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The combined use of two-dimensional NMR and lanthanide shift reagents for the characterization of ethylene – vinyl acetate copolymers

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Summary

Two-dimensional NMR and lanthanide shift reagents have been combined for the first time for NMR spectral assignments. The combined approach permitted very detailed interpretation to be made of the one-dimensional ^1H and ^{13}C spectra of ethylene-vinyl acetate copolymers.

INTRODUCTION

Two-dimensional[1-3] (2D) NMR has been extensively used, and the technique is fairly routine for many applications. One consequence of the increasing use of 2D NMR is a revival of interest in ^1H NMR for polymer studies. Yet, a major drawback of ^1H NMR remains its limited chemical shift range, such that in complex molecules the resonances of different protons are frequently overlapped or incompletely resolved. We shall show in this work that the use of lanthanide shift reagents (LSR) combined with two-dimensional NMR can alleviate this difficulty in suitable cases. As far as we know, this is the first report of the combined use of shift reagents and 2D NMR for any system, organic or polymeric.

RESULTS AND DISCUSSION

We have chosen ethylene-vinyl acetate copolymers (EVAc) for our studies because this is a deceptively simple polymeric system. The copolymer has been studied by both ^1H and ^{13}C NMR[4-6]; however, several aspects of polymer structural and spectral assignments still attract attention[6].

In view of the many comonomer sequences possible in ethylene-vinyl acetate copolymers, a consistent nomenclature is needed for these sequences. In this work, we shall borrow the terminology from ethylene-propylene copolymers[7]. The backbone methine and methylene protons are represented by T and S respectively. Greek subscripts are used to indicate the distances the nearest methines are from the carbon in question. Some examples are shown in Figure 1. Note that this terminology is different from those reported by others[5b].

Figure 2 shows the effect of the addition of ytterbium and europium shift reagents on the ^{1}H NMR spectra of EVAc. In agreement with a previous work [4d], the addition of shift reagents causes a number of resonances to emerge and shift downfield from the large upfield resonances at 1.26 ppm. The ytterbium shift reagent[8], Yb(fod)$_3$, gives larger lanthanide induced shifts, and also provides better separation of overlapped resonances. At a shift reagent/substrate molar ratio (ρ) of ca.0.0015, we observe a number of distinct spectral features (Figure 2f).

Previously it has been shown that the ^{13}C-^{1}H heteronuclear shift correlated experiment (CSCM) can be a useful tool for polymer microstructural studies[9]. By correlating the chemical shifts of directly bonded ^{13}C and ^{1}H, one can combine the information on spectral assignments for ^{1}H and ^{13}C to obtain a more complete interpretation of both spectra. We can use the same approach for the ^{1}H NMR spectra shifted by lanthanide shift reagents. The CSCM contour map for a Yb(fod)$_3$-shifted ^{1}H spectrum is given in Figures 3-4. On the basis of the 2D data, we can then make line-to-line correlations and provide assignments. For convenience, this is summarized in a graphical form in Table I.

From the ^{13}C-^{1}H shift correlation, the LSR-shifted ^{1}H NMR spectrum can be fully interpreted. Not surprisingly, the methine is shifted the most at ca. 6.0 ppm. Rather detailed sequence information is available from this ^{1}H spectrum. Note that $T_{\beta\beta}$ is the most upfield resonance, followed by $T_{\beta\delta}$ and $T_{\delta\delta}$. This is the same trend as ^{13}C NMR, but reversed from the normal (i.e. no LSR) ^{1}H spectrum. The acetate is now split into three resonances at ca. 2.74 ppm. Furthermore, $S_{\beta\beta}$ and $S_{\beta\delta}$ are all separately resolved.

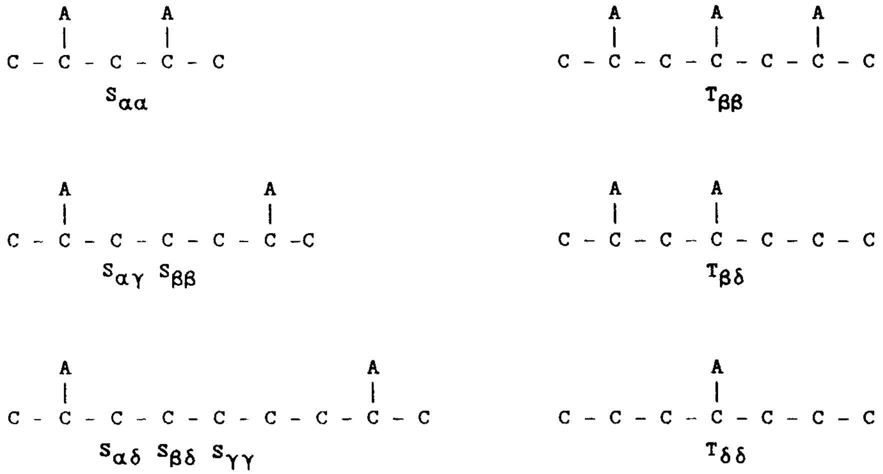


Figure 1. Nomenclature Used for the EVAc Sequences; A = OAc Group

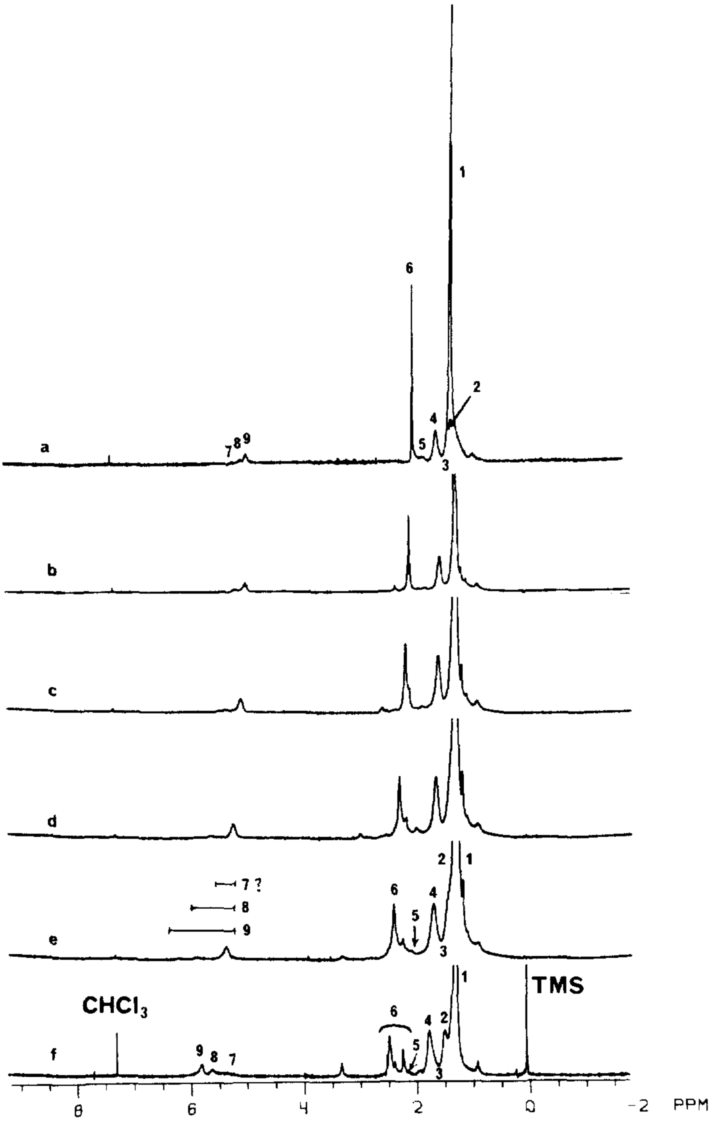
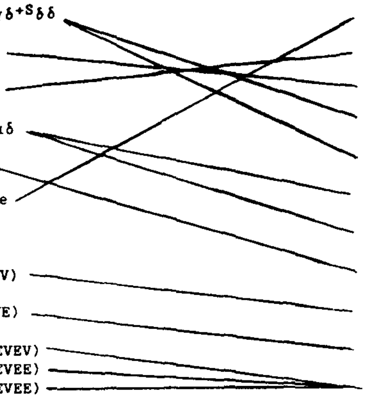


Figure 2. Effect of shift reagents on the ^{1}H spectrum of EVAc: (a) $\rho=0$, (b) $Eu(fod)_3$, $\rho=0.00182$, (c) $Eu(fod)_3$, $\rho=0.00364$, (d) $Eu(fod)_3$, $\rho=0.00546$, (e) $Eu(fod)_3$, $\rho=0.00728$, (f) $Yb(fod)_3$, $\rho\sim0.0015$.

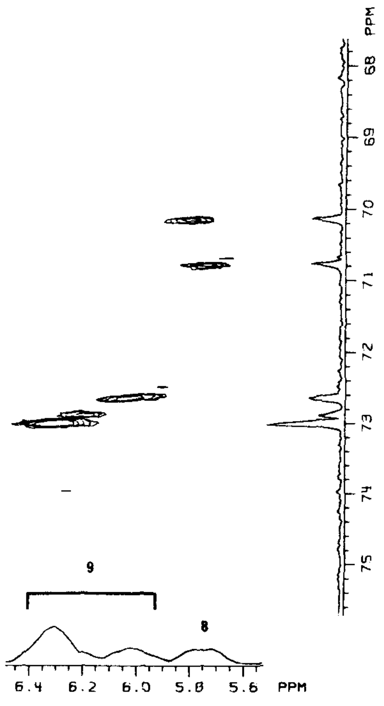
Table I. ^{13}C and ^{1}H NMR Assignments in EVAc Copolymers

No.	^{1}H Shift [ρ=0]	^{1}H Shift [$Yb(fod)_3$]^{a}	Sequence
1	1.26	ca. 1.26	$S_{\gamma\gamma}+S_{\gamma\delta}+S_{\delta\delta}$
2	1.33	1.60	$S_{\beta\delta}$
3	1.40	ca. 1.70	$S_{\beta\beta}$
4	1.50	1.93	$S_{\alpha\gamma}+S_{\alpha\delta}$
5	1.73	2.08	$S_{\alpha\alpha}$
6	1.92	2.58 2.74 2.90	Acetate
7	5.15	5.35	$T_{\beta\beta}$(VVV)
8	5.03	5.75	$T_{\beta\delta}$(VVE)
9	4.90	5.90 6.00 6.30	$T_{\delta\delta}$(VEVEV) $T_{\delta\delta}$(VEVEE) $T_{\delta\delta}$(EEVEE)



^{13}C Sequence	^{13}C Shift
Acetate	21.0
$S_{\beta\beta}$	21.5
$S_{\beta\delta}$	25.7
$S_{\gamma\gamma}+S_{\gamma\delta}$	29.8
$S_{\delta\delta}$	30.0
$S_{\alpha\delta}$	34.7
$S_{\alpha\gamma}$	35.2
$S_{\alpha\alpha}$	39.6
$T_{\beta\beta}$	ca. 68
$T_{\beta\delta}$	71
$T_{\delta\delta}$	73

^{a} Shift observed with $Yb(fod)_3$ added, ρ = 0.00235.



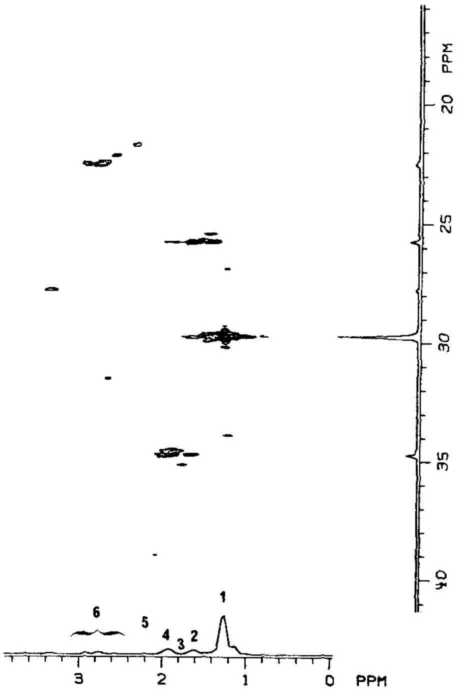


Fig. 3. ^{13}C-^{1}H CSCM plot of the methylene region of EVAc with $Yb(fod)_3$ added (ρ=0.00235).

Fig. 4. ^{13}C-^{1}H CSCM plot of the methine region of EVAc with $Yb(fod)_3$ added

Using the data from the 2D/shift reagent work, we can provide detailed spectral assignments of the normal (i.e. no LSR) one-dimensional ^1H and ^{13}C spectra of EVAc. For compactness, the ^1H assignments are included in the second column of Table I. As expected, the ^1H resonances of many sequences are overlapped. Note that $S_{\beta\beta}$ occurs at 1.40 ppm (between $S_{\alpha\gamma}/S_{\alpha\delta}$ and $S_{\gamma\gamma}$), instead of 1.47 ppm as reported in the literature[4a]. Similarly, $S_{\beta\delta}$ occurs at 1.33 ppm, instead of 1.26 ppm as previously reported[4a].

The assignments of the comonomer sequences in the ^{13}C NMR generally agree with those of the previous works [5,6]. A bonus of the 2D/shift reagent work is that additional features can be noticed. The complete ^{13}C NMR interpretation of EVAc, including several new assignments, is given in Table II. Two copolymers with different compositions have been used. The ^{13}C spectra (Figure 5) show distinctive differences; these are due both to the intensity differences in backbone carbons and to the differences in chain branching, which occurs at low VAc concentrations.

EXPERIMENTAL SECTION

The polymers were purchased from Aldrich Chemical Company (Metuchen, NJ). They were dissolved as 15% (w/w) solutions in deuterochloroform. The $Eu(fod)_3$ and the $Yb(fod)_3$ shift reagents were obtained from Aldrich (Metuchen, NJ) and Norell (Landisville, NJ), respectively. They were used without further purification. All ρ values are calculated for a EVAc copolymer with 40 wt % VAc. For $Yb(fod)_3$, $\rho = 0.00235$ corresponds to 6.9 mg $Yb(fod)_3$/112.3 mg EVAc.

The NMR spectra were obtained on a GE/Nicolet NT-300 spectrometer operating at 75.46 MHz. Unless specified otherwise, all samples were run at 50°C. The (one-dimensional) quantitative spectra were obtained with 90°-pulses and 20-second delays with 32K memory points. The ^{13}C CSCM spectra were obtained using a sweep width of 6 kHz and 4K data points. A total of 128 spectra were used to provide the equivalent of 1.5 kHz sweep width in the ^1H frequency dimension. Free induction decays in the ^1H frequency dimension were zero-filled before Fourier transformation and the spectra displayed in the absolute value mode.

CONCLUSION

In this work it is shown that the combined use of lanthanide shift reagents with the 2D CSCM experiment can provide detailed assignments (at the polymer microstructural level) of the ^1H and the ^{13}C spectra of ethylene-vinyl acetate copolymers. In addition, comonomer sequence distribution can be obtained from the LSR-shifted ^1H spectrum of EVAc. Other 2D approaches (e.g. COSY and NOESY) can also be used in conjunction with lanthanide shift reagents. Application of this combined shift reagent/2D method to other chemical systems should be straightforward.

Table II. Detailed Assignments of ^{13}C Resonances in EVAc Copolymers

No.	Assignments				^{13}C Shift (ppm) Sample A	^{13}C Shift (ppm) Sample B
			A. Backbone Carbons			
1a	CH	EVE			73.8 - 74.6	73.8 - 74.6
1b		VVE			70.0 - 71.8	70.0 - 71.8
1c		VVV			---	ca. 67.7
2a	CH_2	$S_{\alpha\alpha}$ - VVVE[a]			---	39.9
2b		$S_{\alpha\alpha}$ - EVVE[a]			---	39.2
3a	CH_2	$S_{\alpha\gamma}$ [a]			---	ca. 35.2
3b		$S_{\alpha\delta}$			ca. 34.7	ca. 34.7
4a	CH_2	$S_{\delta\delta}$			30.0	30.0
4b		$S_{\gamma\delta}$ [c]			29.8	29.8
5a	CH_2	$S_{\beta\delta}$ - VEEE[a]			25.8	25.8
5b		$S_{\beta\delta}$ - VEEV[a]			25.7	25.7
6	CH_2	$S_{\beta\beta}$			---	21.5
7	CH_3 (acetate)				21.0	21.0
			B. Carbons Due to Chain Branching[b]			
a	Bu-br,	Am-br			38.2	38.2
b			Me-α		37.8	--
c	Bu-α,	Am-α Am-5		L-α	34.6	34.6?
d	Bu-4,				34.1	34.1
e			Me-br		33.3	--
f		Am-3			32.8	--
g				L-3	32.3	--
h	Bu-3				30.0	30.0
i	Bu-β,	Am-β,		L-β	27.5	27.3
j		Am-4,	Me-β		26.8	--
k	Bu-2				23.5	23.5
l		Am-2,		L-2	22.9	--
m			Me-1		20.0	--
n	Bu-1,	Am-1,		L-1	14.0	14.1

[a] Assignments made in this work.

[b] Terminology follows that of low-density polyethylene[10].

[c] Possible overlap due to $S_{\alpha\beta}$ (due to inversion of VAc).

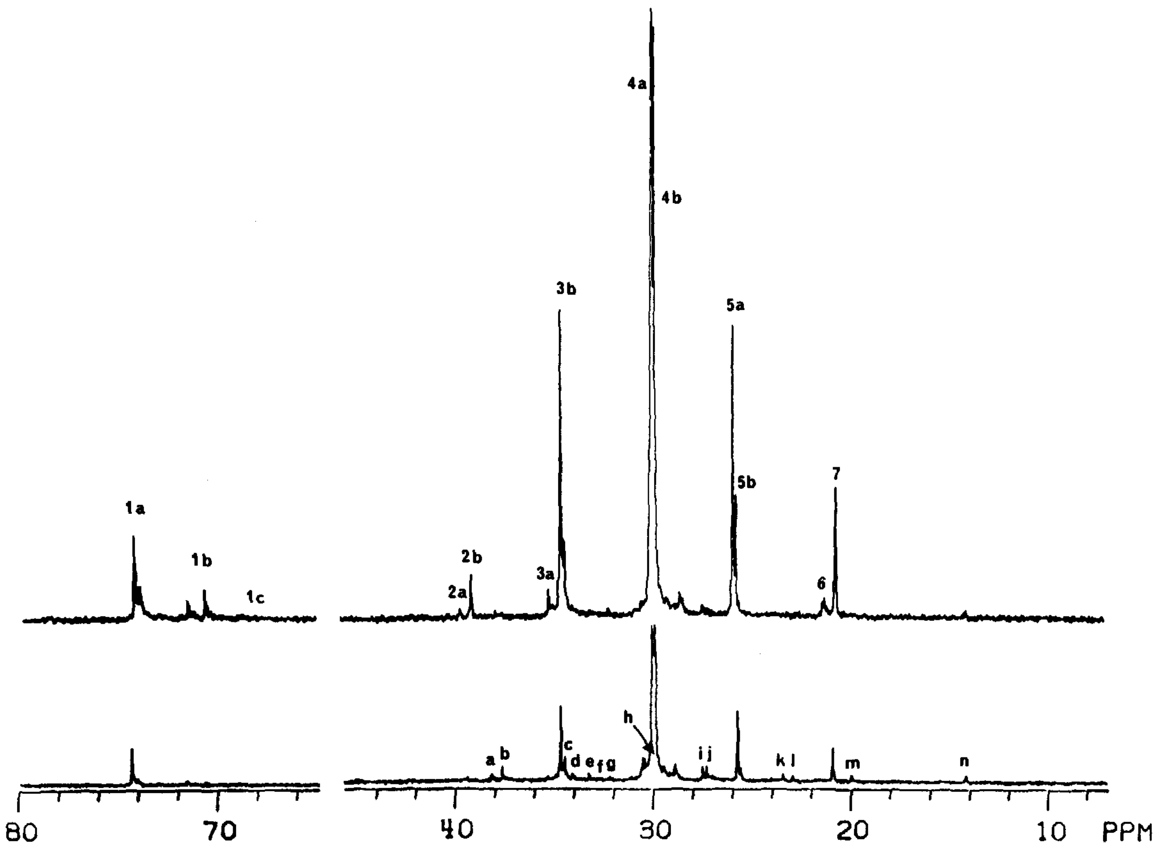


Figure 5. ^{13}C NMR spectra of two samples of EVAc copolymers. Upper trace, 40 wt % VAC; lower trace 12 wt % VAC; line numbers (given in Table II) are used in spectral assignments.

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