Quantitative Determination of the Distribution of Free Hydroxylic and Carboxylic Groups in Unsaturated Polyester and Alkyd Resins by ^{31}P-NMR Spectroscopy

A. SPYROS

NMR Laboratory, Department of Chemistry, University of Crete, 71409 Heraklion, Crete, Greece

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ABSTRACT: Quantitative ^{31}P-NMR spectroscopy is used to measure the hydroxyl and carboxyl content of some polyester resins (short- and long-oil alkyds, polyols, polyesters) through derivatization of the —OH protons with 2-chloro-4,4,5,5-tetramethyldioxaphospholane **I**. This methodology is shown to be superior to titration methods, since it can (a) discriminate between primary and secondary hydroxyl groups, (b) identify individual alcohols and acids present, (c) measure the amount of free fatty acids in oil-modified alkyds, and (d) provide lower limits for the number-averaged molecular weight of the resins and exact values for linear polyesters. A major advantage of the technique is that the NMR measurements are made on unmodified resins in their final product form supplied by the manufacturer. The information obtained is important for the characterization of the alkyd resins and affects drastically their physical properties and performance as products. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1635–1642, 2002

Key words: ^{31}P-NMR spectroscopy; polyesters; alkyd resin; polymer NMR

INTRODUCTION

Alkyd resins are complex network polyesters widely used in the paint and coatings industry.[1] They are prepared through a reaction among fatty acids (vegetable oils such as soya, seed, or tall oil), polyols (i.e., glycerol, pentaerythritol, trimethylolpropane, ethylene glycol), and a dibasic acid or anhydride, such as phthalic anhydride, maleic anhydride, or isophthalic acid.[2,3] Their main difference with other polyester resins is that they contain unsaturated fatty acid side groups. Apart from the resin, alkyd paints contain a suitable solvent (hexane or mineral spirits), a set of driers, such as various metal naphthenates, and pigments, as well as other additives which improve performance.[4] In the presence of atmospheric oxygen, alkyd paints dry (or more accurately harden) through a complex free-radical crosslinking reaction of the side-chain fatty acid double bonds.[5] The role of the drier is to catalyze the decomposition of the hydroperoxides, initially formed by addition of oxygen to the double bond, into free radicals. The rapidity of the drying process as well as the hardness of the final coating depend on the amount of oil fatty acids incorporated into the alkyd resin (the oil length) and their degree of unsaturation. Long-oil alkyds contain 60% fatty acid by weight: medium-oil, 40–60%; and short-oil, less than 40%. Alkyd resins that contain only saturated fatty acids are not able to dry at room temperature and are used mainly as plasticizers or in oven-dried coatings.[3,4] Polyols are alkyd resins with a specified high

Correspondence to: A. Spyros (aspyros@chemistry.uoc.gr).

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Table I Composition Data of Polyester Resins S1–S5

Sample	Oil Type	Oil Length (%) (Approx.)	Phthalic Anhydride (%)	Polyol[a]
S1	Soya	63	24	PE
S2	Linseed/tung	36	34	GL
S3	Castor + linoleic acid	41	38	PE
S4	Lauric acid	25	50	TMP
S5	—	—	33[b]	PG, DEG
			16[b] (maleic)	

[a] PE, pentaerythritol; GL, glycerol; TMP, trimethylolpropane; PG, propylene glycol; DEG, diethylene glycol.
[b] By ^{1}H-NMR spectroscopy.

hydroxyl content that can react with compounds containing epoxy, isocyanate, or melamine groups and produce hybrid coatings with superior performance.

Unsaturated polyester resins are linear copolymers free of oil modifiers and capable of crosslinking through reactive double bonds incorporated into the polyester backbone. Most commonly, they are prepared by phthalic anhydride and various diols, with maleic anhydride providing the double-bond functionality. Unsaturated polyesters are dissolved in a monomer such a styrene and are copolymerized directly in the mold in combination with glass-fiber reinforcement.[4]

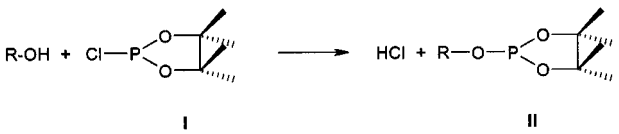
The need to reduce the volatile organic content (VOC) of alkyds for environmental reasons[6] has led to further research toward water-reducible alkyd resins. One way of achieving this goal is to introduce an excess of carboxyl groups, which make the alkyd resin water-reducible in the presence of a base. The amount of free hydroxyl and carboxyl groups of alkyd resins is expressed as the hydroxyl value (HV) and the acid value (AV) in equivalent milligrams KOH per gram of solid resin, respectively. HV and AV are important structural parameters for both simple and modified alkyd resins for several reasons: First, they indicate the level of conversion achieved in the polymerization reaction. Second, since polyols are used as prepolymers for the preparation of hybrid resins, the exact quantity of free —OH groups can be used to calculate the correct stoichiometry of the second polymerization step. In water-reducible alkyd resins, AV is of prime importance because it is related to their water solubility and affects the physical properties and performance of these polymer systems.

We report here a powerful methodology for the simultaneous quantitative determination of the hydroxyl and carboxyl content of polyester resins based on the derivatization of the labile —OH and —COOH protons with 2-chloro-4,4,5,5-tetramethyldioxaphospholane **I** (Scheme 1) and the detection of their phosphitylated derivatives **II** with ^{31}P-NMR spectroscopy. This method appears to be superior to traditional titration methods, since, in addition to the total —OH and —COOH content, it provides a wealth of information regarding the distribution of different types of —OH (i.e., primary and secondary alcohols) and —COOH (aromatic and fatty acids) present in the polyester resins. This is possible because the phosphitylated derivatives of the various alcoholic and carboxylic groups appear in the ^{31}P-NMR spectrum at different frequencies, affording their quantification through integration of the appropriate signals and the use of a suitable internal standard. The ability of the present ^{31}P-NMR methodology to provide quantitative information has been already demonstrated in wood,[7] polymer,[8,9] and food science.[10,11]

EXPERIMENTAL

Materials

Table I summarizes the available chemical composition data of the polyester resins used in this study. All samples were diluted in white spirit or xylenes as supplied by the manufacturer, INTERCHEM HELLAS. S1 is a long-oil alkyd



Scheme 1

resin, and S2, a short-oil; S3 and S4 are short-oil polyols; and S5 is an oil-free polyester resin. Glycerol (GL), pentaerythritol (PE), and trimethylolpropane (TMP) were also the grades used in the industrial preparation of the alkyd resins. Other standard compounds were of reagent grade (Aldrich, Germany) and were used as received.

A stock solution (10 mL) composed of pyridine and $CDCl_3$ in a 1.6:1 volume ratio containing 0.6 mg $Cr(acac)_3$ (0.165 μM) and 13.5 mg cyclohexanol (0.135 mM) as the internal standard was prepared and protected from moisture with 5A molecular sieves. A predeterminated quantity of the model compound (1–5 mg) or 30–60 mg of the polymer resin was placed in a 5-mm NMR tube. The required volume of the stock solution (0.4 mL) and an excess of the reagent **I** (5–30 mL, depending on the number of the functional groups) were added. The reaction mixture was left in the NMR tube to react for 0.5 h at room temperature. Upon completion of the reaction, the solution was used to obtain the ^{13}P-NMR spectra. The presence of excess reagent **I** in the tube after completion of the reaction, verified by its ^{13}P-NMR peak at δ 174.9, ensures that all functional groups of interest have been phosphitylated.[10]

NMR

^{31}P-NMR spectra were obtained on a Bruker AMX-500 spectrometer operating at 202.2 MHz for the ^{31}P nucleus. The probe temperature was 30°C. To eliminate NOE effects, the inverse gated decoupling pulse sequence was used. Typical spectral parameters for quantitative studies were 90° pulse width, 12.5 μs; sweep width, 10 kHz; relaxation delay, 30 s; 16K data points (zero-filled to 32K). Line broadening of 1 Hz was applied and a drift correction was performed prior to Fourier transform. A polynomial fourth-order baseline correction was performed before integration. For each spectrum, 32 and 64 transients were acquired for model compounds and polymer samples, respectively. All chemical shifts reported are relative to the product of the reaction of **I** with water, which has been observed to give a sharp signal in pyridine–$CDCl_3$ at 132.2 ppm.[7]

RESULTS AND DISCUSSION

^{31}P-NMR Spectra Analysis

Table II reports the ^{31}P-NMR chemical shifts of phosphitylated derivatives of several aliphatic alcohols used as starting materials in the industrial preparation of the alkyd resins studied. Also, Table II includes the ^{31}P shifts of the derivatives of some representative fatty acids and several mono- and diglyceride model compounds.[10] Such compounds are produced through the transesterification of oil triglycerides that takes place during the preparation of the alkyd resins. From the data reported in Table II, it is evident that primary alcohols are easily distinguished from secondary alcohols, since the former appear at chemical shifts above δ 147.0 in all cases. Furthermore, the secondary —OH of propylene glycol (PG) appears at δ 145.7, while those of glycerol and mono- and diglycerides at δ 146.4–146.7, thus affording the easy discrimination of this diol in the polyester resins.

Table II ^{31}P-NMR Chemical Shifts δ of Phosphitylated Derivatives of Model Compounds

Compound	⟩CHOH	—CH_2OH	—COOH
GL	146.4	147.4	
PE		147.0	
TMP		147.0	
Ethylene glycol		147.0	
PG	145.7	147.4	
DEG		147.2	
1,3-Diolein[a]	146.7		
1,2-Diolein[a]		148.2	
1-Monoolein[a]	146.4	147.6	
2-Monoolein[a]		148.0	
Stearic acid[a]			134.8
Oleic acid[a]			134.8
Linoleic acid[a]			134.8

[a] Ref. 10.

Free Hydroxyl Groups

Figure 1 illustrates the aliphatic alcohol region of the ^{31}P-NMR spectra of the derivatized polymer resins. The appearance of broad signals, common in the NMR spectra of many polymers even in solution, is due to the multiplicity of different magnetic environments present in the macromolecules because of their inherent heterogeneity and the effects of molecular weight, tacticity, crosslink density, etc. The sharp peak at δ 145.2 seen in all spectra of Figure 1 belongs to cyclohexanol, which is the internal standard used throughout this work. Integration of the spectra can thus provide quantitative information regard-

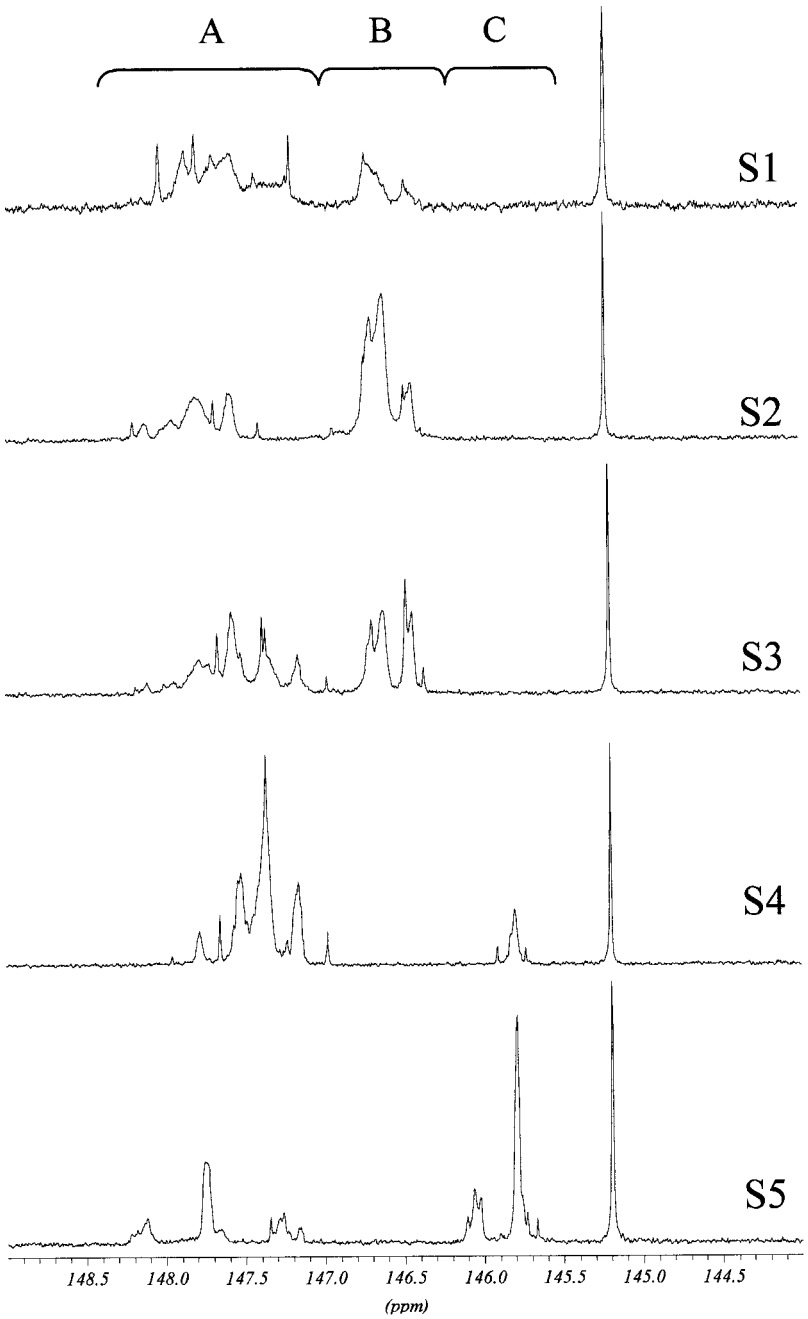


Figure 1 Alcoholic region of the 202.2 MHz ^{31}P-NMR spectra of derivatized unsaturated polyester and alkyd resins S1–S5. Regions A, B, and C are defined in the text. The signal at δ 145.2 is due to derivatized cyclohexanol, used as the internal standard.

ing the total —OH content of the resins. In addition, ^{31}P-NMR spectroscopy provides information regarding the distribution of different types of hydroxyl groups in the polymer resins. There are several sources of free —OH groups in the resins after the completion of the polymerization reaction. These are (a) unreacted —OH from mono- or diglycerides formed by incomplete transesterification of oil triglycerides, (b) residual —OH from completely or partially unreacted polyalcohols that were utilized for the synthesis of network resins, and (c) end-group —OH's in the case of linear polyesters.

Three main subregions are discerned in the aliphatic region of the ^{31}P spectra: region A (δ 147.0 to δ 148.4), region B (δ 146.2 to δ 147.0), and

region C (δ 145.5 to δ 146.2). Region A incorporates all primary —CH_2OH groups, while secondary >CH(OH) groups appear in regions B and C. Comparison with the model compounds of Table I shows that the secondary >CH(OH) group of mono- and diglycerides appears in region B, while that of PG, in region C at δ 145.7. Residual polyols that have not reacted at all should appear at their respective chemical shifts reported in Table II. Inspection of Figure 1 provides some interesting features of the hydroxyl group distribution in the resins studied:

(a) Completely unreacted polyols are not incorporated into the alkyd resins S1 and S2. Polyols S3 and S4 contain small amounts of unreacted GL, PE, and TMP, as evidenced by the appearance of small peaks at ~ δ 147.4 and δ 147.0, respectively.

(b) The alkyd resins (S1 and S2), and also polyol S3, which contains some castor oil, show signal intensity in regions A and B. Polyol S4 and polyester S5, which were prepared without the use of any oil, show no intensity in region B. This observation indicates that the ^{31}P-NMR signals in region B are due to mono- and diglycerides derived from the oil used in the preparation of samples S1–S3. The signals observed in region A of the spectra of samples S4 and S5 are then due to residual —OH groups from the polyols and diols, respectively, used in the polymerization.

(c) Two separate signals appear in region B of the spectra of S1–S3, where secondary alcohols appear. By comparison with the mono- and diglyceride model compounds in Table I, they are assigned as follows: The peak at δ 146.65 to (1→3) glycerol links [~OCH_2—CH(OH)—CH_2O~] and that at δ 146.45 to [~OCH_2—CH(OH)—CH_2OH] moieties of the crosslinked resins. The primary —OH of the [~OCH_2—CH(OH)—CH_2OH] moieties appears at δ 147.55 in region A of the same spectra, and its intensity increases on going from S1 to S3 (see Fig. 1) in parallel with the intensity increase of the peak at δ 146.45, thus further supporting the assignment. The broad nature of the ^{31}P-NMR spectra does not allow the discrimination between different —CH_2OH groups. However, the limited signal intensity around 148.2 ppm implies a small concentration of (1→2) glycerol links [~OCH_2—CH(CH_2OH)~] in the resins studied.

(d) The ^{31}P-NMR spectrum of S5, prepared using PG as the major diol, shows a large signal in region C, indicating the presence of residual secondary >CH(OH) groups from PG in this polyester. This is confirmed by the ^{1}H-coupled ^{31}P-NMR spectrum of S5 (not shown), which shows that the peak at δ 145.8 is a doublet. This observation leads to the conclusion that a small amount of PG was used in the preparation of resin S4, since its ^{31}P-NMR spectrum also shows a signal in region C.

Free Carboxyl Groups

Possible sources of free —COOH groups in these resins are (a) fatty acids produced through the transesterification of oil triglycerides in the alkyd resins (S1 and S2), (b) residual fatty acids in polyols (samples S3 and S4), and (c) carboxyl groups from the anhydrides used in the preparation of S1–S4 (phthalic) and S5 (maleic), present as end groups. The spread of ^{31}P chemical shifts of the derivatives of different acids (δ 134.5–135.5) is much smaller than that of alcohols (δ 146–149).[7,10] It is known that fatty acids appear at δ 134.8 (ref. 10) and a-vinyl acids, such as monoreacted maleic acid, around δ 135.2.[11] Aromatic acids do not show any consistent trend and, depending on phenyl ring substitution, appear in the range δ 134.5–135.2, most commonly around δ 135.0.[11]

The carboxyl region of the ^{31}P-NMR spectra of the resins is depicted in Figure 2. The spectra of resins S1–S4 all show a signal at δ 134.8, which is attributed to free fatty acids added (per se or by oil triglyceride transesterification) as starting materials for the resin polymerization reaction. This assignment is supported by the lack of this peak in the ^{31}P-NMR spectrum of S5, which is a polyester without any oil modification. The broad peak at δ 135.0 is assigned to the free carboxylic phthalic acid end groups of the resins. The ^{31}P-NMR spectrum of S5 in Figure 2 consists of two composite signals, at δ 135.2 and δ 134.9–135.0, corresponding to maleic and phthalic free carboxylic groups, respectively. The ratio of free phthalic/maleic —COOH ^{31}P-NMR signal areas is 1.2:1, although the ratio of the two acids in resin S5 was calculated to be 2.1:1 by ^{1}H-NMR spectroscopy. This indicates that maleic acid is more abundant as a carboxylic end group in polyester S5. The

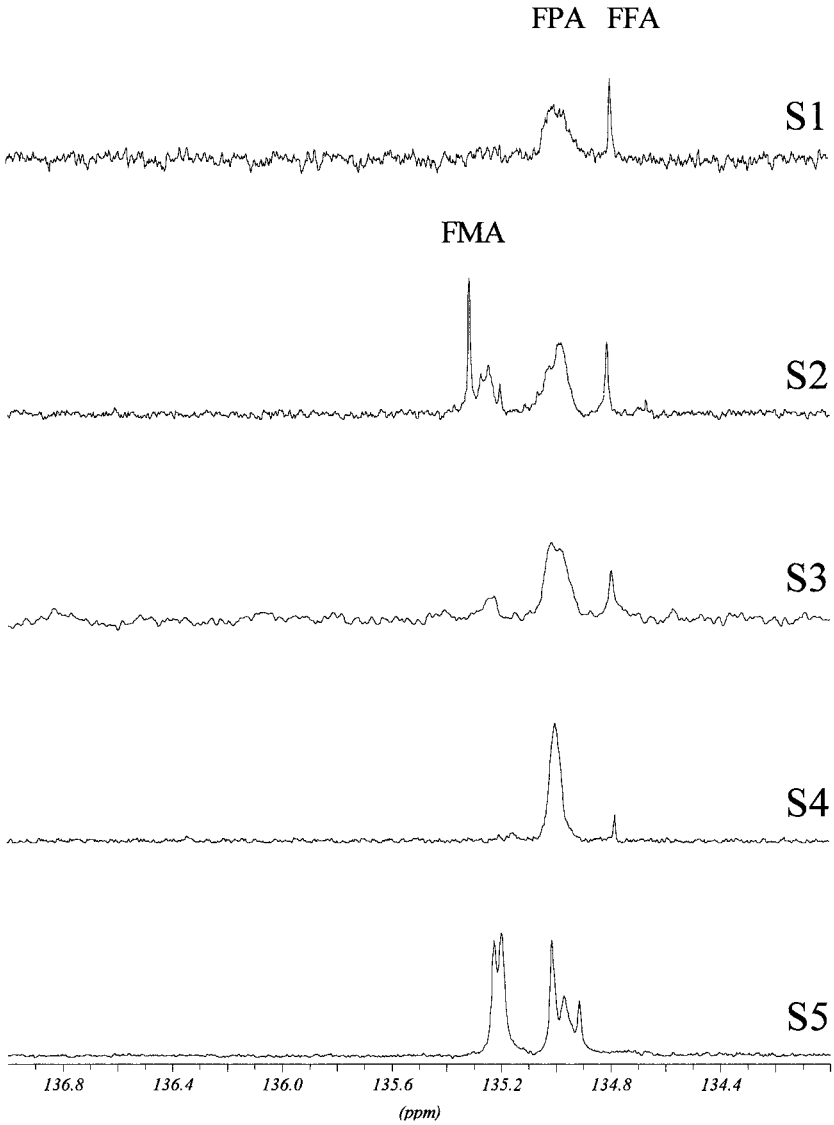


Figure 2 Carboxylic region of the 202.2 MHz ^{31}P-NMR spectra of derivatized unsaturated polyester and alkyd resins S1–S5. FFA, FPA, and FMA stand for free fatty acids and free phthalic and maleic end groups, respectively.

signals at δ 135.3–135.4 in the spectrum of S2 cannot be assigned in accordance to the suggested composition of the resin. Their presence indicates that maleic anhydride was also used in the preparation of resin S2, in addition to phthalic anhydride. This was confirmed by the resin manufacturer.

Quantitative Analysis of ^{31}P-NMR Data

Table III summarizes the quantitative results of our ^{31}P-NMR study of polyester resins S1–S5, obtained through integration of signals in the appropriate regions of the ^{31}P-NMR spectra of Figures 1 and 2. The results are reported as the average of two different measurements for each resin. They can be compared with data supplied by the manufacturer for the maximum AV of these resins, AV_{max}, and for the HV of the polyols S3 and S4. As can be seen, all resins are found to lie closely below the upper AV limits specified by the manufacturer, that is, AV $< AV_{max}$ in all cases. For HV, good agreement is obtained for S4, while for S3, a higher HV is measured by ^{31}P-NMR spectroscopy. Judging by the good reproducibility of the data in Table I, we believe that the NMR value is representative of the —OH content of resin S3.

Table III Quantitative Results of the Hydroxyl and Carboxyl Group Distribution in Polyester Resins Obtained by ^{31}P-NMR Spectroscopy (± standard deviation, n = 2)

Sample	Free >CH_2OH	Free —CHOH	Residual Polyols	HV	FFA[a]	FFAn[a]	FPA[a]	AV	AV_{max}	Minimum M_n (g/mol)
S1	72 ± 1	22 ± 1	0	94 ± 1	1.9	2.9	7.4	9.3 ± 0.1	12	7400
S2	35 ± 1	67 ± 2	0	102 ± 3	2.3	6.4	8.9	18.2 ± 0.3	22	6300
S3	107 ± 3	75 ± 2	2	184 ± 5 (132 ± 5)[b]	1.4	3.4	6.7	9.3 ± 0.2	15	8400
S4	84 ± 4	8 ± 0.5	1	94 ± 4 (95 ± 5)[b]	0.7	2.9	8.8	14.8 ± 0.4	15	4400
S5	24 ± 2	29 ± 2	0	53 ± 4	—	—	20.9	40.7 ± 0.4	40	1300 ± 100[c]

All values in mg KOH per g of solid resin.
[a] FFA, free fatty acids; FFAn, (100 × FFA)/(oil length), oil length values from Table I; FPA, free phthalic acid.
[b] Data in parentheses supplied by the manufacturer.
[c] Exact value.

Apart from the total hydroxyl or carboxyl group content of the resins, ^{31}P-NMR can provide information regarding the distribution of the different types of —OH and —COOH groups, that is, the ratio of primary to secondary [—CH_2OH versus >CH(OH)] hydroxyls, which is not accessible by titration methods. The results in Table III reveal that resin S2 is the only polymer with a higher concentration of secondary rather than primary hydroxyl groups. This observation can be explained by the fact that glycerol has been used as the polyol in the preparation of the resin and by the oil modification, which introduces —CH(OH) groups through transesterification of triglycerides. Resin S4, prepared with TMP and without oil modification, has only ~10% secondary —OH groups, while S1, synthesized with PE but oil-modified, has about 23%. This value is 40% for S3 because of the extra —CH(OH) groups of ricinoleic acid, which is the main component of castor oil.[12] Finally, for the polyester S5, the high quantity of secondary —OH is due to PG, which was the major diol used in its preparation.

The type of hydroxyl groups prevailing in a resin is of prime importance, especially in the case of polyols such as S3 and S4 which are used as prepolymers for the preparation of hybrid resins. Since primary —OH groups are less sterically hindered than are secondary ones, their ratio in the polyol is expected to affect the rate and conversion of the polymerization reaction with compounds containing epoxy, isocyanate, or melamine groups.

The quantification of different types of carboxyl groups by integrating the appropriate ^{31}P-NMR signals of the resins also affords some interesting features not attainable by titration. One can obtain directly the amount of free fatty acids (FFA) present in the oil-modified resins by integrating the signal at δ 134.8 in Figure 2. This information is important because unsaturated fatty acids are incorporated into the polymer chain to affect drying of the alkyd paint through further interchain radical polymerization of their double bonds. However, FFA do not contribute in further crosslinking the resin, although they may polymerize during the drying process, so resins with large FFA would show poor performance as alkyd paints. The results in Table II show that none of the studied resins contains significant amounts of FFA. In general, FFA account for ~15–20% of the total free carboxylic groups, AV, except for the polyol S4, where FFA is 5% of the total acidity. However, if the different oil length of the resins (see Table I) is taken into account (FFAn in Table III), then it is observed that alkyd resin S2 is the exception, having twice the FFAn value of the rest of the resins. This could be due to a larger free acidity in the specific oils used for the modification of S2, although differences in the glyceride transesterification step of the polymerization reaction cannot be excluded.

The knowledge of the quantities of —OH and —COOH groups of a polyester allows, in principle, the determination of its number-averaged molecular weight.[9] However, an exact knowledge of the end-group distribution is required first. Polyester S5 is linear (synthesized by using diols only), and its AV and HV values are very similar (see Table III), so it is safe to assume that S5 possesses one hydroxyl and one carboxyl end group per resin macromolecule. Averaging the —OH and —COOH values, an M_n of 1300 ± 100 is obtained, a value quite reasonable for a polyes-

ter intended to further copolymerize with styrene in a mold. For the alkyd resins S1–S4, this type of calculation is not possible because these polymers are crosslinked. The ^{31}P-NMR data of Table III show that not only polyols S3 and S4, but also alkyd resins S1 and S2 have significantly larger amounts of free —OH groups than free phthalic —COOH groups, HV $\gg$ FPA. This is expected since typical alkyd formulations have an [OH]/[COOH] (mol ratio) of 1.15–1.4. Also, free —OH groups may lie anywhere on the network macromolecule, while free phthalic acid —COOH groups can only be found at the branch ends of a crosslinked chain. One can obtain an indicative lower limit for the M_n of the resins by assuming at least one phthalic end group per macromolecule. These lower-limit number-averaged molecular weights of the resins are summarized in Table III.

CONCLUSIONS

This study describes the use of ^{31}P-NMR spectroscopy as a tool for the characterization of alkyd resins, polyols, and polyesters utilized in the coating industry. Through a fast derivatization reaction completed in the NMR tube, this methodology allows not only the measurement of the total free hydroxyl and carboxyl content of the resins, but, more importantly, the determination of the distribution of different types of labile proton groups, —OH and —COOH, present in the resins. This technique allows a clear discrimination of primary and secondary hydroxyl groups, and the identification of specific —OH groups, for example, PG in resin S5. Furthermore, the present technique allows the discrimination among FFA, phthalic, and maleic carboxyl groups of the resins.

In summary, it was shown that this technique is able to provide a wealth of information regarding the structure and properties of polyester resins in about the same time as a usual —OH and —COOH titration would take (average time for obtaining a ^{31}P-NMR spectrum: ~15min). It must be stressed that no time-consuming purification steps are needed for the ^{31}P-NMR analysis, so that the resins can be studied as prepared by the manufacturer in their final form.

The present technique would be valuable for the study of new and improved polymeric coating formulations that introduce carboxyl groups on the resin as a means of improving its water solubility. Further results of the characterization of polyester alkyd resins by employing ^{1}H- and ^{13}C-1D-NMR spectroscopy and 2D-NMR techniques (^{31}P, ^{1}H, ^{13}C homo- and heteronuclear correlation) will be reported in a subsequent publication.

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