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polymer papers

Quantitative valuation of composition in vinylformal, vinylacetate and vinylalcohol ter-copolymers by ^{1}H- and ^{13}C-n.m.r. spectroscopy

Pedro Ortiz del Toro[a], Alberto Suzarte[b],*, Iván Sergio Colás[b], Carmen Zaldívar[b] and Arístides Rosado[a]

[a]*Department of Physical Chemistry, School of Chemistry, University of Havana, Havana 10400, Cuba*
[b]*Polymer Laboratory, National Center For Scientific Research, Havana 6880, Cuba*
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The ^{13}C-n.m.r. signals were assigned to the composing structural groups of the copolymers. The composition of the copolymers was determined by ^{13}C n.m.r. using the NOE extinction technique. The analyzed samples were synthesized under normal and relatively mild reaction conditions. Despite this and purification methods that avoided elevated temperatures, it was not possible to find hemiformal groups in any amount. Therefore it is possible to analyze these copolymers composed of formal, vinylacetate and vinylalcohol structural groups in a relatively easy way by means ^{1}H n.m.r. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Polyvinylformals are well-known ter-copolymers with vinylformal, vinylalcohol and eventually vinylacetate and hemiformal monomeric units. These copolymers, by virtue of a sufficiently high degree of formalization, are only soluble in a few solvents and show good temperature stability. It seems interesting to relate the solubility behaviour and the thermal stability to the composition and microstructure of these polymers. Knowledge of the microstructure of the polymer chains allows the interpretation and prediction of the behaviour and properties of these substances. Normally the work needed for this aim is not simple[1]. n.m.r. is the most suitable technique for this purpose[2-4]. Only a few papers are reported in the literature in which polyvinylformals are studied by means of n.m.r.[5,6]. The aim of this initial work is to develop a reliable and simple method for the determination of the monomeric unit composition by using ^{13}C n.m.r. and/or ^{1}H n.m.r.

EXPERIMENTAL SECTION

Materials

Three copolymer samples (PVF-2, PVF-3, PVF-4) were synthesized by polymerizing vinylacetate and performing thereafter the acid hydrolysis and simultaneous formalization of poly(vinylacetate) (PVAc, Mw = 25 000). In both cases there was a small remnant of vinylacetate in the reaction mixtures after polymerization. This monomer can hydrolyse and is a source of small quantities of acetaldehyde. In the case of PVF-3 additional acetaldehyde was added to the reaction mixture after polymerization. The PVF-1, PVF-5, and PVF-6 samples were synthesized from purified PVAc (Mw = 25 000). All reactions have taken

place at 60–70°C in a single phase with acid catalysis and withdrawing part of the reaction water. The reaction mixture was neutralized, and the copolymers were thereafter precipitated in distilled water, redissolved and reprecipitated in water. The sample PVF-1 was dried under vacuum at room temperature. All other samples were dried in a vacuum oven at 1–2 mm Hg and 80°C. All samples were dried until weight constancy was achieved.

N.m.r. experiments

N.m.r. spectra were recorded with a Bruker AC-250F spectrometer equipped with an ASPECT 3000 computer, at the frequencies of 250 MHz (^{1}H n.m.r.) and 62.89 MHz (^{13}C n.m.r.) and a temperature of 42°C. The copolymers were dissolved in CDCl$_3$ in concentrations ranging from 9 to 12% w/v. TMS was used as internal reference and chemical shifts were reported in ppm. The nature of each carbon atom was determined using the distortionless enhancement by polarization transfer (DEPT) technique, with proton pulses at $\theta = 135°$ and $\theta = 90°$, respectively. The quantitative measurements were carried out by recording the ^{13}C-n.m.r. spectra using the inverse gated decoupled technique with a relaxation $D_1 = 10$ s, in order to fulfil the condition $D_1 > 5T_1$ (maximum); for hydrogenated carbons, T_1 is the spin-lattice relaxation time. The calculations were always carried out with signals which correspond to protonated carbons. Each integrated intensity value corresponds to the statistical mean of several measurements made with different degrees of expansion of the spectral recording. This procedure minimizes the error originated by base line alterations.

Mass spectrometric experiments

The thermolysis of the samples were carried out in a mass spectrometer JEOL DX300 with programmable heating (16 and 32 deg min^{-1}). The decomposition vapours were
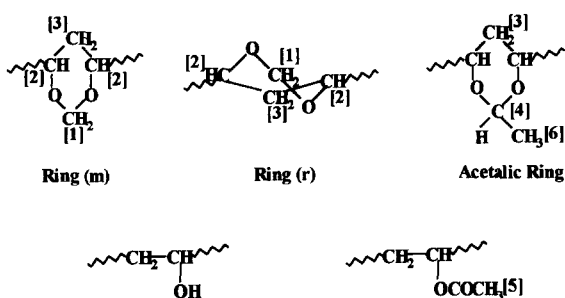
Figure 1 Structural groups present in the copolymers

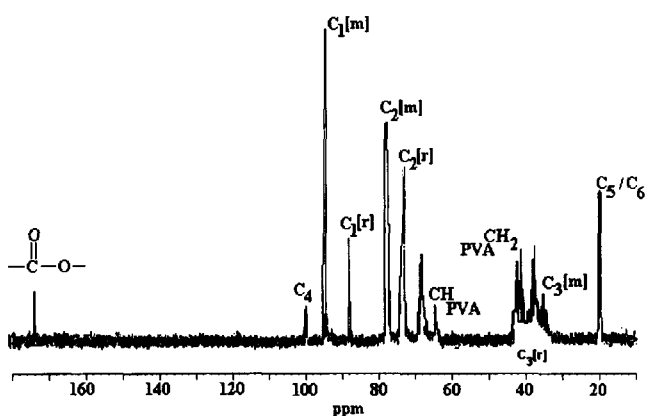**Figure 2** ^{13}C-n.m.r. spectra of a sample of PVF2 in CDCl$_3$

conducted to the ionization chamber and the thermogram recorded for total ionic current and the corresponding to the ions from $m/z = 30$.

RESULTS AND DISCUSSION

These kinds of copolymers present a complex structure with several possible monomeric units: cis and trans formal rings, acetate and alcohol groups and eventually hemiformal groups. On account of this and the great number of sequences and stereosequences either the ^{13}C-n.m.r. or ^{1}H-n.m.r. spectra show considerable complexity. For an easier discussion of the n.m.r. spectra, the carbon atoms of the

groups involved in the copolymer structures were numbered as can be seen in *Figure 1*.

In our study the ring conformation designated as meso and racemic indicates that the ring conformation originates from the addition of formaldehyde to either the meso or racemic dyad of the parent poly(vinylalcohol).

The qualitative analysis of the structural group composition of the sample was performed as follows. *Figure 2* shows the ^{13}C-n.m.r. spectrum of the sample PVF-2. The expanded spectra using the DEPT technique ($\theta = 135°$ and $\theta = 90°$) can be seen in *Figure 3*. The signals at $\delta = 93.37$ ppm (CH$_2$) and $\delta = 87.00$ ppm (CH$_2$) were used for the assignment of the (m) and (r) rings respectively, according to reported data for poly(vinylbutyrals)[7]. Taking into account that the ring (m) is sterically more favoured, it is expected that its signal should be the most intensive. The rest of the signals of these rings and those corresponding to the other groups (vinylacetate and alcohol structural groups), were assigned according to reported data[7–9]. The presence of small amounts of acetaldehyde in the reaction mixture causes the formation of acetalic rings, whose signals in the spectrum were assigned using reported spectral data of model compounds[10]. So, the estimated value for the carbon atom C$_4$ of this structural group match with the signal at 98.52 ppm (C$_4$) and the signal at 21.13 ppm (methyl group, CH$_3$, overlapped with the methyl group of the acetate group).

In *Figure 4* is shown the ^{13}C-n.m.r. spectrum of the sample PVF-3 (synthesized with the addition of acetaldehyde to the reaction mixture). It confirms the prior assignment, since the signals assigned to the acetal structure are more intense in comparison with those in the spectrum of sample PVF-2. This can be better seen by comparing the ratios of intensities of the signals at 98.52 ppm and 87.00 ppm, and the ratios of intensities for the signals at 170.45 ppm (COO$^-$) and at 21.13 ppm (C$_5$/C$_6$) in the spectra of both samples, PVF-2 and PVF-3.

Table 1 summarises the ^{13}C-n.m.r. data obtained from the spectra of the analyzed copolymer. It is important to notice that in all spectra shown in *Figures 1–4* there is no signal that could be assigned to the carbon atom of the hemiformal group (–O–CH$_2$–OH). This means that this group can only be present in the samples of copolymers in a very small amount, so that it cannot be detected by means of the
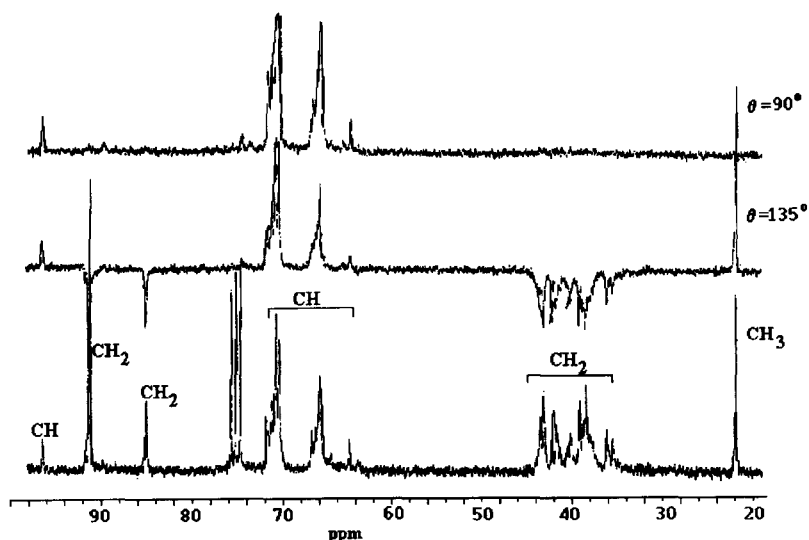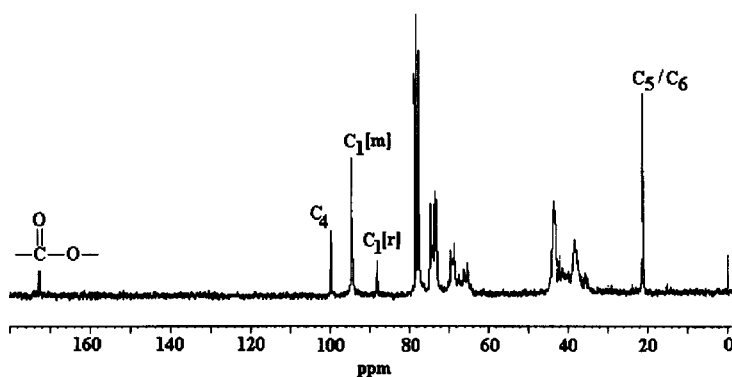

Figure 3 DEPT spectra of a sample of PVF2

Table 1 Chemical shifts δ (ppm) of the ^{13}C-n.m.r. spectra of each polymer dissolved in CDCl$_3$

PVF-1	PVF-2	PVF-3	PVF-4	PVF-5	PVF-6	ASSIGNMENT
–	170.5	170.5	170.5	–	–	–COO–
–	98.5	98.5	98.5	–	–	CH[4]
93.4	93.4	93.3	93.3	93.4	93.1	CH$_2$[1] m
87.1	87.0	87.1	87.0	87.1	86.9	CH$_2$[1] r
–	76.6	76.5	76.5	–	–	CH (acetate)
73.8–72.8	73.8–72.8	73.4–72.8	73.8–72.7	73.7–72.7	73.6–72.8	CH[2] m
68.6–67.2	68.8–67.7	68.7–67.8	68.7–67.7	68.6–67.1	68.6–67.0	CH[2] r
44.0–35.0	44.0–35.0	44.0–35.0	44.0–35.0	44.0–35.0	44.0–35.0	CH$_2$ (chain)
–	21.2	21.2	21.1	–	–	CH$_3$ (acetate, acetal)

Figure 4 ^{13}C-n.m.r. spectra of a sample of PVF3 in CDCl$_3$
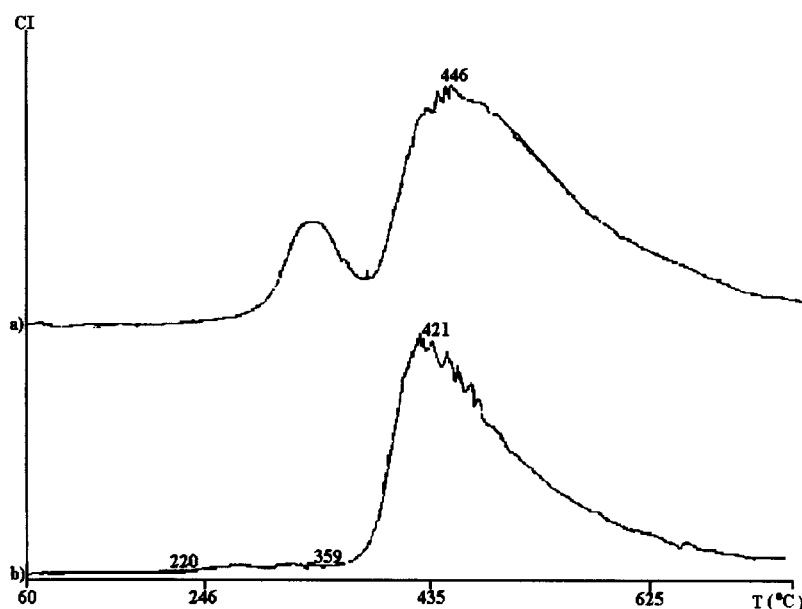
Figure 5 Thermolysis of PVF1. Heating rate, 32 deg min^{-1}. Curve (a) and (b) correspond to the total ionic current and to the ionic current from ion $m/z = 30$ respectively

^{13}C-n.m.r. technique. In order to confirm this statement the thermolysis of the samples under high vacuum in conjunction with mass spectrometry was performed. It is well known that the hemiformal group is less stable than the formal rings. So, it is reported[11,12] that the hemiformal group formed from cyclohexanol and formaldehyde decomposes at 125–160°C, and the hemiformal from polyglicolether decomposes at 120°–140°C. The mentioned decomposition implies the formation of formaldehyde.

In *Figure 5* can be observed the thermogram of the thermolysis of sample PVF-1. No formaldehyde formation can be detected at temperatures below 220°C.

Figure 6 shows the same kind of thermogram obtained for the sample PVF-3, a sample with a smaller degree of formalization than sample PVF-1. Below 170°C no formaldehyde was found; it is possible to consider that the small peak, seen between 170 and 188°C, could be derived from the existence of hemiformal groups. In that case these groups would account for only 0.96% of the total
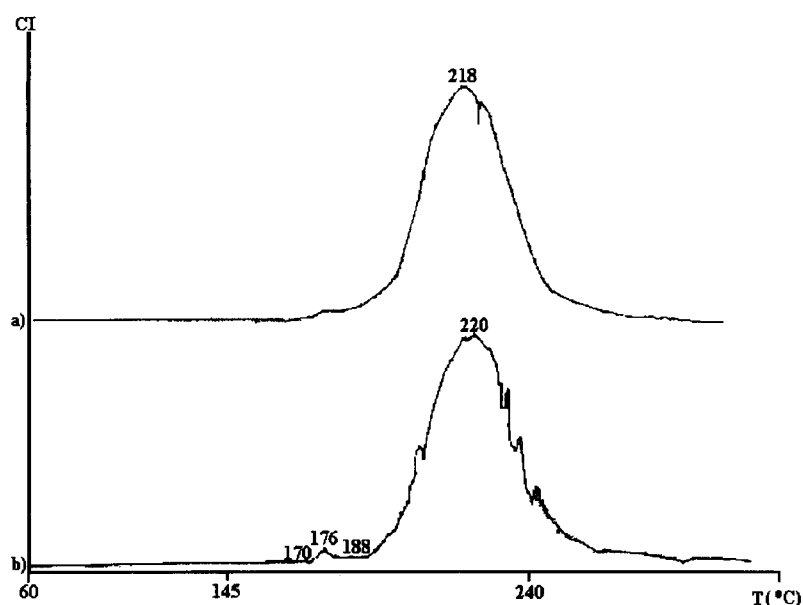
Figure 6 Thermolysis of PVF3. Heating rate, 16 deg min^{-1}. Curve (a) and (b) correspond to the total ionic current and to the ionic current from ion $m/z = 30$ respectively

Table 2 Group compositions in the samples are given in the table as the percentage of the vinylacetate monomeric units that were transformed into the respective group

Sample	Formal ring (m) (%)	Formal ring (r) (%)	Acetalic ring (%)	Vinyl acetate units (%)	Vinyl alcohol units (%)
PVF-1	64	18	–	–	18
PVF-2	49	17	7	22	5
PVF-3	39	13	17	12	11
PVF-4	44	15	13	14	14
PVF-5	62	22	–	–	16
PVF-6	66	18	–	–	16

Table 3 Quantitative evaluation of the percentage of formalization of the samples by ^{1}H- and ^{13}C-n.m.r. spectroscopy

Sample	^{1}H n.m.r.	^{13}C n.m.r.
PVF-1	84	82
PVF-5	84	82
PVF-6	84	83

formaldehyde bonded within the copolymer, and this amount is hardly seen using ^{13}C n.m.r.

Table 2 shows the quantitative composition of the copolymer samples determined from ^{13}C-n.m.r. spectra, using the NOE extinction technique. The quantitative signal response was checked calculating the intensity ratios of the signals at 93.37 ppm C_1 (m) and at 72–74 ppm C_2 (m), which corresponded in all cases to the theoretical value $I_{C_{2(m)}}/I_{C_{1(m)}} = 2$.

Since no hemiformal groups were detected by means of ^{13}C n.m.r. and the thermolysis mass spectrometric technique gives evidence of their absence or small significance for all the analyzed samples, it can be assumed that all copolymers synthesized by the described technique in the absence of vinylacetate monomer or added acetaldehyde can be analyzed by means of ^{1}H n.m.r.. So, the ratio of the integrated signals of CH_2 formal protons (4.5–5.5 ppm) to the integrated signals of the CH chain protons (3.5–4.3 ppm) gives, multiplied by 100, the percentage of formalization of the sample.

The quantitative analysis of the comparison of samples PVF-1, PVF-5, and PVF-6, following the procedure described above gave results that agree with the results of the quantitative analysis by ^{13}C n.m.r.. This can be seen in *Table 3*.

CONCLUSIONS

The assignment of the ^{13}C-n.m.r. signals to the structural groups present in these copolymers and the use of the NOE extinction technique allow an accurate determination of the composition, although the method is time consuming and is almost impracticable for dilute solutions.

The absence of hemiformal groups of ter-copolymers synthesized and purified under rather mild conditions allows determination of the degree of formalization by means of ^{1}H n.m.r. in a relatively easy way.

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