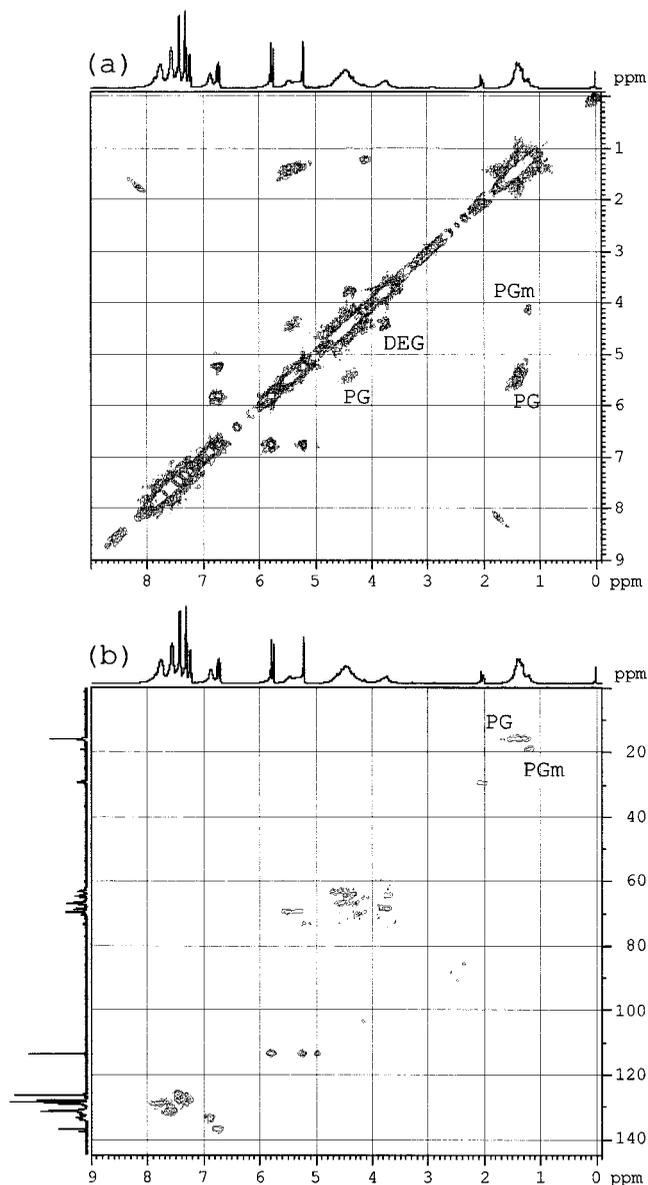


Figure 2 (a) 1H - 1H homonuclear gCOSY 2D NMR spectrum of polyester S5. Labels indicate crosspeaks by alcohols PG, DEG, and PGm end groups (see text). (b) 1H - ^{13}C heteronuclear gHMQC 2D NMR spectrum of polyester S5. Labels indicate the methyl peaks of backbone PG and PGm end groups.

relate carbon atoms with their directly bonded protons, thus allowing the assignment of both 1H and ^{13}C 1D spectra. The monomer units detected with the help of 2D NMR in the resins are reported in Table I, along with their 1H - and ^{13}C -NMR chemical shifts in the 1D spectra acquired in acetone- d_6 .

Polyester S5

Figure 2(a) presents the 2D gradient 1H - 1H gCOSY spectrum of polyester S5. The observation of crosspeaks attributed to vicinal J-coupling between the

CH/CH₂ and CH/CH₃ protons of propylene glycol (PG) incorporated in the polyester backbone allows the assignment of PG.¹⁰ The methylene protons H-1 and H-2 of backbone diethylene glycol (DEG) are also identified¹⁰ by their crosspeak in the spectrum of Figure 2(a). Furthermore, the small methyl signal at δ 1.2 shows connectivity with a proton at δ 4.1. These two signals are assigned to CH₃ and CH protons belonging to PG end groups of the polyester S5, denoted as PGm in Figure 2 and Table I. The ¹H-¹³C gHMQC spectrum of Figure 2(b) shows two peaks in the methyl region (top right), thus proving the existence of two distinct types of methyl group in the polyester, originating from PG and PGm units of the resin. Moreover, this spectrum makes possible the assignment of the carbon and proton signals of PG, PGm, ethylene glycol (EG), DEG, PHT, and MA groups in the 1D NMR spectra, reported in Table I.

Polyols S3 and S4

The 2D ¹H-¹H gCOSY and ¹H-¹³C gHMQC spectra of polyol S4 are presented in Figure 3(a) and (b), respectively. Starting with the spectrum in Figure 3(b), the presence of two types of methyl groups is noted, which correspond to TMP and lauric ester units.^{11,13} These can be differentiated by their large ¹³C-NMR chemical shift differences: TMP methyl (C-4) at δ 7.5 and lauric ester methyl at δ 14.0. Both methyl peaks show the expected connectivities in the gCOSY spectrum of Figure 3(a): TMP H-4 with H-3, and lauric ester methyl group with the intense methylene peak at δ 1.2. Another salient feature of the gCOSY spectrum is the connectivities of the proton peak at δ 5.4 with protons at δ 1.4 and 4.4. This proton system is assigned to PG, which is verified as a minor alcohol constituent present in polyol S4. This finding is in agreement with a recent ³¹P-NMR analysis of phosphitylated S4.¹⁴ This assignment was further supported by observing the signal corresponding to the methyl group of PG at δ 16.2 in the ¹³C-NMR spectrum of S4 (not shown). PG and TMP end groups were also identified in polyol S4, as reported in Table I.

Figure 4 presents the 2D ¹H-¹H gCOSY spectrum of polyol S3. Crosspeaks in this spectrum can be divided in two groups, originating from either linoleic or ricinoleic ester groups incorporated in the polyol. The broad ¹H peak at δ 3.6 contains a proton that correlates with a carbon at δ 71.0 in the gHMQC 2D spectrum of resin S3 (not shown), and is identified as the -CH(OH)- proton of ricinoleic acid,¹³ which is the main fatty acid in castor oil. This assignment is verified by the crosspeaks at δ 3.6/2.25 (-CH₂-CH(OH)-CH₂-V) and δ 3.6/1.39 (-CH₂-CH(OH)-CH₂-V) in the 2D ¹H-¹H gCOSY spectrum of S3 in Figure 4 (marked as RIC). Other crosspeaks observed in this spectrum originate from the protons of linoleic acid at

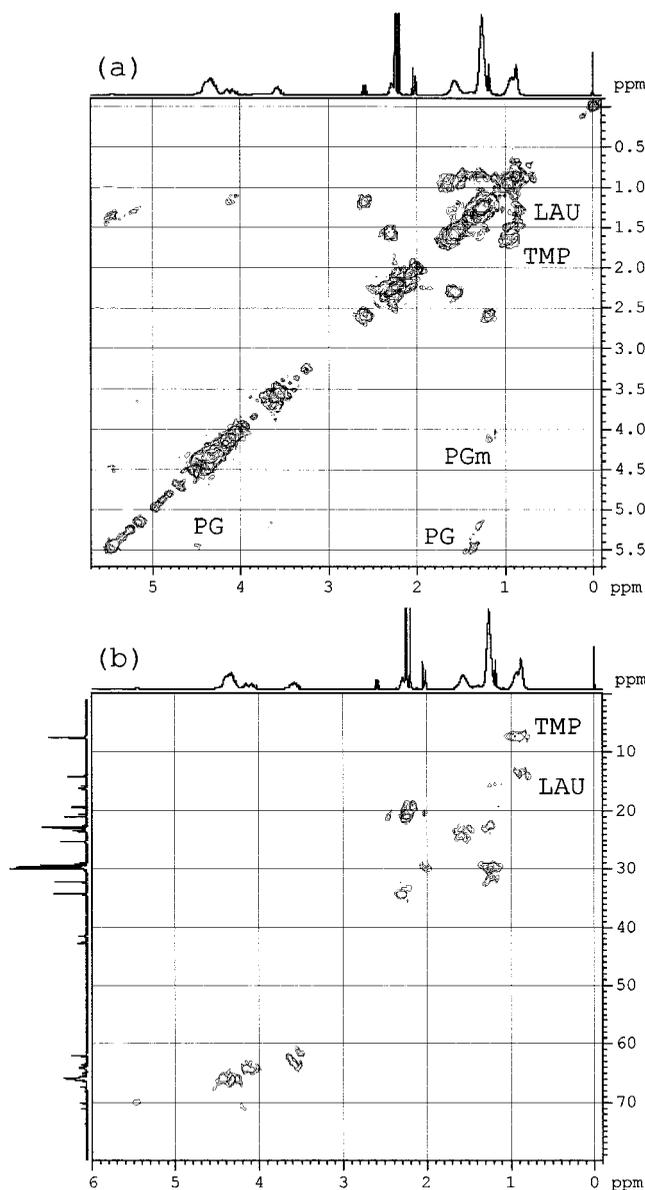


Figure 3 (a) ¹H-¹H homonuclear gCOSY 2D NMR spectrum of polyol S4. Labels indicate crosspeaks by lauric ester protons (LAU), and alcohols TMP, PG, and PGm (see text). (b) ¹H-¹³C heteronuclear gHMQC 2D NMR spectrum of polyester S4. Labels indicate the methyl peaks of lauric ester (LAU) and TMP.

well-expected positions,^{11,12} except from the characteristic H-4/H-3 crosspeak of TMP [compare with Fig. 3(a)], which indicates that TMP is a minor component of resin S3. The alcoholic regions of the ¹H spectra of S3 and S4 are almost identical, containing mainly -CH₂-OCOR units at δ 4-5 and free -CH₂OH units at δ 3.6 originating from TMP and PE, at well-expected positions.¹³

Alkyd resins S1, S2

Figure 5(a) depicts the 2D ¹H-¹H gCOSY spectrum of alkyd resin S2. Several overlapping methyl peaks are

observed in the region δ 0.85–1.0 of the ^1H -NMR spectrum. The methyl peak at about δ 0.95 in Figure 5(a) correlates with a proton peak at δ 2.0, which proves that linolenic acid's characteristic fragment $\text{CH}_3\text{—CH}_2\text{—CH=CH—}$ is present in resin S2. The correlation of the methyl peak at δ 0.85 with the intense methylene peak at δ 1.3 is attributed to oleic, linoleic, and saturated fatty acids, as expected for a linseed oil-modified alkyd resin.¹¹ The rest of the crosspeaks in the 2D gCOSY spectrum of Figure 5(a) also originate from linseed oil unsaturated fatty acids present in resin S2 (compare with Fig. 4). Figure 5(b) presents the vinyl region of the 2D ^1H - ^{13}C gHMQC spectrum of resin S2. Of special interest are the two peaks marked with an arrow, corresponding to vinyl carbons with chemical shifts of δ 120.9 and 123.2, which are assigned to the vinyl carbons of abietic acid,¹³ the major constituent of rosin. Close examination of the ^{13}C spectrum of resin S2 at increased vertical scale revealed the presence of several small intensity peaks originating from the rest of the carbon atoms of abietic acid at the expected chemical shift positions.¹³ Also, the isopropyl methyl groups of abietic acid were detected in the broad methyl proton resonance at δ 1.0 [Fig. 5(a)], thus verifying that resin S2 was modified with small amounts of rosin. The presence of another fatty acid, eleostearic acid (and thus, modification of S2 with tung oil) was indicated by noting the presence of two carbon peaks at δ 32.2 and 32.8 in the ^{13}C -NMR spectrum of S2. Linseed oil fatty acids do not contribute in

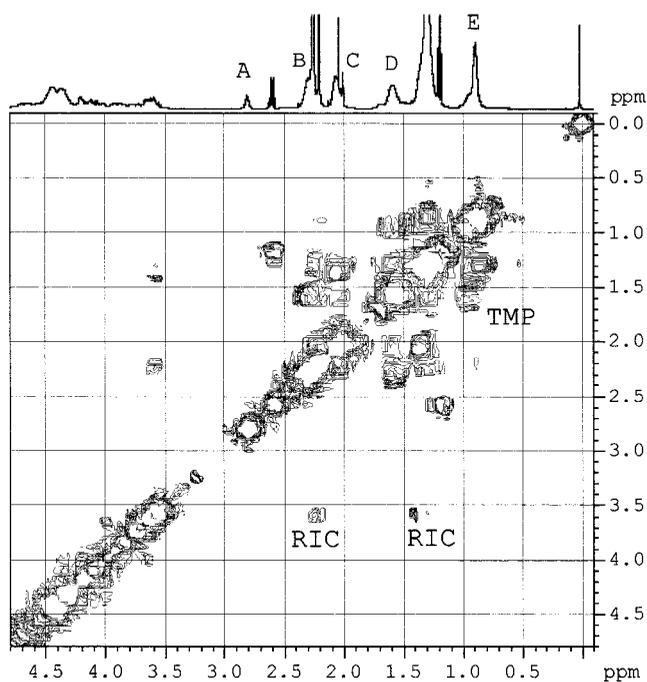


Figure 4 ^1H - ^1H homonuclear gCOSY 2D NMR spectrum of polyol S3. Crosspeaks attributed to ricinoleic acid (RIC) and TMP are labeled. For labeling of linoleic acid protons see text.

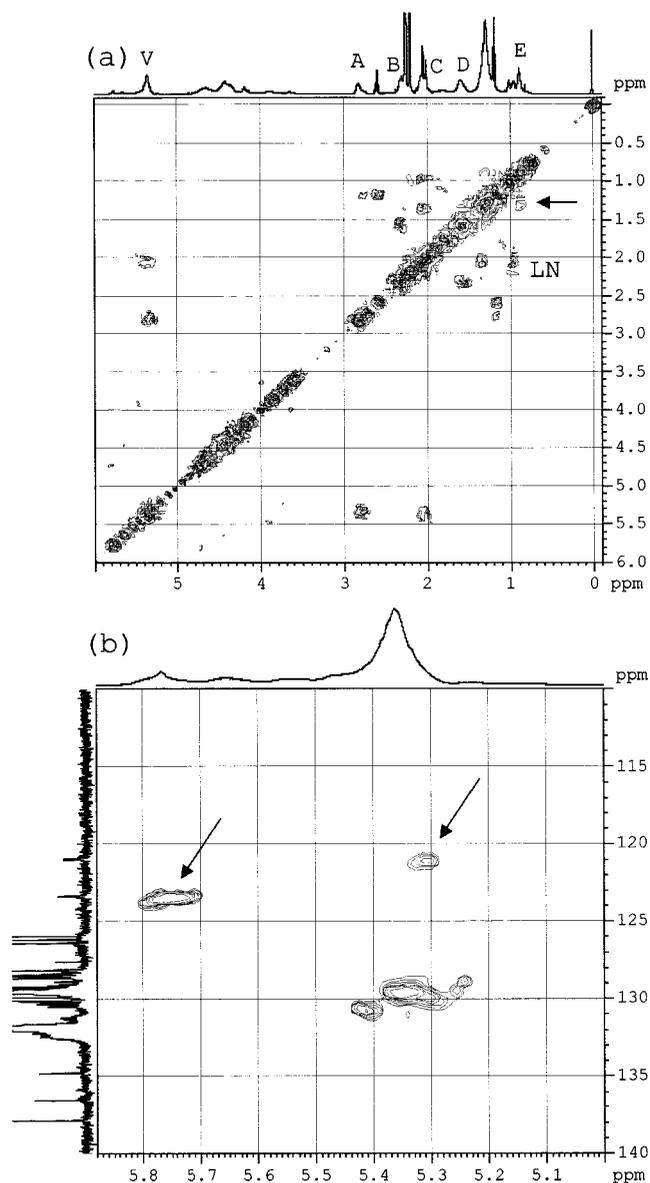


Figure 5 (a) ^1H - ^1H homonuclear gCOSY 2D NMR spectrum of alkyd resin S2. The methyl crosspeak of linolenic acid (LN) is labeled, whereas an arrow indicates the methyl crosspeak attributed to other fatty acid methyl groups. For labeling of fatty acid protons see text. (b) Vinyl region of the ^1H - ^{13}C heteronuclear gHMQC 2D NMR spectrum of alkyd resin S2. Arrows indicate peaks of the vinyl carbons of abietic acid.

this spectrum region,¹¹ where methylene carbons C-15 and C-16 of eleostearic acid are expected. Finally, main-chain and end-group pentaerythritol and various glyceride structures were identified in this resin (see Table I) with the help of its ^1H - ^{13}C gHMQC spectrum.

Resin S1 is a soya oil-modified resin, and thus crosspeaks from linoleic acid, pentaerythritol, and phthalate groups dominate its 2D NMR gCOSY and gHMQC spectra (not shown), as expected. No minor

TABLE II
Chemical Composition (mol %) of Polyester and Alkyd Resins by ¹H-NMR Spectroscopy^a

Resin	Diacid (mol %)			Fatty acid (FA) ^c (mol %)	Alcohol (mol %)						UN ^d	TUN ^d
	PHT	MA	Total ^b		GL	PE	TMP	PG	DEG	Total		
S1	24	—	24 (24)	49 (63)	17	10	—	—	—	27	0.71	0.35
S2	32	—	32 (34)	34 (36)	35	—	—	—	—	35	1.03	0.32
S3	38	—	38 (38)	26 (41)	2	22	12	—	—	36	0.75	0.20
S4	43	—	43 (50)	19 (25)	—	—	33	5	—	38	—	—
S5	33	16	49	—	—	—	—	37	14	51	—	—

^a GL is the glycerol content; for other abbreviations used see Table I.

^b The phthalic anhydride content (wt %) in the feed is given in parentheses.

^c Resin S2 contains 3.5% abietic acid; S3 contains 6.5% linoleic acid and 19.5% ricinoleic acid; S4 contains only lauric acid. Oil lengths (wt %) are given in parentheses.

^d UN is the average number of double bonds per fatty acid molecule, and TUN = (UN × FA)/100. NMR integration error ~ 5%, leading to errors of <10% for the % molar composition.

components were identified in this resin by its NMR spectra.

Resin chemical composition by ¹H-NMR

Once the components of the ¹H-NMR peaks have been determined with the help of 2D NMR techniques, their integrals, which are related to the molar concentration of each type of proton in the resin, can be used to extract chemical composition information. Phthalate and maleate ester units were quantified by their corresponding aromatic proton peaks, whereas the fatty acid content FA was calculated from the methylene proton peak D (see Fig. 1 for peak positions). The molar ratio of the different alcohols present in the resins was calculated from the corresponding methylene integrals in the region δ 3.5–4.5 (PE, GL, DEG) and/or the region δ 1.0–1.6 (TMP). When an oil has been used for the modification, the intensity of glycerol protons introduced by oil triglycerides was taken into account. Abietic acid in S2 was quantified by its isopropyl methyl groups at δ 1.0. Only linoleic acid contributes to peak A (Fig. 1), so this peak was used to calculate the amount of linoleic acid in S3. The molar ratios of the different components of resins S1–S5, as calculated by ¹H-NMR, are presented in Table II. It is interesting to note that the NMR molar percentage of phthalate esters PHT in Table II is similar to the percentage of phthalic anhydride in the polymerization feed, whereas FA is always found to be smaller compared to the percentage oil length of the resins. This is expected, given that fatty acids and triglycerides both have larger molecular weights than that of PHT, and their weight percentage in the feed overestimates their molar ratio in the final polymer.

The abundance of double bonds in alkyd resins is directly related to their drying and hardening properties, given that in general an increasing number of double bonds will lead to faster hardening through crosslinking of neighboring fatty side chains during

drying. Table II reports the values of UN, which is the average number of double bonds per fatty acid molecule in each resin. This parameter is calculated by comparing the integral ratio of peak V (vinyl protons) to peak D [see Fig. 1(a)], the latter peak referring to all fatty acids present in a resin. Resin S2 has the highest value of UN in Table II because of its high content in linolenic and eleostearic acid, both of which have three double bonds per fatty acid molecule. Additionally, the presence of conjugated double bonds in eleostearic acid gives S2 very fast drying capabilities. However, the actual number of double bonds in a resin also depends on the molar percentage of oil in the resin (i.e., long versus short oil alkyds). To take this factor into account, we calculated TUN, the total unsaturation of a resin as (UN × FA)/100, which is a parameter properly normalized to the mol % of fatty acids in the resins, as measured by ¹H-NMR. As can be seen in Table II, the alkyd resins S1 and S2 now have the highest total unsaturation, TUN, whereas polyol S3 has a much lower TUN value of 0.20. The order S1 > S2 is in agreement with the superior hardening properties of resin S1 versus S2, as specified by the resin manufacturer, showing that TUN can serve as a useful index of the hardening properties of alkyd resins.

CONCLUSIONS

This study describes the application of advanced 1D and 2D ¹H- and ¹³C-NMR techniques for the characterization of various alkyd resins, polyols, and polyesters used in the coatings industry. 2D NMR allows the spreading of chemical shift information in two dimensions, and is ideal for polymers exhibiting complex 1D NMR spectra with broad and/or featureless peaks. NMR spectroscopy can thus provide a wealth of information regarding the chemical composition of the resins (i.e., the type of polyols, fatty acids, and vegetable oils used in the preparation of the resins).

^{13}C -NMR spectroscopy, with its wide chemical shift range, is ideally suited for the detection of materials present in small quantities. For example, the presence of eleostearic and abietic acids in resin S2 points to the modification of the resin by tung oil and rosin, respectively. ^1H -NMR, on the other hand, provides quantitative information about the molar percentages of resin components on the final product. This type of information is valuable because the weight percentage of monomers in the feed is only an approximation to the final resin composition. ^1H -NMR also provides information regarding the double bond content of the alkyd resins, which is useful to evaluate their hardening and drying properties. Further work in the direction of characterizing the oxidation and crosslinking products of alkyd resins on exposure to light, using high-resolution and solid-state NMR spectroscopy, is in progress in our laboratory.

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