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Applications of DEPT Experiments to the ^{13}C NMR of Copolymers: Poly(styrene-*co*-maleic anhydride) and Poly(styrene-*co*-acrylonitrile)

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ABSTRACT: The DEPT technique for the generation of CH, CH_2, and CH_3 ^{13}C NMR subspectra has enabled the resolution and assignment of broad and overlapping aliphatic resonances in copolymers. For styrene–acrylonitrile copolymers, the CH_2 resonances gave dyad fractions that were in agreement with the previously established copolymer structure. For styrene–maleic anhydride copolymers, three broad resonances were observed in the methylene subspectrum. These resonances were assigned to SSS, SSM and MSS, and MSM triads in preference to SS, *trans*-MS, and *cis*-MS dyads on the basis of a variety of evidence. This sequence information can be applied to the study of the mechanism of copolymerization. Partial esterification of the anhydride unit in some styrene–maleic anhydride copolymers was detected by generating the CH_3 subspectrum. A modification of the DEPT sequence to obtain partially relaxed subspectra enabled T_1 and T_2 relaxation times of both ^{13}C and ^{1}H nuclei to be measured for each of the resolved resonances.

Introduction

Over the last decade ^{13}C NMR spectroscopy has become an important technique for investigations of the structure of polymers and copolymers. The significant effects on chemical shifts of tacticity and, in copolymers, of monomer sequence rearrangements have enabled important information on these parameters to be obtained. However, along with the large natural line broadening from rapid spin–spin relaxation, these factors can also result in extremely complex spectra through peak overlap.

For those polymers with broad, poorly resolved resonances the assignment technique of single-frequency, off-resonance decoupling to determine peak multiplicities is rarely useful. Any technique which does allow simplification of such polymer spectra is obviously of considerable value. In recent papers the spin-echo,[1] INEPT,[2] and DEPT[3] techniques have been used to assign peak multiplicities via generation of CH_n (n = 0–3) subspectra in studies on small molecules.

Bendall and co-workers[1] have used spin-echo methods to generate accurate quaternary, CH_2, and CH/CH_3 subspectra which are relatively insensitive to modest variation of the single bond ^{13}C–^{1}H coupling constant. However, CH and CH_3 subspectra cannot be separated with the same degree of accuracy using this technique.

Both the INEPT[2] and DEPT[3] techniques utilize polarization transfer, which provides a significant sensitivity advantage over the spin-echo technique. However, the INEPT sequence is less accurate than the spin-echo technique due to its greater sensitivity to $^1J_{C-H}$ variations. The DEPT sequence, written as

$$^1\text{H:}\quad \frac{\pi}{2}(y)-\frac{1}{2J}-\pi(x)-\frac{1}{2J}-\theta(\pm x)-\frac{1}{2J}-\text{BB}$$

$$^{13}\text{C:}\quad -\frac{\pi}{2}(\pm x,\pm y)-\pi(\pm x,\pm y)-\text{acquire}$$

may be used to obtain CH_n (n = 1, 2, and 3) subspectra by combination of the three spectra obtained with $\theta = \pi/4$, $\pi/2$, and $3\pi/4$. Hence the editing depends on a pulse angle rather than a J-modulation period as in INEPT. DEPT provides more accurate subspectra because (1) it has a lower sensitivity to $^1J_{C-H}$ variations and (2) by using fewer pulses it is less sensitive than INEPT to pulse missetting and inhomogeneity.

In this work we report on the use of the DEPT technique to generate accurate subspectra of copolymers, demonstrating the simplification of spectra which is achieved and the sequence distribution information which is obtained for copolymers of styrene with maleic anhydride or acrylonitrile. The quantitative aspects of the technique are investigated.

Experimental Section

Copolymerizations. Styrene (S)–acrylonitrile (AN) and styrene–maleic anhydride (MAn) copolymers were produced by polymerization in the absence of solvent at 60 °C with benzoyl peroxide as initiator. The copolymers were twice purified by reprecipitation into methanol from chloroform (S–AN copolymers) or acetone (S–MAn copolymers) solutions.

NMR. ^{13}C NMR spectra were obtained on 10% w/v solutions in $CDCl_3$ (S–AN copolymers) or acetone-d_6 (S–MAn copolymers) using a Bruker CXP-300 spectrometer at 75.46 MHz with a standard, fixed frequency, ^{13}C observe/^{1}H decouple 10-mm probe. ^{1}H and ^{13}C $\pi/2$ pulse times were 22 and 15 μs, respectively. Experiments were performed at 37 °C using a 2-s recycle time.

The J-modulation time for the DEPT sequence was set to 3.7 ms, equivalent to J = 135 Hz. No detectable differences were observed in experiments performed with an assumed J of 125 Hz.

DEPT subspectra were generated from the following combinations of the $\pi/4$ (θ_1), $\pi/2$ (θ_2), and $3\pi/4$ (θ_3) experiments.

$$CH = \theta_2 - c(\theta_1 + a\theta_3)$$

$$CH_2 = \theta_1 - a\theta_3$$

$$CH_3 = \theta_1 + a\theta_3 - b\theta_2$$

where a, b, and c have theoretical values of 1.0, 0.707, and 0, respectively. However, in practice, slightly different values are necessary due to differences in probes and spectrometer setup. In this work the values used were ca. 1.15, 0.75, and 0.10, respectively.

Results and Discussion

Styrene–Maleic Anhydride Copolymer. The ^{13}C NMR spectrum of the aliphatic region of these copolymers has not previously been assigned. The normal spectrum (Figure 1d) of a sample S–MAn 1 with polymer composition of 52% styrene consists of three broad resonances, each displaying fine structure. As well as signals arising from the methine and methylene carbons of the styrene unit, separate resonances should be exhibited by the methine carbons of each maleic anhydride unit, one being

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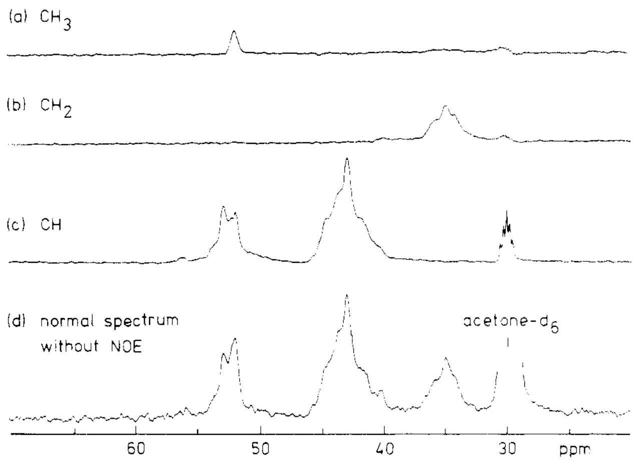


Figure 1. Aliphatic region of ^{13}C NMR spectrum of styrene–maleic anhydride copolymer (S–MAn 1): (a–c) subspectra generated by DEPT sequence; (d) normal spectrum obtained with gated decoupling to remove nuclear Overhauser enhancement, pulse angle = 90°, recycle time = 2 s.

attached to a methylene and one to a methine carbon of an adjacent styrene residue. Thus some overlap of resonances must be present in the spectrum. Further effects of the relative configurational arrangement of the monomer units in the chain would lead to peak multiplicities.

The three subspectra (Figure 1a–c) show the separation of the resonances which can be achieved, making assignments far easier and uncovering signals from defects in the regular chain structure.

The CH subspectrum shows good cancellation of the high-field methylene peak and of the $(CD_3)_2C{=}O$ solvent resonance. The multiplet at ~29 ppm is clearly the incompletely deuterated CD_3COCHD_2 impurity in the solvent. The peaks at ~44 and ~52 ppm are shown to belong to methine carbons with that at 44 ppm exhibiting good line-shape agreement with the normal spectrum.

From the CH_2 subspectrum the signal at ~35 ppm is identified with the methylene carbons. It also shows good line-shape agreement with the normal spectrum and clearly has a component extending to ~41 ppm. This extension is not obvious in the normal spectrum due to overlap by the methine resonance.

The CH_3 subspectrum shows the excellent cancellation of the methine and methylene resonances which is obtained. It reveals the difference in the signal in the region of ~52 ppm in the CH subspectrum as being due to the presence in the same region of a methyl signal resulting from esterification of the anhydride group during the isolation and purification steps of copolymer preparation where methanol was used as precipitant. It is well recognized[4] that these copolymers will form the half-ester of the anhydride unit in the presence of alcohols. This assignment was confirmed by observing the enhancement of the methyl signal when the copolymer was subjected to stirring in a large excess of methanol for long time periods. The DEPT sequence enables the detection of small amounts of ester impurities in these copolymers for which conventional techniques such as infrared spectroscopy[5] may not be sufficiently sensitive. (Copolymers for which sequence distributions are reported later in this work did not contain methyl ester impurity.)

The methylene subspectra from four copolymers with different composition are shown in Figure 2. Three broad signals are observed at 33–37, 37–42, and 42–47 ppm. The methylene subspectrum of a solution of copolymer to which polystyrene was added showed enhancement of the resonance at 42–47 ppm only.

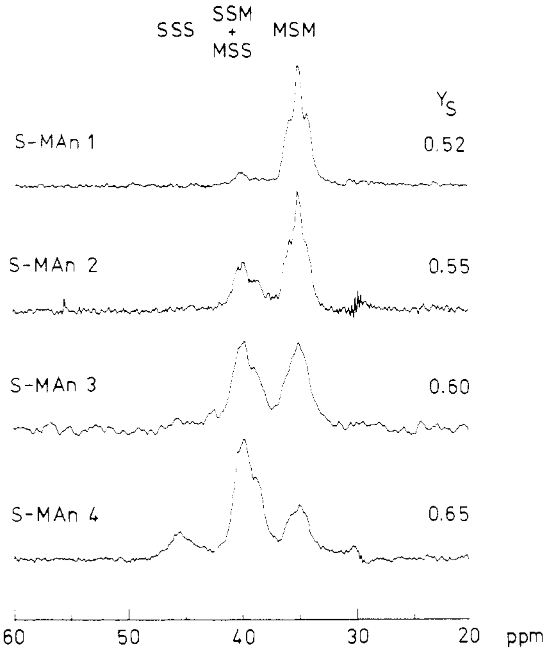


Figure 2. Methylene subspectra of styrene–maleic anhydride copolymers showing variation in triad sequence distribution with polymer composition (Y_S = mole fraction of styrene in copolymer).

Table I
Copolymer Composition Expressed As Mole Fraction of Styrene, Y_S, and Resonance Areas for the Methylene Subspectrum from the ^{13}C NMR of Styrene–Maleic Anhydride Copolymers

	Y_S			CH_2 resonance areas[d]		
code	*a*	*b*	*c*	42–47[e]	37–42[e]	33–37[e]
S–MAn 1	0.517	0.51_5	0.50_0	0	12	88
S–MAn 2	0.548	0.55_8	0.50_9	3	35	62
S–MAn 3	0.601	0.60_8	0.53_3	12	47	41
S–MAn 4	0.654	0.65_0	0.545	17	59	14

[a] Calculated from the carbonyl and aromatic signals of a separate ^{13}C NMR experiment,[9] ±0.01. [b] Calculated from CH_2 resonance areas on the basis of triad assignments (eq 2). [c] Calculated from CH_2 resonance areas on the basis of dyad assignments with cis/trans effect (eq 1). [d] Expressed as percentage of total CH_2 area; ±5%. [e] Range in ppm.

There are two different ways in which these methylene resonances could be assigned.

(A) The methylene resonances of vinyl polymers are expected to be sensitive to dyad effects. Since the MAn residue has no methylene carbons, only two dyad resonances, corresponding to SS and MS, should be present. The chemical shift of a methylene carbon adjacent to MAn which is in the cis form is expected to be lower than the shift of a carbon which is adjacent to MAn in the trans form by ca. 3 ppm based on changes observed in model succinimide compounds[6,7] and ethylene–maleic anhydride oligomers.[8] Thus, although this shift difference is somewhat less than that observed between the two upfield resonances, the three methylene resonances could be assigned to dyad sequences as follows: SS, 42–47 ppm; *trans*-MS, 37–42 ppm; *cis*-MS, 33–37 ppm.

The relative intensities of the two resonances at 37–42 and 33–37 ppm change markedly with copolymer composition (see Table I), thus indicating a large change in cis/trans content based on the assignments above. Olson and Butler[7] have reported a large change in cis/trans content with change in initial monomer feed composition in copolymers of *N*-phenylmaleimide with chloroethyl vinyl ether. Their results were based on changes in the relative intensities of two of the carbonyl resonances, which they assigned on the basis of epimerization studies to cis and trans arrangements about the maleimide unit. If complex participation occurs during propagation and if incorporation of the complex leads to predominantly cis or trans arrangement of the MAn residue, then a change in cis/trans content with monomer feed composition might result.

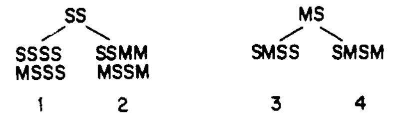
The methine and carbonyl carbons of the MAn residue should also display cis/trans effects of the order of 2–5 and ≈1 ppm, respectively, based on model compound studies.[6,7] While the resonances of these carbons do exhibit fine structure, the small changes observed in the shape of these resonances as the composition changes are not consistent with the large change in the ratio of peak intensities predicted if the methylene residues are assigned to cis and trans sequences.

Because of its low tendency to homopolymerize, MAn can be assumed to be present as single unit sequences in copolymers produced from monomer feeds containing an excess of styrene, as was the case for the copolymers discussed here. The compositions of these copolymers can therefore be calculated from the relative magnitudes of the dyads SS and MS:

$$F_S/F_M = 1 + A_{SS}/A_{MS} \qquad (1)$$

where F_S/F_M is the mole ratio of residues in the copolymer and A_{MS} and A_{SS} are the relative areas of the resonances assigned to the respective dyad fractions. The results of this calculation given in Table I show poor agreement with compositions determined independently,[9] consistently predicting a much lower styrene content. The evidence above suggests that assignment of the three resonances to SS, *trans*-MS, and *cis*-MS dyads would be inappropriate.

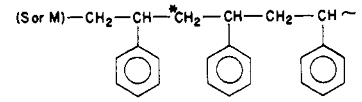
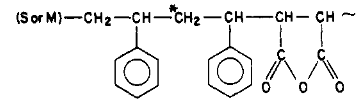
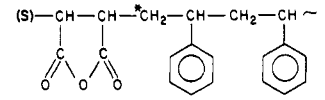
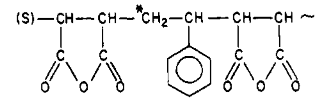
(B) The methylene group may also be sensitive to the nature of the residues beyond its adjacent substituents in the chain. Six different tetrads are predicted from SS and MS dyads, if it is assumed that only single MAn units are present. These tetrads may be divided into four groups



where the two groups from each dyad are differentiated by the presence of C═O substitution at the γ position relative to the CH_2 group under consideration, as shown in Table II. This γ substitution could shield the CH_2 to the extent that two separate resonances are observed for each dyad. The four resonances would correspond to the triad sequences shown in Table II.

It has been observed in the course of this work that the dyad sequences in the methylene subspectrum of styrene (S)–diethyl fumarate (D) copolymers are separated in this way.[10] The diethyl fumarate is a 1,2-disubstituted residue which resembles the MAn residue but does not produce the cis/trans effect. Three distinct CH_2 regions are observed in the spectra of these copolymers, 30–35, 32.5–42.5, and 40–45 ppm. They can be assigned to DSD, DSS and SSD, and SSS triad sequences respectively, since tacticity effects are expected to be smaller than observed shift differences and the relative intensities of the three regions change with copolymer composition in a way which is consistent with sequence distribution effects. The three resonances overlap and, because DSS and SSD triads are always equal in magnitude, it is not possible to separate their contribution to the resonance at 32.5–42.5 ppm.

Table II
Separation of the Tetrad Sequences into Four Triad Sequences Based on Substitution at the γ Position to the Methylene Carbon of the Styrene Residue of Stryene (S)–Maleic Anhydride (M) Copolymers

tetrad	triad	structure
SSSS or MSSS	SSS	
SSSM or MSSM	SSM	
SMSS	MSS	
SMSM	MSM	

For S–MAn copolymers, assignment of the methylene subspectrum to triad sequences requires that the chemical shift of the CH_2 in MSS and SSM sequences is different by less than 5 ppm: SSS, 42–47 ppm; SSM, MSS, 37–42 ppm; MSM, 33–37 ppm. The compositions of these copolymers can be calculated from the relative areas of the triad resonances according to the following formula:

$$\frac{F_S}{F_M} = 1 + \frac{2A_{SSS} + A_{SSM+MSS}}{2A_{MSM} + A_{SSM+MSS}} \qquad (2)$$

The calculated compositions of Table I show excellent agreement with the compositions determined by independent techniques, supporting these triad sequence assignments in the methylene region, rather than the assignments based on dyad fractions with cis/trans effects.

The calculation of the sequence distribution of styrene units in these copolymers represents a significant advance toward an understanding of the mechanism of copolymerization of these two monomers. Styrene and maleic anhydride produce equimolar copolymers for a major part of the monomer feed composition range. Only at high styrene concentrations in the feed are styrene sequences of length greater than one produced. The distribution of these sequences was predicted[11] to enable discrimination between the penultimate and complex participation models, which have been postulated as alternative mechanisms to explain the copolymerization behavior.

Styrene–Acrylonitrile Copolymer. The styrene–acrylonitrile copolymer system has been well characterized by ^{13}C NMR. The quaternary aromatic carbon resonances at 139–145 ppm and the nitrile carbon resonances at 117–120 ppm are sensitive to the distribution of styrene- and acrylonitrile-centered monomer sequences, respectively. The relative intensities of the resonances in these regions can be used to calculate the monomer sequence distributions for the copolymers.[12-14]

The aliphatic region (as displayed in the normal spectrum, Figure 3d) is not well understood and conflicting assignments have been reported in the literature.[12,13] The multiplet at ~27 ppm is known to be the methine carbon of the acrylonitrile residue and its fine structure is the result of sensitivity to both configurational and monomer sequence arrangements.

The collection of resonances at 30–45 ppm consists of the methine carbon of the styrene residue and the methylene carbon signals. As shown in Figure 3 the DEPT experiment enables the separation of the three broad resonances of the methylene carbons from the styrene methine resonance. The variation of the relative intensities

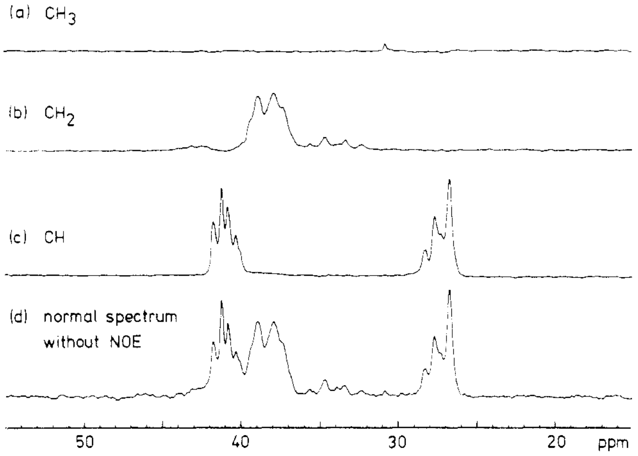


Figure 3. Aliphatic region of ^{13}C NMR spectrum of styrene-acrylonitrile copolymer (S-AN 3): (a-c) subspectra generated by DEPT sequence; (d) normal spectrum obtained with gated decoupling to remove nuclear Overhauser enhancement, pulse angle = 90°, recycle time = 2 s.

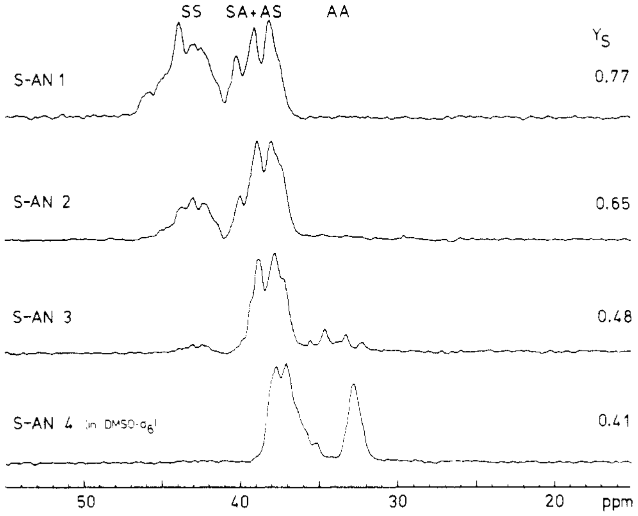


Figure 4. Methylene subspectra of styrene-acrylonitrile copolymers showing variation in dyad sequence distribution with polymer composition (Y_S = mole fraction of styrene in copolymer).

of the three methylene resonances with polymer composition is shown for four samples in Figure 4. On the basis of this variation and the known homopolymer chemical shifts[12,13,15] these three resonances are assigned as monomer sequence dyads according to the nature of the substituents of the neighboring methine carbons as shown in Table III. These assignments confirm those of Sandner et al.[12] over those of Pichot and Pham[13] whose interpretation was obviously hampered because of the Me_2SO-d_6 solvent overlap in this region.

The dyad fractions calculated from the relative intensities of the methylene carbons displayed in Figure 4 are presented in Table IV. The triad fractions determined from the quaternary aromatic and nitrile carbon resonances as previously described[14] can be used to calculate the dyad fraction distribution according to the formulas

$$F_{SS} = Y_S(F_{SSS} + \tfrac{1}{2}F_{SSA+ASS})$$

$$F_{SA+AS} = Y_S(F_{ASA} + \tfrac{1}{2}F_{SSA+ASS}) + Y_A(F_{SAS} + \tfrac{1}{2}F_{SAA+AAS}) \quad (3)$$

$$F_{AA} = Y_A(F_{AAA} + \tfrac{1}{2}F_{SAA+AAS})$$

where Y_S and Y_A are the mole fractions of styrene and acrylonitrile, respectively, in the copolymer; F_{SSS}, $F_{SSA+ASS}$, and F_{ASA} are the styrene-centered triad fractions, and F_{AAA}, $F_{SAA+AAS}$, and F_{SAS} are the acrylonitrile-centered triad fractions. The results of these calculations are given in Table IV for comparison with the experimental values.

Table III
Dyad Sequence Assignments for the Methylene Subspectrum of Styrene-Acrylonitrile Copolymers

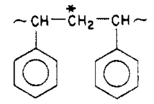
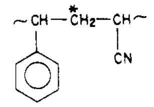
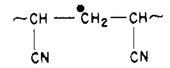
dyad	chem shift, ppm	structure
SS	41-45	
SA or AS	36-41	
AA	31-36	

Table IV
Comparison of Dyad Fractions Calculated from Methylene Subspectra Generated by DEPT with Those Calculated from Quaternary Aromatic and Nitrile Carbon Resonances for Styrene-Acrylonitrile Copolymers of Various Compositions

		dyad fractions					
		b			*c*		
sample	compn[a]	F_{SS}	F_{SA+AS}	F_{AA}	F_{SS}	F_{SA+AS}	F_{AA}
S-AN 1	0.772	0.53	0.47	0.00	0.52	0.48	0.00
S-AN 2	0.650	0.30	0.69	0.01	0.28	0.68	0.04
S-AN 3	0.476	0.06	0.84	0.10	0.06	0.80	0.14
S-AN 4	0.406	0.03	0.74	0.23	0.00	0.73	0.27

[a] Expressed as mole fraction of styrene, from %N elemental analysis.[10] [b] From triad distributions of quaternary aromatic and nitrile carbon resonances, by formulas given in text. [c] From CH_2 subspectra.

The dyad fractions determined by the separate NMR methods show good agreement. This supports the techniques used to make these sequence assignments and gives greater reliability to the calculated monomer sequence distributions. Recently, Hill et al.[14] have used triad fractions determined by ^{13}C NMR of the aromatic and nitrile resonances to distinguish between the penultimate and complex participation models for the copolymerization of acrylonitrile and styrene. The two models cannot be distinguished on the basis of their fit to the composition data alone. However, the sequence distributions show good agreement with the predictions of the penultimate model while being substantially different to those of the complex participation model.

The triad fractions are preferred in testing copolymerization mechanisms since they contain more information than dyad fractions. However, the reactivity ratios calculated by Hill et al. also predict quite different distributions of dyad fractions for the two copolymerization models applied to this copolymer system. The experimental dyad fractions obtained from the methylene subspectra independently discriminate in favor of the penultimate model. Other copolymer systems in which substituent carbon atoms are not sensitive to triad sequence effects but which exhibit a sensitivity to dyad sequences among the main chain carbon atoms could be investigated, using the DEPT sequence to separate and quantify these sequence effects.

Relaxation Time Measurements. ^{13}C and ^{1}H relaxation time measurements can provide important structural and dynamic information on polymers in solution.[16]

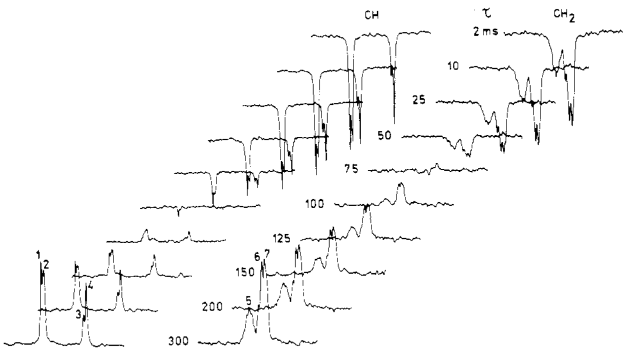


Figure 5. Partially relaxed CH and CH_2 subspectra for measurement of ^1H T_1 relaxation of styrene–acrylonitrile copolymer (S-AN 2), generated by preceding the DEPT sequence with a ^1H π–τ– sequence.

However, accurate measurements for different resonances can be severely hampered by resonance overlap. Fortunately, simple extensions of the DEPT sequence, analogous to modified cross-polarization pulse sequences used in the solid state,[17] enable partially relaxed subspectra to be generated which reflect either directly ^{13}C spin–lattice or spin–spin relaxation or indirectly ^1H spin–lattice or spin–spin relaxation.

For example, ^1H T_1 measurements can be made by preceding the DEPT sequence by a ^1H π–τ– sequence. Performance of all three DEPT experiments (θ_1, θ_2, and θ_3) for an appropriate range of τ values allows generation of CH_n subspectra in the usual manner for each τ value. Figure 5 shows such sets of CH and CH_2 partially relaxed subspectra for the S-AN copolymer. They were generated from the addition and subtraction, respectively, of only the $\pi/4$ and $3\pi/4$ experiments which is possible due to the absence of methyl carbon resonances. Measurement of the individual ^1H T_1's directly from the ^1H spectrum is not feasible due to the lack of resolution. With partially resolved peaks in Figure 5 and analysis via nonlinear least-squares regression, T_1 values of approximately 110 ms for the CH_2 protons and approximately 150 ms for the CH protons are obtained (Table V). Similarly, ^1H T_2 values for individual protons (but modulated by ^1H–^1H homonuclear coupling) are obtained by replacing the initial ^1H $\pi/2$ pulse by a ^1H $\pi/2$–τ–π–τ– sequence. A value of 14 ms results for each of the protons. An alternative, preferred since no extra pulses are added, involves adding a τ–π–τ sequence to the DEPT sequence just prior to the $\pi/2$ carbon pulse. This renders the original ^1H π pulse redundant.

Similarly, ^{13}C relaxation parameters may be determined from partially relaxed CH_n subspectra. Spin–lattice relaxation rates can be determined by the addition of a $\pi/2$ phase-shifted ^{13}C $\pi/2$–τ–$\pi/2$ pulse sequence with ^1H broad-band decoupling between the final $(2J)^{-1}$ period and acquisition. As ^{13}C spin–spin relaxation times for polymers in solution can be very short, appropriate cycling of the additional $\pi/2$ pulse phases and the receiver phase is necessary to remove the effects of residual transverse magnetization.[18] Performance of $\theta = \pi/4$, $\pi/2$, and $3\pi/4$ experiments at each τ delay enables generation of partially relaxed subspectra in the usual manner. Likewise, ^{13}C spin–spin relaxation rates can be measured by insertion of a ^{13}C τ–π–τ pulse sequence, again with broad-band decoupling. Partially relaxed CH and CH_2 subspectra obtained in this manner for the S-AN copolymer are shown in Figure 6. Again, it was only necessary to perform $\theta = \pi/4$ and $3\pi/4$ experiments as there were no methyl resonances. Experimental T_2 and T_1 values for CH and CH_2 carbons are displayed in Table V.

Table V
^{13}C and ^1H Relaxation Times[a] Measured for Individual Resonances of Styrene–Acrylonitrile Copolymer Using Modifications of DEPT Sequence

peak[b]	chem shift, ppm	T_1 (^1H), ms	T_1 (^{13}C), ms	T_2 (^{13}C), ms
CH				
1	41.0	170	225	120
2	40.2	140	230	115
3	27.7	155	250	130
4	26.7	140	240	110
CH_2				
5	43.1	115	140	75
6	39.0	110	135	65
7	38.0	105	130	70

[a] ±10%. [b] Numbers assigned as in Figures 5 and 6. T_2 (^1H) = 14 ms for all resonances.

Quantitative Aspects. The DEPT sequence allows accurate generation in terms of signal cancellation of CH, CH_2, and CH_3 subspectra. Normal ^{13}C NMR spectra of polymers and copolymers can provide important quantitative information on structure, if differences in spin–lattice relaxation times of different carbon environments are allowed for in the acquisition of the spectra. However, because of the polarization transfer nature of the DEPT sequence and its length, any attempt to quantitatively interpret DEPT subspectra must involve consideration of the time parameters characterizing polarization transfer and ^{13}C and ^1H relaxation during the sequence. Significant differences in $^1J_{CH}$ values will not affect cancellation of unwanted multiplicities in subspectra generation. However, they will result in differing extents of polarization transfer, and hence signal intensities will not be comparable. Likewise, if relaxation times are short and vary with carbon environment, differential signal loss during the DEPT sequence will also prevent quantitative use of signal intensities. It is important to note that during the DEPT sequence, both ^{13}C and ^1H magnetization are, at different stages, along the z axis and in the xy plane of the rotating frame. Hence the spin–lattice and spin–spin relaxation times of both nuclei need to be considered. The broad lines often observed in ^1H and ^{13}C spectra of polymers are indicative of short spin–spin relaxation times, T_2, due to slow molecular correlation times. Hence, relaxation times may be a considerable problem in quantitative interpretation of DEPT subspectra of polymers.

We have observed in our work that it not possible to compare the intensity of signals in a CH_2 subspectrum with those in a CH subspectrum, the overall integrated intensity of the former being too low. For the S-AN copolymer where there are equal numbers of methine and methylene carbons, the CH_2 subspectrum has only 75% of the intensity of the CH subspectrum.

Bendall and Pegg,[19] in a detailed analysis of errors in DEPT subspectra, have estimated the loss of intensity as a function of delay misset (or variation of $^1J_{CH}$ from assumed value) in CH_n subspectra. Methylene intensity was found to be more sensitive than methine to delay misset but only to a minor extent. For example, a 10% variation in $^1J_{CH}$ from the assumed value results in approximately 5% and 2.5% intensity loss for CH_2 and CH, respectively. Hence, the intensity difference which might result from different CH and CH_2 J values is far less than that observed for the S-AN copolymer. Furthermore, as the $^1J_{CH}$ value for the methine carbons is more likely to differ significantly due to the phenyl and nitrile substituents from the value of 135 Hz assumed, an excess of methylene over methine intensity would be expected. Finally, DEPT ex-

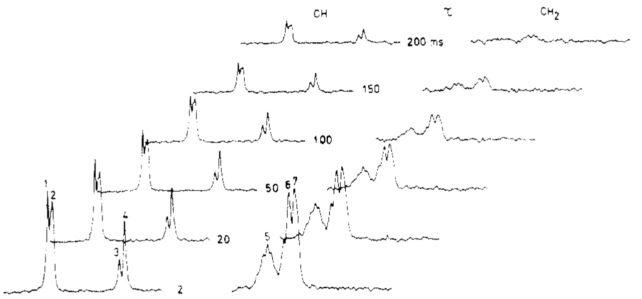


Figure 6. Partially relaxed CH and CH_2 subspectra for measurement of ^{13}C T_2 relaxation of styrene–acrylonitrile copolymer (S–AN 2), generated by inserting a ^{13}C $-\tau-\pi-\tau-$ pulse sequence after the final $(2J)^{-1}$ period of the DEPT sequence.

periments on the S–AN copolymer performed with assumed $^1J_{CH}$ values of 125 or 145 Hz yield similar CH/CH_2 intensity ratios.

Bendall and Pegg have previously observed a measurable loss of intensity in DEPT experiments on cholesterol due to relaxation during the pulse sequence. As described in the preceding section on relaxation time measurements, we have determined both ^1H and ^{13}C relaxation times of methine and methylene resonances in the S–AN copolymer. Both ^{13}C spin–spin and spin–lattice relaxation times are shorter for methylene carbons than for methine. Methylene T_1's are approximately 135 ms while methine T_1's are approximately 240 ms. Even more significantly, methylene T_2's are approximately 70 ms compared with approximately 120 ms for methine resonances. Such short relaxation times till result in observable loss of magnetization. More importantly, due to shorter ^{13}C relaxation times, loss of methylene intensity will be greater. From the observed ^{13}C T_2 values it can be calculated that methylene signal lost due to spin–spin relaxation during the DEPT sequence will be greater than methine intensity lost by ca. 5%. ^1H T_1 values from CH_2 resonances ($\sim$110 ms) are also significantly shorter than those of the methine resonances ($\sim$150 ms) which may also result in a slightly greater loss of CH_2 intensity. Measured ^1H T_2 values are all ca. 14 ms due to modulation via homonuclear coupling and will therefore not result in any differential signal loss. Consequently, relaxation during the DEPT pulse sequence will result in observably greater loss of methylene intensity than methine in the S–AN copolymer, but only of the order of 10% or less.

While relaxation has been shown to result in some relative loss of CH_2 intensity, the amount is insufficient to account for the total observed loss of 25%. A feasible cause of this further loss can be found in the polarization transfer observed as a function of θ pulse angle and the effect of inhomogeneity of this pulse across the sample. First, as demonstrated by Bendall and Pegg, the divergence of θ across the sample becomes more significant as pulse length is increased. As the generation of the CH_2 subspectrum requires the use of a $\theta = 3\pi/4$ experiment in conjunction with the $\theta = \pi/4$ experiment, whereas the CH spectrum is basically obtained directly from the $\theta = \pi/2$ experiment, the former will suffer more from pulse inhomogeneity. Second, the rate of change of signal intensity for CH_2 intensity as a function of θ is far greater in the region of $\theta = \pi/4$ and $3\pi/4$ than for CH intensity at $\theta = \pi/2$. Hence, the loss of CH_2 intensity at these values of θ will be enhanced by the existence of a range of θ values across the sample. In demonstrating the effects of pulse inhomogeneity, Bendall and Pegg have observed a loss of CH_2 intensity of ca. 15% at $\theta = 3\pi/4$ relative to CH intensity at $\theta = \pi/2$ for a number of resonances in cholesterol. This loss is of the magnitude we have observed in copolymer subspectra.

Hence, while quantitatively reliable information may be obtained from individual subspectra where no significant differences in $^1J_{CH}$ or T_2 values exist, results obtained by comparing intensities from more than one subspectrum appear to suffer in accuracy largely as a result of the different sensitivities of the different carbon atoms to θ pulse inhomogeneity and, to a lesser extent, differential relaxation.

Conclusions

The DEPT technique for generation of ^{13}C CH_n subspectra when applied to copolymers, where resonances are broad and exhibit severe overlap, is able to provide accurate spectral editing, even though ^{13}C and ^1H transverse relaxation rates are fast and different for different carbon types. The utility of the technique in assisting interpretation of ^{13}C spectra of copolymers has been clearly demonstrated and the technique should be generally applicable. However, reliable quantitative information requires the consideration of a number of factors including variation of single bond ^{13}C–^1H scalar coupling, relaxation during the polarization transfer pulse sequence, and the effects of pulse inhomogeneity. The DEPT technique can also be used to measure relaxation times through partially relaxed CH_n subspectra.

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Registry No. (S)·(AN) (copolymer), 9003-54-7; (S)·(MAn) (copolymer), 9011-13-6.

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