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Compositional Assignments for Chemically Modified PVC by Two-Dimensional NMR Spectroscopy

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ABSTRACT: The chemical microstructure of vinyl chloride–vinylthiobenzene copolymers prepared by the nucleophilic substitution reaction of poly(vinyl chloride) and that of vinyl thiobenzene homopolymer is analyzed by monodimensional ^{1}H and ^{13}C and two-dimensional inverse heteronuclear NMR spectroscopy. In this work the correct assignments of $-CHCl-$ and $-CHSC_6H_5-$, methine carbons at 62.0–57.0 and 47.5–45.5 ppm, respectively, are shown. The results of this work support the stereoespecific character of the PVC substitution reaction given in the past; however, they also demonstrate the necessity for a re-interpretation of the ^{13}C-NMR spectroscopic signals of the vinyl chloride–vinylthio derivate copolymers previously studied.

Introduction

Although many chemical modification reactions have been carried out on poly(vinyl chloride) to improve the polymer properties, only few NMR spectroscopic analyses on the microstructure and stereochemistry of chemically modified poly(vinyl chloride) have been reported. To our knowledge, the only complete works of this kind refer to the nucleophilic substitution, described later, and to the chemical reduction of PVC.[1–5] Many studies of the comonomer and stereosequence distribution of ethylene/vinyl chloride (EV) copolymers, were made by Tonelli et al. and Starnes et al., among others, and later by Pourahmady et al. using ^{13}C-NMR spectroscopy. The ability of Tonelli et al. to predict the ^{13}C chemical shifts for various microstructures occurring in E–V copolymers enabled them to make the assignments of VVV, EVV, EVE, VEV, VEE, and EEE triads and therefore to determine the comonomer distribution in the copolymer. They also concluded from the ^{13}C-NMR analysis that in the reduction of PVC and PVC model compounds with reagents such as tri-*n*-butyltin hydride or sodium tetrabutyl hydride, m VV diads are preferentially removed relative to r VV diads. From the comparison of triad sequences observed in PVC and PVC model compounds, they found an independence of comonomer sequences longer than triads.

A large amount of substitution reactions of PVC with a variety of thiolate derivatives has also been carried out by Millán et al.[6–13] with the double purpose of improving polymer properties and studying the nucleophilic substitution mechanism. Nowadays this kind of study is of extreme interest in the investigations of fundamental aspects and properties of this polymer. In this regard it has been reported by Mijangos et al. that the controlled substitution reactions on PVC is a new way to study (i) the gelation mechanism of this polymer,[14,15] (ii) the dependence of the glass transition temperature of the chemically modified PVC with the microstructure and the reaction medium,[16,17] and (iii) the improvement of polymer properties under industrial conditions.[13,18,19] Similar modified PVC has also been employed by Scherrenberg et al.[20] to investigate the structural order in this polymer and by Millán et al.[6,7] in the study of conformational aspects of substitution reactions. These studies implied a systematic analysis of chemically modified PVC by ^{13}C NMR spectroscopy, particularly with sodium thiobenzene as reactant. The corresponding vinyl chloride–vinylthiobenzene (VC–VTB) copolymers were analyzed in terms of the stereochemistry of unreacted methine carbons, mm, mr, and rr triad configurations, allowing the description of a stereospecific mechanism in this nucleophilic reaction, in which mm > mr ≫ rr in all reactions conditions: solution, melt and temperature.

Nevertheless, in order to give a correct ^{13}C-NMR verification and quantification of the microstructure of VC–VTB copolymers, the absolute assignments of newly formed structures in these copolymers, that is the $-CHSC_6H_5-$ structure, is required. To obtain a more consistent interpretation of the VC–VTB copolymer spectra, two methods were undertaken. One is the synthesis of the VTB homopolymer and examination of the ^{13}C and ^{1}H spectra, and the second is the direct study of these copolymers by two-dimensional heteronuclear ^{13}C ^{1}H NMR spectroscopy. Two-dimensional heteronuclear correlation spectroscopy has been successfully applied[21–24] to provide tacticity assignments in PVC and microstructure analysis of a few copolymer systems. Nevertheless, it has never been applied to PVC copolymers, although peak assignments are made independent of empirical shift rules and propagation statistics.

In this work we show the correct assignment of ^{13}C-NMR spectra for VC–VTB copolymers and evidence for the necessity of revising the NMR results concerning the evolution of tacticity in the nucleophilic substitution of PVC.

Experimental Section

Reagents. Poly(vinyl chloride) (PVC) was supplied from Rio Ródano Industries, Spain. The (*S*)-vinylthiobenzene (vinyl phenyl sulfide) monomer (VTB) was supplied by Fluka. The sodium benzenethiolate (NaBT) was synthesized from the corresponding thiol by reaction with metallic sodium in *p*-xylene, as described elsewhere.[11,12] Tetrahydrofuran (THF) was distilled in the presence of lithium aluminum hydride. Cyclohexanone was purified by double distillation from the commercial product.

Synthesis of Poly(vinylthiobenzene). The synthesis of poly(vinylthiobenzene) (PVTB) was carried out by radical homopolymerization of vinylthiobenzene monomer. The po-

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lymerization was carried out in the presence of AIBN as initiator in a glass ampule at 55 ± 0.5 °C in a nitrogen atmosphere. After 48 h of reaction time the sample was diluted with THF and precipitated with a large excess of methanol. The precipitate was purified twice by dissolving the isolated samples in THF and precipitating in methanol. Finally, it was dried to constant weight under vacuum at a temperature of 40 °C. The PVTB was characterized by ^{1}H and ^{13}C spectroscopy.

Synthesis of Vinyl Chloride−Vinylthiobenzene Copolymers. The vinyl chloride−vinylthiobenzene (VC−VTB) copolymers were obtained by substitution reactions of PVC and NaTB, in an equimolecular concentration, in cyclohexanone, 8 g/L, at 60 °C. At progressively increasing reaction intervals, samples were withdrawn, precipitated in methanol, and purified twice with THF/MeOH as the solvent−precipitant system. The (VC−VTB) copolymers were characterized by ^{1}H- and ^{13}C-NMR spectroscopy.

The degree of conversion, expressed in mol %, refers to the number of chlorine atoms displaced by the $-SC_6H_5$ group. Therefore, it also expresses the molar composition of VC−VTB copolymers.

NMR Spectroscopy. ^{1}H-NMR spectra of PVC, PVBT, and VC−VTB copolymers were recorded at 25 °C on 5% w/v deuterated nitrobenzene−deuterated chloroform mixture solutions with a Varian Gemini 200 MHz, operating at 200 MHz, under standard conditions.

^{13}C-NMR spectra of PVC, PVBT, and VC−VTB copolymers were recorded at 90 °C on 10−20% w/v in deuterated dioxane solutions with a Varian XL-300 MHz spectrometer operating at 75.5 MHz under conditions previously described.[16,17]

Two-dimensional inverse proton detected heteronuclear shift correlation spectra were obtained on a Varian unity 500 operating at 500 MHz, using the HMQC pulse sequence. Deuterated nitrobenzene was used as a solvent. Data were collected in an 1024 × 512 matrix with a spectral width of 4110 Hz in the proton domain, and 4918 Hz in the carbon domain, and processed in a 1024 × 1024 matrix. The experiment was optimized for a one-bond heteronuclear coupling constant of 140 Hz. The null time was empirically optimized at 300 ms.

Results and Discussion

^{1}H Spectroscopy. Figures 1a−c show the ^{1}H-NMR spectra of poly(vinyl chloride), vinyl chloride−vinylthiobenzene copolymer (90:10), and vinyl chloride−vinylthiobenzene copolymer (70:30), respectively. The 5.0−4.0 ppm region represents the resonance peaks of $-CH^{*}Cl-$ protons, and the 2.5−1.5 ppm region, those of $-CH^{*}_2-$ protons. In Figure 1b,c, it can be observed that the substitution of Cl atoms by $-SC_6H_5$ leads to new resonance bands from 4.0 to 3.4 ppm, which have been assigned to the less deshielded protons of tertiary carbons substituted by the thiobenzene. The area of the region 4.0−3.4 ppm related to the total area 5.0−3.4 ppm, and expressed in %, gives the degree of modification (molar composition). The 4.0−3.4 ppm region corresponds to the contribution of compositional and configurational effects, although at present it cannot be analyzed more precisely. Nevertheless, this region is of great importance in the 2D heteronuclear spectroscopy analysis.

In Figure 1d is shown the ^{1}H-NMR spectrum of poly(vinylthiobenzene). The region 4.4−3.4 ppm reproduces the $-CH^{*}SC_6H_5-$ protons, and the 2.5−1.6 ppm region, that of $-CH^{*}_2-$ protons. These results confirm the correct assignment previously made for the 4.0−3.4 ppm region, to $-CHSC_6H_5-$ in the VC−VTB copolymer.

^{13}C Spectroscopy. Figures 2a−c show the ^{13}C-NMR spectra of poly(vinyl chloride), vinyl chloride−vinylthiobenzene (90:10), and vinyl chloride−vinylthiobenzene (70:30) copolymer, respectively. In Figure 2a the 59.7−57.3 ppm and the 49.5−47.0 ppm regions represent the methine and methylene carbons, respectively, of PVC in agreement with already published data.[8−13] The methine carbon region has been applied very successfully to the determination of configurational monomer sequences in the polymer, and it consists of three well-separated main peaks centered at 59.3, 58.5, and 57.5 ppm characteristic of rr, rm, and mm triads.

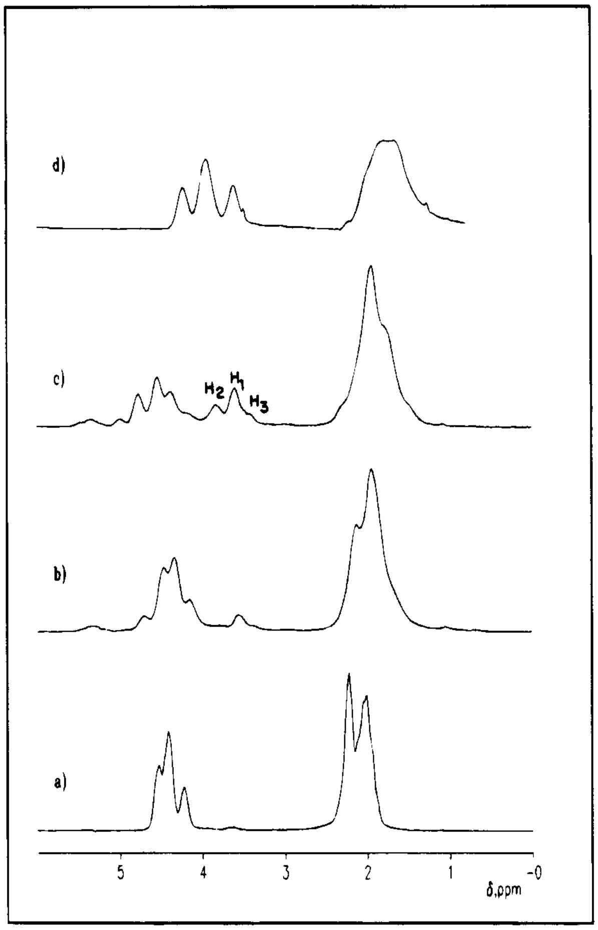

Figure 1. ^{1}H-NMR spectra of poly(vinyl chloride) (a), vinyl chloride−vinylthiobenzene (90:10%) (b), vinyl chloride−vinylthiobenzene (70−30%) (c), and poly(vinylthiobenzene) (d).

In the past, the ^{13}C-NMR spectra of chemically modified PVC, that is VC−VTB copolymers, have only been analyzed for the 62.0−57.2 ppm region corresponding to the methine carbons. It was found in spectra similar to these, although less resolved, that, firstly, this region was sensitive to the modification (broadening of the bands) as is observed in Figure 2b, in which new resonance bands appear at 60.1 ppm. As the degree of modification increases, other bands appear at 61.1 ppm (spectrum 2c). Secondly, whatever the degree of composition, α, the percentage of new triads found, C_4 and C_5, was ≃α, while the number of triads centered on a VC unit was ≃100 − α.[8−14] Then it was assumed that the resonances corresponding to the $-CHCl-$ centered triads were C_1, C_2, and C_3 bands while those corresponding to the $-CHSC_6H_5-$ centered triads lied under the peaks C_4 and C_5. On the basis of the evolution of these triads, the stereospecific mechanism of PVC nucleophilic substitution was established.

In the present study we focus our attention on all of the ^{13}C-NMR resonance bands of chemically modified PVC, as displayed in Figure 2a−c. We can observe a broadening in the $-CH_2-$ region as the degree of

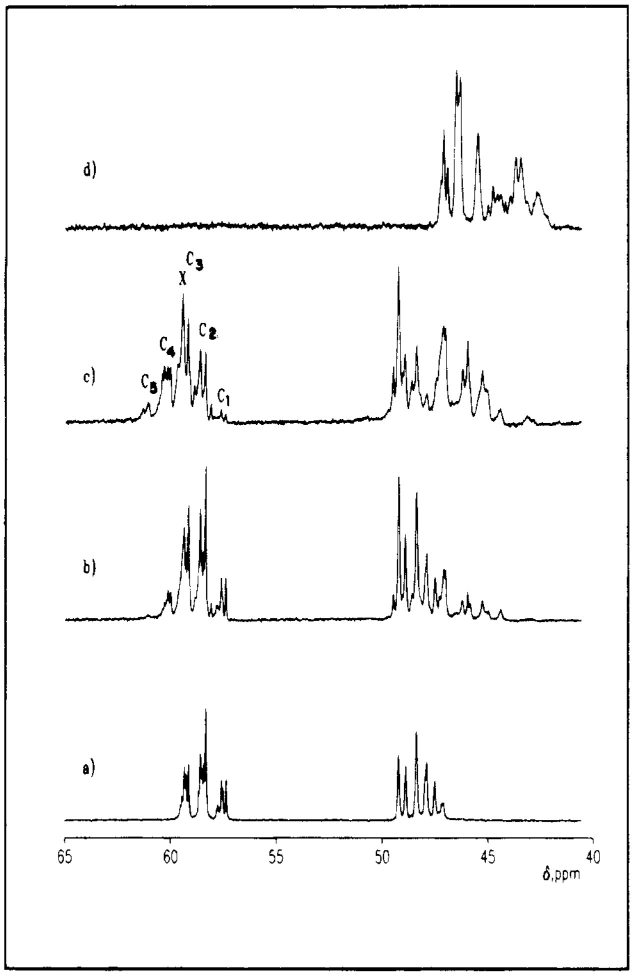

Figure 2. ^{13}C-NMR spectra of poly(vinyl chloride) (a), vinyl chloride–vinylthiobenzene (90:10%) (b), vinyl chloride–vinylthiobenzene (70–30%) (c), and poly(vinylthiobenzene) (d).

modification increases. In fact, this enlargement is higher than that observed in −CH− region. We will return to this point later.

In order to obtain a more consistent interpretation of the above spectra we synthesized and examined poly(vinylthiobenzene), that is, a 100% modified PVC. In Figure 2d the carbon resonance of PVTB is shown. As we can see, all of the resonance peaks of this polymer lie in the small region from 47.5 to 42 ppm. Although there are not two clearly separated regions corresponding to methine and methylene carbons, as for other vinyl homopolymers, we assume by analogy that the 47.5–45.1 ppm region corresponds to the tactic placements of $-CHSC_6H_5-$ carbons, that is, rr, mr, and mm triads, and that of 45.1–42.0 ppm to the $-CH_2-$ carbons. This assumption will be confirmed by two-dimensional inverse heteronuclear correlation spectroscopy.

The most outstanding finding observed in this spectrum is that, contrary to what might be expected and what we have always considered, no single band is found in the 62–57 ppm region. The comparison of the PVTB spectrum with those of VC–VTB copolymers oblige us to reconsider the interpretation of methine carbons given until now.

For this reason, in the present study, the following assumptions for spectra of Figures 2a–d and others not shown, are made.

—Firstly, all of the resonance peaks from 62.0 to 57.3 ppm in the VC–VTB copolymers are only due to the centered −CHCl− methine carbons.

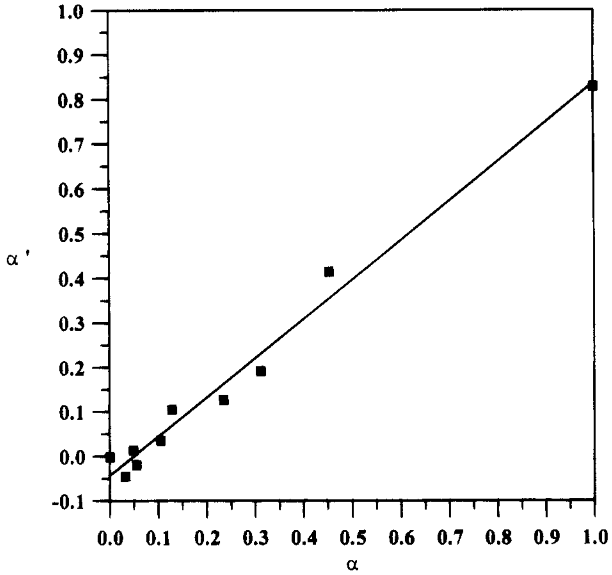

Figure 3. Correlation ^{1}H spectroscopy and microanalysis composition, α, with ^{13}C spectroscopy composition, α′.

—Secondly, all the peaks corresponding to centered $-CHSC_6H_5-$ methine carbons resonate in a zone in the 48.0–42.0 ppm region, although they cannot be more precisely assigned. We consider, moreover, that all the $-CH_2-$ carbons must appear in this region, that is, from $-CH_2-CHCl-$ and $-CH_2-CHSC_6H_5-$ units.

If this assumption is true, from the ^{13}C spectrum calculation one should be able obtain, in some way, the degree of modification (molar composition), although a 100% agreement is not expected because experimental conditions are not ideal for quantitative evaluations.

Thus by a simple calculation, the degree of modification, α′, can be derivated as follows:

$$\alpha' = \frac{B - A}{B + A} 100 \qquad (1)$$

where α′ is the degree of modification expressed in percent mole, *A* is the area of the 62–57.3 ppm region, and *B* is the area of 48–42 ppm region.

In Figure 3 the degree of composition, α′, calculated from eq 1 versus the degree of composition, α, obtained from microanalysis and ^{1}H spectroscopy, for a variety of VC–VTB copolymers of different molar compositions is plotted. The following conclusions can be drawn from the plot: Firstly, as the degree of conversion, α, increases, the value of α′ also increases. Secondly, there is a linear relation between α and α′ with a factor of almost 1. As previously stated, a 100% agreement is not expected due to experimental conditions.

Therefore one can say that the two considerations made are true. Consequently, the triads centered on $-CHSC_6H_5-$ methine carbons resonate in the 50.0–45.0 ppm region, presumably at the lowest field shifts of $-CH_2-$ carbons, around 46 ppm, although we cannot assign their exact position. A more precise determination will be obtained by 2D heteronuclear spectroscopy in the next section.

The ^{13}C resonances of the 62–57.3 ppm region only correspond to triads centered on −CHCl− methine carbons formed by the compositional triads, VC–VC–VC, VC–VC–VTB, and VTB–VC–VTB, each including the respective configurational triads. Nevertheless, they are not susceptible to a more detailed analysis at the present, because of the following reason. One can

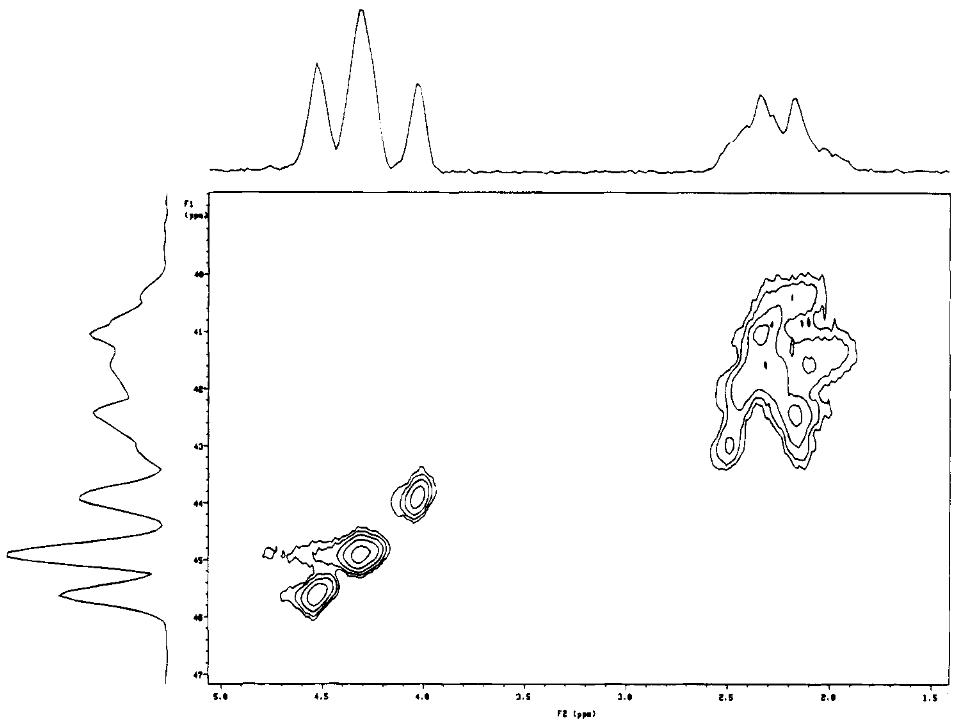

Figure 4. 2D $^{13}C-^{1}H$ heteronuclear correlation NMR spectrum of poly(vinylthiobenzene).

easily assume that the bands, in Figure 2c, can be assigned in the following way: C_5 to VTB–VC–VTB triads, C_4 to VC–VC–VTB triads, and C_1, C_2, and C_3 to VC–VC–VC triads. There are arguments in favor of this assignment. One is the analogy with the ^{13}C-NMR analysis of EV copolymer made by Tonelli et al., among others,[1,2] and the second is that we do not find any new bands beyond C_5 even at conversions of 66%. But, there are also arguments against this assignment. One is, that due to the small shift of new bands, it is likely that some of them can also be overlapped with those corresponding to the unreacted chlorines. In fact we observe in Figure 2a–c, that band X in the rr configuration of VC carbons increases as the degree of modification increases. Another comes from the fact that if we plot the evolution of VC–VC–VC, VC–VC–VTB, and VTB–VC–VTB triads, assumed to be C_1–C_3, C_4, and C_5 bands, respectively, as a function of the degree of conversion, the evolution is far removed from what, in principle, one might expect for a random distribution of comonomer sequences. However, if we consider that band X corresponds to some of the configurational bands of VC–VC–VTB triads, the results are improved. We do not have definite conclusions to show that the PVC reaction mechanism with NaBT follows a random or block substitution model, since some uncertainties still exist which prevent the accurate quantitative analyses of VT–VTB copolymers in terms of stereosequence and comonomer sequence distribution. Nevertheless, there is evidence, from ^{1}H-NMR and glass transition temperature studies, now underway, in favor of a Bernouillian rather than block substitution.

Be as it may, it is beyond doubt that in the nucleophilic substitution of PVC with these new results, not only the stereospecific mechanism is valid but also the role of isotactic and heterotactic triads in the reaction is reinforced, since their evolution rate is now higher.

2D NMR Spectroscopy. An unambiguous method to verify the correct assignments of the $-CHSC_6H_5-$ carbons was undertaken with the aid of 2D heteronuclear spectroscopy, by means of single-bond proton–carbon correlation. This technique makes it possible to correlate the directly bonded proton and carbon atoms.

Figures 4–6 show the 2D heteronuclear $^{13}C-^{1}H$ inverse correlation spectra of PVTB, VC–VTB copolymer (90:10), and VC–VTB copolymer (60:40). In Figure 4 it can be observed that the protons of methylene carbons from 2.6 to 1.8 ppm are correlated to carbons in the 43.5–40.0 ppm region, and the protons of $-CH^{*}SC_6H_5$ methine carbons, from 4.7 to 3.9 ppm, to carbons in the 46.0–43.5 ppm region. Therefore these two zones, 43.5–40.0 and 46.0–43.5 ppm, correspond to the resonance of methylene and methine carbons, respectively, in the monodimensional ^{13}C spectrum of PVTB. This chemical shift corresponds to the spectra in nitrobenzene. The exact position corresponding to dioxane solutions must be taken from the ^{13}C-NMR spectrum, Figure 2d. These results also confirm the assignments given previously in the ^{13}C spectrum of this homopolymer (Figure 2d), i.e., methine carbons in the region 47.0–45.1 ppm and methylene carbons in the region 45.1–42 ppm.

Figure 5 shows the 2D heteronuclear NMR spectrum of VC–VTB copolymer (90:10). It can be seen that the unique proton resonance band of $-CH^{*}SC_6H_5-$ methine carbons is correlated to two bands of methine carbons at 44.0 and 45.0 ppm, presumably due to configurational effects of the VC–VTB–VC triads. In dioxane, the corresponding shifts are 45.9 and 47.1 ppm, respectively. Methylene bands are not assigned because the corresponding protons in the homonuclear ^{1}H spectrum are not yet resolved.

Finally, Figure 6 shows the contour map of a VC–VTB copolymer (60:40) $^{1}H-^{13}C$ heteronuclear spectrum. One can observe that the three proton bands of the homonuclear spectrum are correlated to five bands in the ^{13}C spectrum, whose assignments are not simple at present. In fact the assignment in the homonuclear ^{1}H spectrum are not completely clarified but are consistent with the following. In Figure 1c, H_1 would correspond to the protons of methine carbon in the VC–VTB–VC triad, H_2 the same in VC–VTB–VTB, and H_3 that in

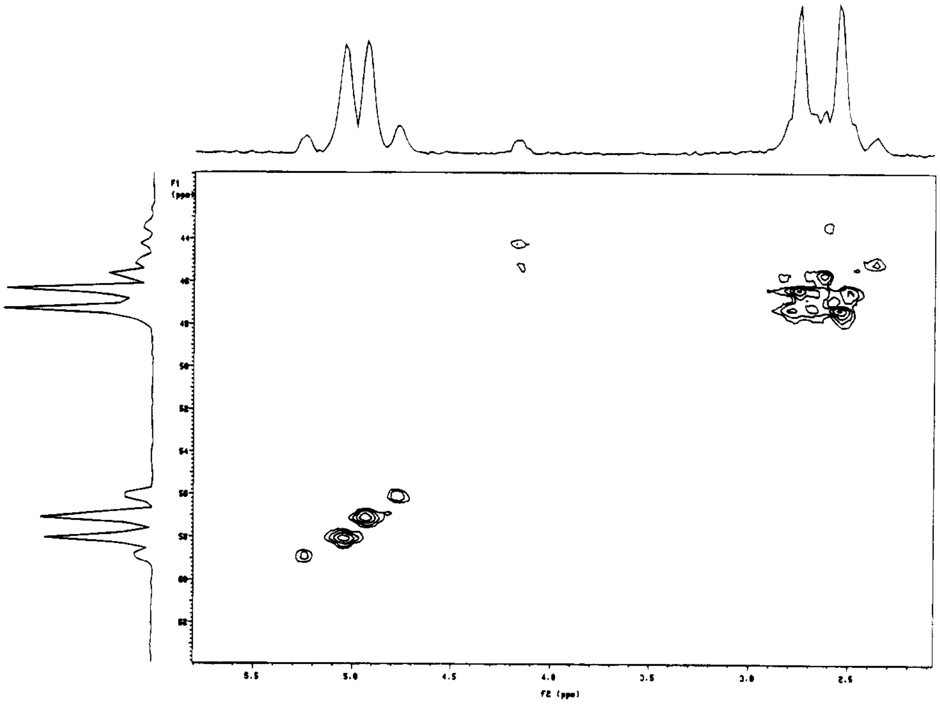

Figure 5. 2D $^{13}C-^{1}H$ heteronuclear correlation NMR spectra of vinyl chloride−vinylthiobenzene copolymer (90:10).

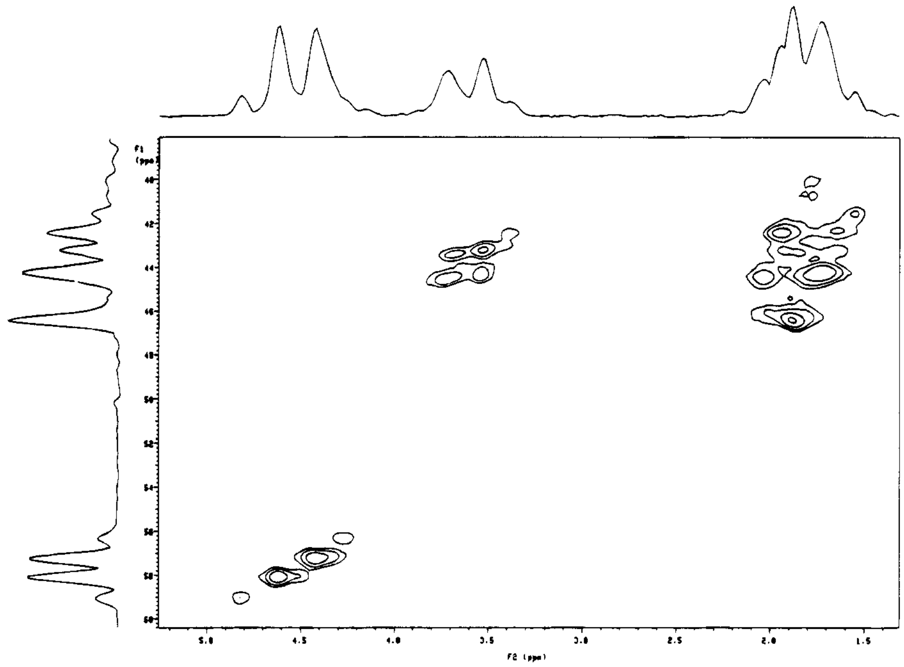

Figure 6. 2D $^{13}C-^{1}H$ heteronuclear correlation NMR spectra of vinyl chloride−vinylthiobenzene copolymer (60:40%).

VTB−VTB−VTB triads. Thus, in Figure 6, the five methine carbon signals must correspond to compositional and configurational effects. If we add the overlapping of $-CH^{*}_2$ methylene carbons, to the above region, the assignments are now quite impossible.

In spite of a relatively great effort which is now underway to determine the microstructures responsible for these signals by experimental measurements, the results of the work presented here represent a new path toward the correct assignments of the ^{13}C spectra for VC−VTB copolymers, and other vinyl chloride−vinylthiolate-derived copolymers. They represent a reinforcement of the stereospecific character of the reaction, as far as configurational control is concerned. Nevertheless, the stereospecific mechanism needs to be revised for other thiolate derivatives.

Conclusions

From monodimensional ^{1}H- and ^{13}C-NMR and two-dimensional inverse heteronuclear NMR spectroscopy of vinyl chloride−vinylthiobenzene copolymers and the vinylthiobenzene homopolymer, the correct assignments of $-CHCl-$ and $-CHSC_6H_5-$ methine carbons at 62.0−57.0 and 47.5−45.5 ppm, respectively, are deduced. Results concerning the stereospecific mechanism of PVC substitution with thiolate derivatives need to be revised.

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