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Characterization of Ketone Resins by Pyrolysis/Gas Chromatography/Mass Spectrometry

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Commercial and synthesized ketone resins are efficiently characterized by pyrolysis/gas chromatography/mass spectrometry. A useful application is analysis of materials used in art painting. Pyrolysis pathways could be proposed upon identification of the pyrolysis products and investigation of resin structures. Resins containing 1,5-diketone patterns were shown to be pyrolyzed via a very efficient cleavage pathway, suggesting a cyclic six-centered mechanism. This pathway was checked on a monomeric compound. Similar cyclic mechanisms may be operative in pyrolysis of 3-hydroxy, 5-hydroxy, and 5,6-unsaturated carbonyl groups, accounting for the main features of the pyrograms obtained.

INTRODUCTION

A variety of synthetic polymers have been used as paints and varnishes by contemporary artists.[1] In order to be able to restore paintings, to examine the effect of aging, and to prove their origin, a reliable identification method is needed for these materials. A major requirement is that the analysis be performed on a very small amount of material so as not to damage the work of art. Pyrolysis coupled to gas chromatography (PY/GC), which is a general method of polymer investigation,[2] has been very satisfactory for this purpose.[3,4] The resulting chromatogram can be considered to be a fingerprint of the material analyzed.

The drawback to PY/GC analysis is that results are strongly dependent on the column used, which makes comparisons between analyses from different sources difficult. Another shortcoming is that it does not provide any structural information. However, combined use of pyrolysis, gas chromatography, and mass spectrometry (PY/GC/MS) overcomes these handicaps. Each peak on the chromatogram is characterized by the corresponding mass spectrum so that (i) the method remains reliable even when comparing results from different GC columns and (ii) the pyrolysis products can be either completely or partly identified from their mass spectrum so that structural information can be gained about the polymer. In the recent years various natural (see for example refs 5-7) and synthetic (see for example refs 8 and

9) polymers, in particular acrylic resins used in art conservation,[10] have been studied by PY/GC/MS.

In this paper we report results concerning PY/GC/MS identification of the structures and pyrolysis mechanisms of some cyclohexanone resins used as components of varnishes.

EXPERIMENTAL SECTION

Measurements were performed with a Nermag R 10-10 B quadrupole mass spectrometer fitted with a Girdel 75 PY 1 pyrolyzing unit and a Girdel 30 gas chromatograph.

The pyrolysis system consists of an electrically heated platinum coil, which allows a continuous temperature range. In order to improve the heat transfer from the filament to the sample, which is a determining factor of pyrolysis reproducibility,[11] the sample of polymer (20-30 μg) was added to a small drop of ethanol deposited on the filament. The filament was then heated to ca. 100 °C for a few minutes to allow evaporation of the solvent before pyrolysis.

Time and temperature of pyrolysis are known to have a strong influence on the pyrogram pattern of polymers.[12,13] The temperature was maintained at 650 °C for 5 s for all experiments, and under these conditions satisfactory pyrograms were obtained for all resins. Since the size of the sample may have an influence on the pyrolysis temperature and hence on the pyrogram pattern, it was checked that variation of the sample amount in the range 5-50 μg did not modify the relative height of the pyrogram peaks.

The capillary column used was a nonpolar WCOT CPSIL 5 CB (Chrompack, Netherlands) of 50-m length, 0.32-mm i.d. and 0.42-μm stationary phase thickness. The carrier gas was helium U (Air Liquide) with 0.6-bar entrance pressure; the splitting ratio was 1:10. The injector temperature was 240 °C. The column temperature was programmed as follows: the initial temperature was set to 80 °C and maintained for 10 min, and then a linear heating rate of 10 °C/min was applied so as to obtain a final temperature of 250 °C. In some of the experiments n-dodecane was added to the sample as an internal standard in order to check the reproducibility of the retention times.

The GC column was connected to the mass spectrometer via a transfer line heated to 300-350 °C. Spectra were recorded in the electron impact mode at 70 eV or in the chemical ionization mode with NH₃ as reagent gas. The mass range of the spectrometer was 50-500. A Sidar PDP 11-23 data system was used for spectra acquisition and data processing.

Direct inlet mass spectra were recorded on a Nermag R 10-10 mass spectrometer allowing a 50-1000 mass range.

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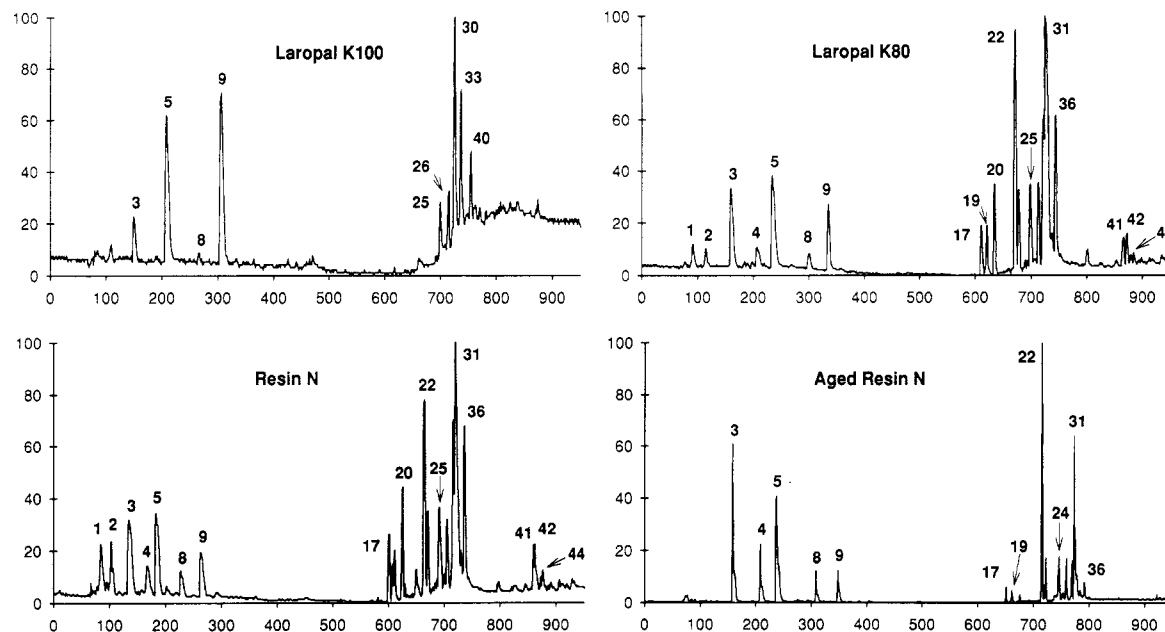(13) Zulaica, J.; Guiochon, G. *Bull. Soc. Chim. Fr.* **1966**, 1343-1351.

Figure 1. Pyrograms of the commerical resins. Peaks are designated by numbers characteristic of each product (first column of Tables I and II).

NMR spectra were performed on a Brüker AC 250 (proton frequency of 250.13 MHz) with deuterated chloroform or deuterated benzene as solvent.

Preparation of Synthetic Resins. The experimental procedure was adapted from ref 14. Organic compounds and concentrated sodium hydroxide solution should be handled with appropriate caution.[15]

Resin A. To a mixture of cyclohexanone (9.8 g, 0.1 mol) and aqueous 5 M sodium hydroxide (50 mL) was added slowly formaldehyde trimer (6.0 g, 2 equiv of CH_2O), producing an exothermic reaction. The mixture was then refluxed for 30 min, yielding a gummy resin which was washed with water and dried in a vacuum dessicator.

Resin B was prepared in the same way, except for the amount of formaldehyde trimer (15 g, 5 equiv) and the reflux time (7 h).

Resin C was prepared under the same conditions as resin A, using a 50–50 mixture of cyclohexanone (4.9 g, 0.05 mol) and 2-methylcyclohexanone (5.6 g, 0.05 mol) instead of pure cyclohexanone.

Procedure for Accelerated Aging of Resin N. Samples of resin N were deposited on a glass plate and irradiated at 60 °C for 200 h in a SEPAP 12-24 irradiation box; this device allowed homogeneous irradiation of the sample at a controlled temperature with wavelengths larger than 290 nm. The irradiation source, a mercury lamp, was designed at the Photochemistry Laboratory of Clermont II University (France).

RESULTS AND DISCUSSION

Nature of the Ketone Resins Studied. Condensation products of cyclohexanone and/or methylcyclohexanone have been widely used in picture varnishes since the 1950s. They are generally sold as additives for paints and lacquers in concentration varying from 5 to 50% to improve physical properties such as gloss and hardness.

Examples of such resins are Ketone resin N, available some years ago from BASF, and Laropal K80, which has now replaced the latter. Both are presented as condensation products from cyclohexanone. We also analyzed Laropal K100, a resin used as a component of varnishes for wood and other materials, which is specified to be a condensation product of cyclohexanone and formaldehyde.

Since the structure of such resins is not necessarily simple and since we had no further information about their synthesis,
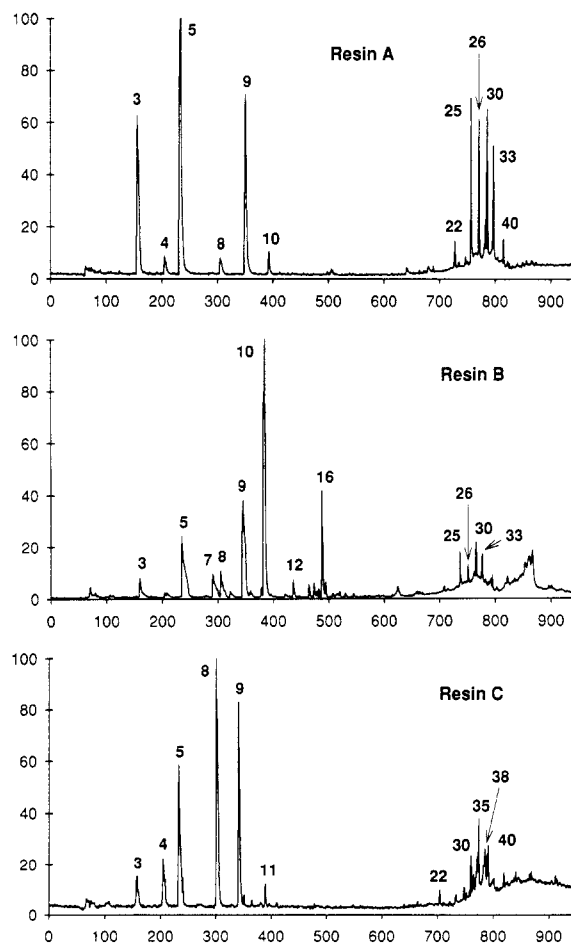
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Figure 2. Pyrograms of the synthetic resins. Peaks are designated by numbers characteristic of each product (first column of Tables I and II).

it seemed interesting to compare their PY/GC/MS analyses with those of similar materials synthesized under known conditions. Cyclohexanone resins have been prepared from cyclohexanone and formaldehyde in the presence of a base.[14] Three samples were synthesized according to this method with the following modifications:

Resin A: 2 mol of formaldehyde per mole of cyclohexanone

Table I. Comparison of the Monomeric Products Obtained from PY/GC/MS of the Different Ketonic Resins[a]

peak	mass	formula	structure	resin N	K80	aged N	K100	resin A	resin B	resin C
1	82	C_6H_{10}	cyclohexene	20	8	–	–	–	–	–
2	94	C_7H_{10}		22	7	–	–	–	0.8	–
3	98	$C_6H_{10}O$	cyclohexanone	30	32	61	34	62	7	12
4	112	$C_7H_{12}O$	3	12	7	22	–	7	–	19
5	110	$C_7H_{10}O$	1	33	36	41	100	100	24	57
6	110	$C_7H_{10}O$		4	–	–	–	–	–	–
7	110	$C_7H_{10}O$		–	–	–	–	–	3	–
8	124	$C_8H_{12}O$	12	10	6	8	–	6	10	100
9	122	$C_8H_{10}O$	2	12	24	12	93	70	34	83
10	122	$C_8H_{10}O$	10	–	–	–	–	9	100	–
11	124	$C_8H_{12}O$		–	–	–	–	–	–	9
12	124	$C_8H_{12}O$		–	–	–	–	–	6	–
15	154	$C_9H_{14}O_2$		–	–	–	–	–	2	–
16[b]	140	$C_8H_{12}O_2$	11	–	–	–	–	–	26	–

[a] Listed in order of elution. For each resin the approximate relative amount of each pyrolysis product is indicated as the height of the corresponding peak in percent relatively to the height of the highest peak of the pyrogram. [b] Other products of mass 140 appearing exclusively in the case of resin B corresponded to peaks 13 (5%) and 14 (5%).

Resin B: 5 mol of formaldehyde per mole of cyclohexanone

Resin C: same conditions as resin A, but with use of a 50/50 mixture of cyclohexanone and 2-methylcyclohexanone instead of neat cyclohexanone.

Finally, the effect of aging on PY/GC/MS spectra of resin N was examined on a sample of resin N which had been submitted to accelerated aging process using UV irradiation.

PY/GC/MS Results. The pyrolysis conditions used (650 °C for 5 s) had been optimized for analysis of acrylic polymers, also used in picture varnishes,[3] and also appeared to give excellent results in the case of ketone resins. These conditions can therefore be considered to be standard conditions for most picture varnish analyses.

The pyrograms obtained exhibited a good reproducibility, provided the amount of sample was low enough.

The PY/GC fingerprints obtained for each sample are shown in Figures 1 and 2. Mass spectra corresponding to each peak established unambiguous matching between the pyrograms. Irrespective of the nature of the pyrolysis products, the following trends are striking:

(A) The pyrogram of resin N is very different from that of Laropal K100, and more complicated, indicating important structural differences between the two resins.

(B) On the contrary, resin N and Laropal K80 have very similar pyrograms, which confirms that the trade name change did not involve major structural modifications of the product.

(C) While none of the resins synthesized have pyrograms of the same type as those of resin N and Laropal K80, the pyrogram of resin A is very similar to that of Laropal K100. Pyrograms of resins B and C each exhibit still different patterns.

(D) Comparison of "aged" and untreated resin N shows that the effect of aging is quite apparent on the pyrogram: the abundance of most products is modified, and new pyrolysis products have appeared with aging process.

The samples were analyzed first with electron impact ionization, which provided the fragmentation spectra and relative amounts of the pyrolysis products, and then in the chemical ionization mode in order to ascertain their molecular weights. Structure assignments have been made either from literature data or by synthesis and GC/MS analysis of authentic samples. The results are summarized in Tables I and II.

1. *Laropal K100 and Resin A.* The pyrograms of Laropal K100 and resin A give unequivocal identification of components such as cyclohexanone,[16] 2-methylenecyclohexanone (1) (major peak), and very probably 2,6-dimethylenecyclohexanone (2) as the most abundant monomeric species. A

trace of 2-methylcyclohexanone (3)[16] is also present. In order to ascertain the structure of 1 we synthesized 2-methylenecyclohexanone;[17] the mass spectrum of 1 is identical to this of the authentic sample, whereas it is very different from the known mass spectrum of 2-methylcyclohexen-2-one.[18]

In the dimer range, compounds of molecular weight 208, 220, and 232 (two isomers each) were detected. The compounds of molecular weight 208 had a fragmentation pattern similar to this reported for 2,2'-methylenebiscyclohexanone (4);[19] this structure was confirmed by comparison with the authentic sample 4a + 4b (two diastereomers).[20,21] According to their fragmentation patterns the other products are likely 5a,b (*m/z* 220) and 6a,b (*m/z* 232).

Resin A exhibits nearly the same pyrogram as Laropal K100, with slight differences in abundance of the products. Traces of 2-methylcyclohexanone also appear in the pyrogram of resin A, even though no methylcyclohexanone was present in the starting monomers.

2. *Resin N and Laropal K80.* The mixture produced by pyrolysis of these resins is more complex than the preceding ones but includes most of the products seen above: cyclohexanone, 2-methylcyclohexanone (the identity of which was confirmed by PY/GC/MS of a mixture of resin N and authentic 2-methylcyclohexanone), 2-methylenecyclohexanone (1), 2,6-dimethylenecyclohexanone (2), and 2,2'-methylenebiscyclohexanone (4). Numerous additional products appear, the most significant being the following: (i) cyclohexene; (ii) *m/z* 94, whose mass spectrum corresponds either to methylenecyclohexene or 1-methyl-1,4-cyclohexadiene; (iii) *m/z* 180 (two isomers with similar spectra), corresponding to molecular formula $C_{12}H_{20}O$: the EI mass spectrum is very different from the known spectrum of cyclohexylcyclohexanone;[22] the fragmentation pattern (H_2O loss, important fragment at *m/z* 81, $C_6H_9^+$) rather suggests cyclohexenylcyclohexanol; (iv) *m/z* 192 ($C_{13}H_{20}O$): several products with very similar fragmentation patterns, very weak H_2O loss, important fragments at *m/z* 111 ($C_7H_{11}O^+$), 98, 79, 81; probably isomeric (cyclohexenylmethyl)cyclohexanones, for example 7, or methylenecyclohexylcyclohexanones; (v) *m/z* 212 ($C_{13}H_{22}O_2$), three peaks with close retention times and identical EI mass spectra; they were identified as 2,2'-methylenebiscyclohexanol (8) (four isomers, appearing as three

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Table II. Comparison of the Dimeric Products Obtained from PY/GC/MS of the Different Ketonic Resins[a]

peak	mass	formula	structure	resin N	K80	aged N	K100	resin A	resin B	resin C
17	180	$C_{12}H_{20}O$		26	20	5	–	–	–	–
18	192	$C_{13}H_{20}O$		13	3	–	–	–	–	–
19	180	$C_{12}H_{20}O$		20	19	5	–	–	–	–
20	192	$C_{13}H_{20}O$		45	35	3	–	2	–	–
21	192	$C_{13}H_{20}O$		10	–	–	–	–	–	–
22	192	$C_{13}H_{20}O$	7?	78	96	100	–	10	2	6
23	192	$C_{13}H_{20}O$		33	32	17	–	–	–	–
24	204	$C_{14}H_{20}O$		–	–	17	–	–	–	–
25	208	$C_{13}H_{20}O_2$	4a	32	32	–	34	65	14	4
26	208	$C_{13}H_{20}O_2$	4b	27	32	16	41	54	8	5
27	204	$C_{14}H_{20}O$		–	–	15	–	–	–	–
28	212	$C_{13}H_{24}O_2$	8	33	34	–	–	–	–	–
29	232	$C_{15}H_{20}O_2$	6a	–	–	–	–	14	2	–
30	220	$C_{14}H_{20}O_2$	5a	–	–	–	80	60	14	16
31	212	$C_{13}H_{24}O_2$	8	100	100	63	–	–	–	–
32	212	$C_{13}H_{24}O_2$	8	14	17	–	–	–	–	–
33	220	$C_{14}H_{20}O_2$	5b	–	–	–	43	43	12	–
34[b]	236	$C_{15}H_{24}O_2$		–	–	–	–	–	–	13
35[c]	234	$C_{15}H_{22}O_2$		–	–	–	–	–	–	25
36	192	$C_{13}H_{20}O$		65	58	6	–	–	–	–
40	232	$C_{15}H_{20}O_2$	6b	–	–	–	33	10	5	15
41[d]	304	$C_{20}H_{32}O_2$	9	19	17	–	–	–	–	–

[a] Listed in order of elution. For each resin the approximate relative amoung of each pyrolysis product is indicated as the height of the corresponding peak in percent relatively to the height of the highest peak of the pyrogram. [b] Another product of mass 236 appearing exclusively in the case of resin C corresponded to the peak 37 (5%). [c] Other products of mass 234 appearing exclusively in the case of resin C correspond to peaks 38 (11%) and 39 (9%). [d] Other products of mass 304 corresponded to the following peaks (respective intensities for resin N; Laropal K80): 42 (8; 11), 43 (6; 5), 44 (8; 6).
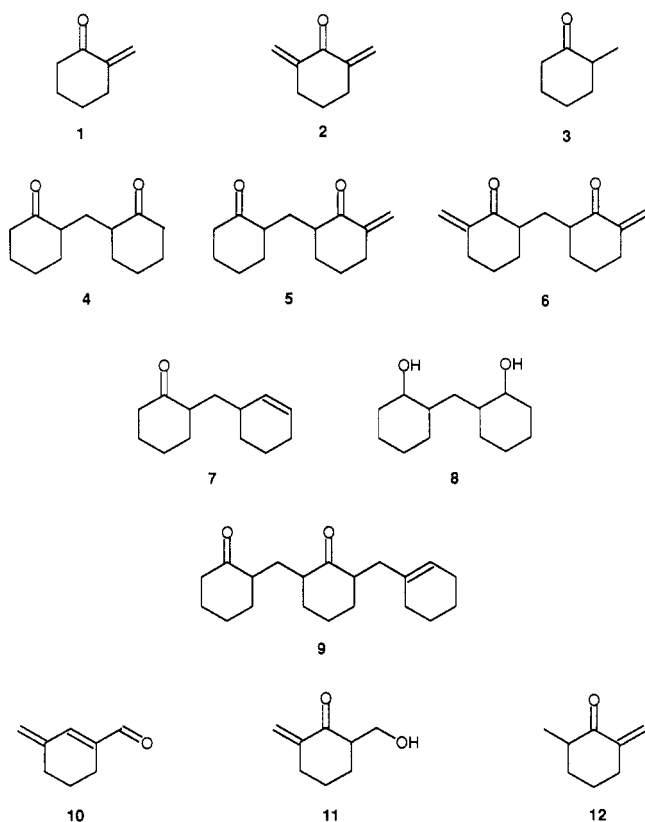
peaks under the GC conditions used) from comparison with an authentic sample prepared by reduction of methylenebiscyclohexanone;[23] (vi) a sizeable amount of trimers with m/z 304 ($C_{20}H_{32}O_2$); structure 9 or analogue may account for their fragmentation patterns.

3. *Resins B and C.* The pyrogram of resin B, synthesized using a large excess of formaldehyde, is characterized by a major peak corresponding to m/z 122 but different from 2, which is also present in the pyrogram. A reasonable possibility

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is structure 10, which is consistent with the observed fragmentation pattern: m/z 107, 93 (base peak, CHO loss), 91, 79, 77, 65, etc. Also characteristic of resin B is the presence of compounds of molecular weight 140. The EI spectrum of the main one, very similar to this of 2, suggests structure 11. The dimers are the same as in resin A but are formed in lower amount.

The pyrogram of resin C, synthesized from a mixture of cyclohexanone and 2-methylcyclohexanone under the same conditions as resin A, showed a major product corresponding to m/z 124 ($C_8H_{12}O$), most probably 2-methyl-6-methylene-cyclohexanone (12). The same compound had been found in a low amount among the pyrolysis products of the other resins. The 2-methylcyclohexanone monomer also appears in the pyrogram of resin C, but it is not much more abundant than in the resins synthesized from cyclohexanone only. A better criterion for identifying syntheses using 2-methylcyclohex-anone as one of starting monomers seems to be the presence of dimers of molecular weight 222, 234, and 236, corresponding respectively to methyl-, methylmethylene- and dimethylmethylenebiscyclohexanone, which are completely absent from the pyrograms of all the other resins studied, and the large amount of $C_8H_{12}O$ compound.

4. *Aged Resin N.* The pyrogram differs from that of resin N regarding the following points: a larger relative amount of monomers, except for cyclohexene and methylenecyclohex-ene is observed; the distribution of m/z 192 isomers is different; and the presence of dimers corresponding to m/z 204 ($C_{14}H_{20}O$), possibly methylene derivatives of m/z 192 compounds is observed.

5. *Comparison of PY/GC/MS Data with Direct Inlet/MS Results.* In order to compare the results of the two methods the CI mass spectra obtained from direct inlet of Laropal K100 and resin N into the ion source were recorded. These spectra are time-dependent: relative intensities of heavy fragments increase with increasing time. In both cases many low and medium molecular weight ions present in the direct inlet mass spectra corresponded to protonated pyrolysis products: m/z 123, 209, 221, and 233 for Laropal K100, m/z 193, 213, and 305 for resin N. The heavier ions, detected up to mass 1000, were generally derived from the preceding ones by mass increments of 110 ($C_7H_{10}O$, corresponding to pattern

A below for R = H) or 140 ($C_8H_{12}O_2$, pattern A for R = CH_2-OH) in the case of Laropal K100, of mass 112 ($C_7H_{12}O$, pattern B below) in the case of resin N.

Direct inlet results are therefore consistent with PY/GC/MS results. The disadvantage of direct inlet compared to PY/GC/MS is that the origin of the ions observed is uncertain: they may correspond (i) to relatively small molecules present in the polymer, in which case they do not reflect the bulk of the polymer but only its most volatile, oligomeric fraction; (ii) to decomposition products of the polymer, formed in the inlet under uncontrolled conditions; or (iii) to fragmentation of heavier ions.

Structure of the Resins and Probable Pyrolysis Mechanisms. Direct interpretation of the PY/GC/MS results reported above in terms of detailed structure for each polymer studied is made difficult by the fact that little is known on the major processes involved in polyketone pyrolysis. Therefore we combined these results with structural information given by ^{1}H and ^{13}C NMR spectrometry, in addition to literature reports concerning the structure of ketonic resins, so that we could propose general pyrolysis mechanisms consistent with experimental data.

1. *Laropal K100 and Resin A.* Formaldehyde–cyclohexanone resins are thought to have the following structure (pattern A):

R = H or CH₂OH
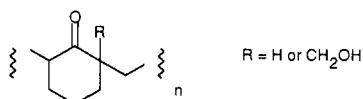
The proportions of hydroxymethyl groups depend on synthetic conditions, in particular the formaldehyde to cyclohexanone ratio.[14,24]
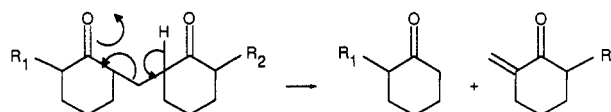
Laropal K100 and resin A exhibit similar ^{1}H and ^{13}C NMR spectra, which confirms the structural similarity already indicated by their pyrograms. These spectra show the following features, in agreement with the structure proposed above: the absence of ethylenic protons (4.5–6 ppm) or carbons (110–140 ppm) and the presence of carbonyl groups (carbons at 215–220 ppm) and of protons α to carbonyl groups (2.2–2.8 ppm).

In addition to the expected signals, all the recorded ^{13}C spectra (Laropal K100, resin C, resin N) present a signal centered at 100 ppm. We assign this signal to carbon atoms bearing two oxygens. Such carbons could be the result of equilibrated hemiacetal formation from ketone and hydroxyl groups in the polymer. The spectra also show the presence of hydroxymethyl groups (carbons at 60–65 ppm and protons at 3.5–3.8 ppm). Integration of the ^{1}H spectrum of Laropal K100, although it is inaccurate, allows to estimate as ca. $^1/_5$ the approximate CH_2OH proportion for the R groups.
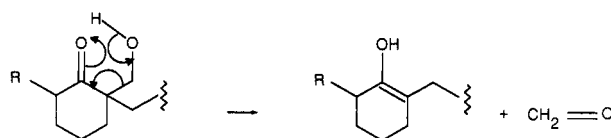
Therefore the carbon–carbon double bonds present in the major pyrolysis products 1 and 2 should be formed during the pyrolysis process. Although no data are available on the pyrolysis of polyketones themselves, pyrolysis of several polymers containing carbonyl groups, such as poly(methyl methacrylate)[25] and polyamides[26] has been studied: concerted mechanisms involving a cyclic six-membered transition state are often invoked for these compounds, contrary to hydrocarbon polymers such as polyethylene which follow radical pyrolysis pathways.[13] Protons α to a carbonyl group are easily transferred to an oxygen atom. We thus propose Scheme I in the case of ketone resins.

This scheme accounts for obtention of cyclohexanone, 2-methylenecyclohexanone, and 2,6-dimethylenecyclohex-
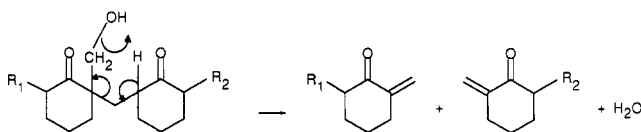
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**Scheme I**

Scheme II

Scheme III

anone as major pyrolysis products. In order to check the possibility of such a mechanism occurring, a sample of methylenebiscyclohexanone **4a,b** was submitted to PY/GC/MS under the same conditions as the resins. Cyclohexanone and 2-methylenecyclohexanone, expected from the above mechanism, were the only products which appeared on the pyrogram in addition to the starting materials. Pyrolysis of aliphatic monoketones has also been shown to lead to unsaturated ketones, likely through a radical mechanism;[27] however, a similar pathway operating in the case of 4 would be expected to give rise to a larger variety of products such as cyclohexenone and open-chain isomers of the starting material.

The pyrolysis products of the resins do not seem to include molecules containing hydroxymethyl groups, although these groups are initially present in the polymers as indicated by NMR spectra. Two possible mechanisms may account for this: (1) retrocondensation leading to loss of formaldehyde (Scheme II) and (2) chain cleavage with dehydration (Scheme III).

2. *Resins B and C.* The same mechanisms as above easily account for the pyrolysis products obtained from resin C, if we assume that the only structural difference between resins A and C is the presence of methyl substituents such as R groups in resin C.

Although resin B has not been submitted to detailed structural investigation, it may reasonably be thought to include the following structural patterns:

R = CH₂OH, sometimes H
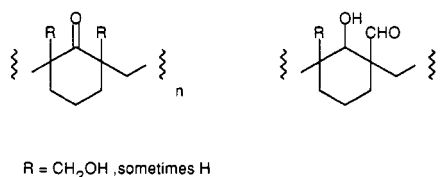
The second structural group may be formed from the first one during the condensation process in basic medium, by an internal hydride transfer reaction from the alkoxide to the ketone group.[28] Pyrolysis according to the same mechanism as in Scheme III would lead to aldehyde 10 (Scheme IV).

3. *Resin N and Laropal K80.* The structure of these resins is obviously more complicated than that of the preceding one. Such resins are obtained by condensation of cyclohexanone in the presence of sodium methoxide at high temperature. Under those conditions methoxide is likely oxidized to formaldehyde, which may take part in the condensation

(27) Boss, B. D.; Hazlett, R. N. *Anal. Chem.* **1976**, *48*, 417–420.

(28) Djerassi, C. *Org. React.* **1951**, *6*, 207–272.

Scheme IV
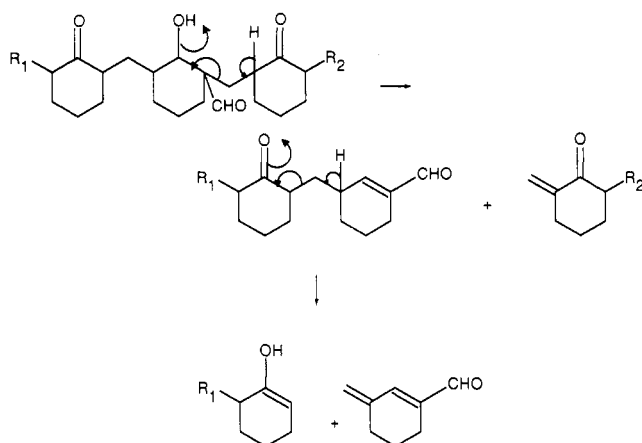
reactions.[29,30] C7 and C13 units found as major pyrolysis products confirm this hypothesis.

The following structural features appear in the NMR spectra of resin N: (a) the absence of ethylenic protons or carbons; (b) the presence of carbonyl carbons, but apparently in lower amount than in the preceding resins; low proportions of protons α to the carbonyl groups are also observed (weak signal at 2.2–2.4 ppm in the proton spectrum); (c) few protons α to oxygen are found in the proton spectrum (weak signal between 3.5 and 4 ppm). However, the carbon spectrum shows signals at 70–80 ppm, corresponding to secondary or tertiary oxygen-bearing carbons. No signal appears in the region of hydroxymethyl carbons (60–65 ppm).
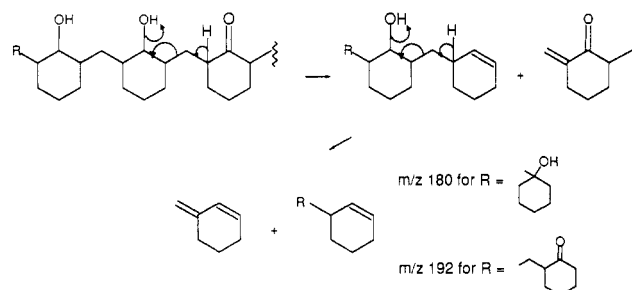
These data suggest that resin N possesses OH groups in secondary and/or tertiary positions and that part of the carbonyl groups initially present in cyclohexanone monomers do not appear in the polymer. Since both C12 and C13 units are found in the dimer products of the pyrogram, it appears that resin N contains both C6–C6 linkages from cyclohexanone autocondensation[31] and C6–C–C6 linkages from cyclohexanone–formaldehyde condensation. Spectral data and the presence of methylenebiscyclohexanol as a major pyrolysis product suggest that in the latter case some of the ketone groups have been reduced (pattern B).
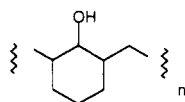
Such a reduction may be encountered either during the polymerization process or in a subsequent step of the resin preparation.[24]

Mechanisms similar to those described above may then account for the observed pyrolysis products (Scheme V).

(29) Mleziva, J. *Collect. Czech. Chem. Commun.* **1954**, *19*, 505–516.
(30) Dolgov, B. N.; Samsonova, I. N. *Zh. Obsch. Kh.* **1952**, *22*, 632–637.
(31) Rollin, P. *Bull. Soc. Chim. Fr.* **1973**, 1509–1514.

Scheme V

The 1,5-diol pattern present in the polymer could conceivably lead to other types of pyrolysis mechanisms, since aliphatic alcohols are cleaved through radical mechanisms under slightly different pyrolysis conditions.[27] In order to answer this question, a sample of methylenebiscyclohexanol was submitted to PY/GC/MS under the same conditions: only the starting materials were detected.

Aged resin N and untreated resin N have distinguishable but similar pyrograms. In view of these similarities and of the uncertainties concerning the detailed structure of resin N, a reliable model for the chemical transformations corresponding to the aging process cannot be proposed from these results.

CONCLUSION

The preceding results show that PY/GC/MS is a satisfactory method for characterizing ketonic resins on a small amount of sample. A useful application is analysis of materials used in art painting.

A very efficient pyrolysis pathway involving abstraction of a proton α to one of the ketone groups via a cyclic six-centered mechanism has been shown to occur in molecules containing a 1,5-diketone pattern. Similar cyclic mechanisms seem to operate in pyrolysis of 3-hydroxy, 5-hydroxy, and 5,6-ethylenic carbonyl groups. The scope and generality of this type of pyrolysis pathway deserves further investigation, which should be easily performed through widespread PY/GC/MS analysis of known molecules or polymers.

The resulting improvements in the knowledge and understanding of pyrolysis mechanisms will in turn make PY/GC/MS a still more powerful tool for structure determination of unknown or modified polymers.

Registry No. Laropal K80, 108334-37-8; Laropal K100, 142797-55-5; (cyclohexanone)(formaldehyde) (copolymer), 25054-06-2; (cyclohexanone)(formaldehyde)(2-methylcyclohexanone) (copolymer), 142723-34-0.