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Assignment of Monomer Sequences in the ^{13}C and ^{1}H NMR Spectra of Several Ethylene-Containing Co- and Terpolymers by Two-Dimensional Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: Two-dimensional nuclear magnetic resonance spectroscopy has been applied to the sequence assignments of the proton and carbon-13 spectra of the ethylene-containing polymers ethylene/methyl acrylate/carbon monoxide, ethylene/carbon monoxide, and ethylene/methyl acrylate. The proton NMR spectra of these polymers are extremely complex due to the occurrence of resonance lines corresponding to many different monomer sequences in a small chemical shift range of the spectra. Despite this complexity, the proton monomer sequence assignments can be made unambiguously at the triad level through application of homonuclear two-dimensional correlated spectroscopy (COSY). Furthermore, several different types of end groups are observed in the proton spectra of these polymers, and these end-group resonances were assigned from the coupling patterns seen in the COSY spectra. Once the proton assignments were known, the carbon-13 assignments were made from two-dimensional ^{13}C–^{1}H heteronuclear shift-correlated spectroscopy. These assignments were confirmed by performing distortionless enhancement by polarization transfer (DEPT) spectroscopy.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for determination of the chemical microstructure of synthetic copolymers since the chemical shift is sensitive to differences in comonomer and stereochemical sequences. However, analysis by NMR requires that the lines in the spectrum be assigned to specific sequences in the polymer. Traditional line assignment techniques, such as theoretical chemical shift calculations, comparison of relative intensities of resonances to those predicted from reaction probabilities, and various synthetic techniques, are often tedious and/or subject to some ambiguity in complex copolymers. Two-dimensional (2D) correlated spectroscopy (COSY) provides an experimental basis for making unambiguous line assignments in the straightforward manner.

Two-dimensional correlated spectroscopy has been applied extensively to line assignment in the NMR spectra of biopolymers,[1-11] but application of these techniques to synthetic polymers has been less widespread. One of the first applications to polymers was by Gerig, who applied ^{19}F–^{1}H correlation NMR to poly(*p*-fluorostyrene).[12] Proton COSY has been applied to stereosequence assignments in poly(vinyl alcohol)[13] and poly(methyl methacrylate).[14] Bruch et al. have applied ^{19}F homonuclear 2D correlated spectroscopy to stereosequence assignments in the ^{19}F spectrum of poly(vinyl fluoride),[15] and Ferguson et al. have applied ^{19}F COSY to poly(vinylidene fluoride).[16] More recently, Cheng and Lee have applied 2D ^{13}C–^{1}H correlated spectroscopy to comonomer sequence assignments in ethylene/propylene copolymers[17] and stereosequence assignments in polypropylene,[18] and Mirau and Bovey have used a variety of 2D correlated techniques to make stereosequence assignments in poly(vinyl chloride).[19]

We report the application of 2D COSY, 2D ^{13}C–^{1}H correlated, and ^{13}C distortionless enhancement by polarization transfer (DEPT) spectroscopy to line assignment in the ^{1}H and ^{13}C spectra of a terpolymer containing ethylene, methyl acrylate, and carbon monoxide (E/MA/CO). This terpolymer is more complex than the homopolymers and copolymers studied previously due to the large number of possible comonomer sequences. Sequences containing methyl acrylate are further complicated by stereochemistry since methyl acrylate has a pseudoasymmetric center. Furthermore, the ^{13}C NMR spectrum of E/MA/CO was previously unassigned. Despite this complexity, ^{1}H and ^{13}C assignments can be made unambiguously at the triad level by a combination of 2D correlated and DEPT experiments on a single sample of E/MA/CO. In addition, several different types of end groups are observed and assigned in the ^{1}H spectrum of E/MA/CO. All of the line assignments are confirmed by COSY spectra and ^{13}C spectra of the two copolymers E/MA and E/CO.

Experimental Section

All spectra were recorded on a Bruker AM-300 spectrometer equipped with an Aspect 3000 computer. Chemical shifts were

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referenced to tetrachloroethane-d_2 (74.2 ppm for ^{13}C, 5.97 ppm for ^1H). All pulse sequences include a 16-cycle phase-cycling routine. Each 2D spectrum was zero-filled in both dimensions prior to Fourier transformation, and the absolute value (magnitude) spectrum was calculated. A sine-bell or phase-shifted sine-bell filtering function was used in both dimensions prior to Fourier transformation to improve resolution. Homonuclear 2D spectra were all symmetrized to eliminate the bands of "t_1 noise" arising from spectrometer instabilities during the extended acquisition times associated with those experiments.[20]

Homonuclear 2D correlated spectroscopy was performed by using the standard sequence RD–90°–t_1–90°–t_2.[21] The first 90° pulse causes each proton to precess at its initial frequency during t_1. The second 90° pulse, or mixing pulse, causes magnetization exchange between protons that are J-coupled to each other, and the final frequency is detected during t_2. Those spins that do not exchange have a final frequency that is equal to the initial frequency. Hence, the COSY spectrum contains the normal spectrum along the diagonal given by $\omega_1 = \omega_2$. Those spins that do exchange due to J-coupling give rise to pairs of cross peaks (off-diagonal peaks) connecting coupled protons. Hence, the COSY spectrum is a map of the complete homonuclear coupling network.

The COSY spectrum of E/MA/CO was obtained on a 5% solution in tetrachloroethane-d_2 at 100 °C. A total of 64 transients were accumulated with a relaxation delay of 3.5 s, which is greater than 3 times the longest measured ^1H T_1. The initial data matrix was 1100 Hz (256 real data points) in both dimensions, and the digital resolution after zero-filling was 2.2 Hz/point. A sine-bell filtering function was used in both dimensions. COSY spectra of E/CO and E/MA copolymers were obtained under essentially identical conditions.

Distortionless enhancement by polarization transfer (DEPT) spectroscopy was performed to determine the multiplicity of each ^{13}C resonance. A standard pulse sequence[22] was employed:

$$^1H:\ \text{RD–90°–}\tau\text{–180°–}\tau\text{–}\theta\text{°–}\tau\text{–decouple}$$

$$^{13}C:\ (\text{RD} + \tau)\text{–90°–}\tau\text{–180°–}\tau\text{–detect}$$

In this sequence, the preparation period is a relaxation delay to ensure that the *protons* are fully relaxed. The multiplicity is determined by varying the proton pulse, θ. When $\theta = 45°$, all protonated signals are observed, but when $\theta = 90°$, only methine carbon signals are observed. When $\theta = 135°$, methine and methyl signals are positive, but methylene signals are negative. Signals corresponding to quaternary carbons have zero intensity for all values of θ.

^{13}C DEPT spectra were obtained on a 10% solution of E/MA/CO in tetrachloroethane-d_2 at 100 °C. A total of 16K data points were accumulated over a sweep width at 6 kHz. A total of 400 transients were accumulated for each spectrum using a recycle time of 7.7 s. The delay time was set to 3.6 ms.

Two-dimensional ^{13}C–^1H correlated spectroscopy was performed with the following standard pulse sequence:[23]

$$^1H:\ \text{RD–90°–}(t_1 + \Delta_1)\text{–90°–}\Delta_2\text{–decouple}$$

$$^{13}C:\ \text{RD–}t_1/2\text{–180°–}t_1/2\text{–}\Delta_1\text{–90°–}\Delta_2\text{–detect}$$

In this sequence, the preparation period ensures that the protons are fully relaxed. The first 90° proton pulse causes the protons to precess at their initial frequencies. The 180° ^{13}C pulse refocuses dephasing that has occurred due to ^{13}C–^1H J-coupling. Consequently, the initial precession frequencies during t_1 depend only on the proton chemical shifts and homonuclear coupling constants. The delay time $\Delta_1 = 1/2J$ is necessary to allow the individual components of a ^1H–^{13}C multiplet to dephase to the antiparallel alignment, which is optimal for polarization transfer. Polarization transfer between protons and directly attached ^{13}C nuclei is caused by the simultaneous ^1H and ^{13}C 90° pulses. The delay $\Delta_2 = 1/4J$ is necessary to ensure optimal detection, and the resultant ^{13}C FID is detected with proton decoupling during t_2. The final frequencies reflect only the carbon chemical shifts corresponding to protonated carbons. The 2D ^{13}C–^1H correlated spectrum maps each proton signal to the carbon-13 signal of the corresponding directly attached carbon.

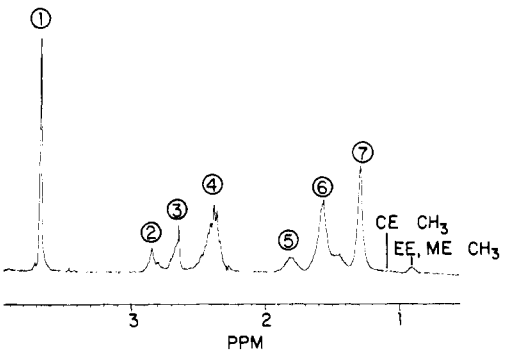


Figure 1. Conventional 300-MHz proton NMR spectrum of a 5% solution of E/MA/CO terpolymer in tetrachloroethane-d_2 at 100 °C.

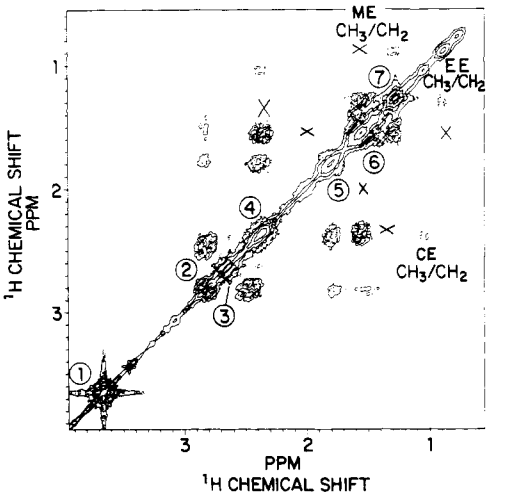


Figure 2. Contour plot of the 300-MHz proton 2D COSY spectrum of E/MA/CO terpolymer. An "×" represents weak peaks visible at lower contour levels.

The 2D ^{13}C–^1H correlated spectrum was obtained on an 8% solution of E/MA/CO at 100 °C. A total of 1600 transients per t_1 value were accumulated with a recycle time of 3 s. The initial data matrix was 6 kHz (2K complex points) in the ^{13}C dimension and 1100 Hz (64 t_1 values) in the ^1H dimension. A sine-bell, phase shifted by 45°, was used as a filtering function in both dimensions. Digital resolution after zero-filling was 4.3 and 6 Hz/point in the ^1H and ^{13}C dimensions, respectively. The delay times Δ_1 and Δ_2 were set to 3.57 and 1.79 ms, respectively.

The E/MA/CO terpolymer and E/MA and E/CO copolymers were obtained from E. I. du Pont de Nemours and Co. The levels of the comonomers methyl acrylate and carbon monoxide in the E/MA and E/CO copolymers are comparable to the level of these comonomers in the E/MA/CO terpolymer. Tetrachloroethane-d_2 was obtained from Merck Isotopes.

Results and Discussion

The proton spectrum of E/MA/CO in tetrachloroethane is shown in Figure 1. The presence of carbon monoxide as one of the components in the polymer causes many sequences to have characteristic chemical shifts and coupling patterns. Consequently, the COSY spectrum of E/MA/CO, shown in Figure 2, can be used to make line assignments. The proton spectrum exhibits primarily diad sensitivity with some sensitivity to triad monomer sequences, whereas the carbon-13 spectrum exhibits triad sensitivity. For simplicity, we shall consider primarily triad monomer sequences throughout the discussion of both the carbon-13 and proton line assignments, and the sequences will be designated by E, M, and C for ethylene, methyl acrylate, and carbon monoxide, respectively.

The most downfield resonance in the proton spectrum of E/MA/CO has a chemical shift of 3.7 ppm and is not

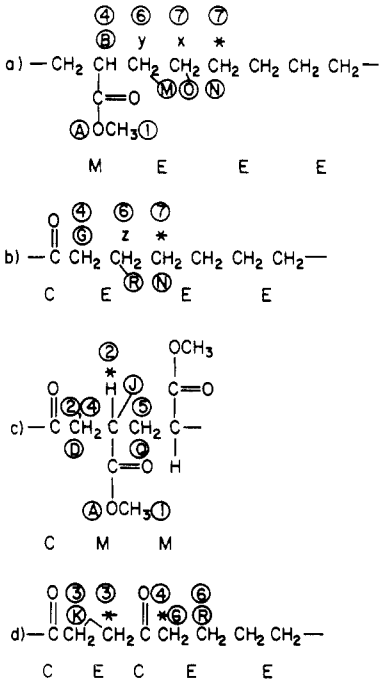


Figure 3. Structure of several monomer sequences in E/MA/CO terpolymer. (a) Structure of MEEE tetrad. The indicated methylenes at the center of an EEE triad are coupled to neighboring x methylenes, and these x methylenes are coupled to neighboring y methylenes in MEE triads. (b) Structure of CEEE tetrad. The indicated EEE methylenes are coupled to neighboring z methylenes in CEE triads. (c) Structure of CMM triad. The central methine is coupled to the methylenes on either side in MM and CM diads. (d) Structure of CECEE pentad. There is weak four-band coupling between indicated α methylenes in CEC and CEE triads.

coupled to any other resonance in the COSY spectrum. Therefore, this resonance, labeled 1 in Figure 3, is assigned to MA OCH_3 protons. The chemical shift of these methyl protons is largely insensitive to monomer sequence effects as evidenced by the lack of fine structure associated with resonance 1.

The downfield resonances from 2.2 to 3.0 ppm (resonances 2–4) have chemical shifts that indicate that these resonances correspond to protons that are α to carbonyl groups. In every sequence involving protons α to carbonyls, except CEC, the α protons are J-coupled to neighboring protons β to the carbonyl which have chemical shifts that differ from those of the α protons. However, in CEC sequences, all four methylene protons are α to a carbonyl and are equivalent (or nearly so) and no J-coupling is observed between these methylenes. Therefore, the methylenes in CEC triads are immediately assigned to resonance 3 because no cross peaks are observed for this resonance in the COSY spectrum.

The remaining resonances in the downfield region can be assigned more easily once the upfield resonances (1.2–2.0 ppm) have been assigned. The resonances in this region must correspond to protons that do not have directly adjacent carbonyl groups. Since polyethylene is known to have a chemical shift of 1.3 ppm,[24] resonance 7 must contain methylene protons in EEE triads. These central methylene protons are coupled to the methylene protons on either side. These neighboring methylene protons can be at the center of two triads other than EEE: MEE or CEE. The coupling pattern for an MEE sequence is shown in Figure 3a. One of the central pairs of equivalent protons is coupled to methylene protons labeled x. These protons have a similar chemical shift to EEE and are assigned to resonance 7. However, methylenes x are coupled to methylenes y, which are shifted downfield by the β carbonyl group. Because of the presence of the acrylate group, the y methylenes are expected to be nonequivalent. In the case of CEE sequences, the central methylenes are coupled to neighboring equivalent methylenes (Figure 3b) which are shifted downfield by the β carbonyl. The COSY spectrum shows coupling from resonance 7 to several resonances, labeled 6, at approximately 1.6 ppm. Hence, these resonances must correspond to y-methylene protons in MEE and β-methylene protons in CEE sequences. The exact location of these methylenes can be determined more precisely from the 2D ^{13}C–^{1}H correlated spectrum discussed later.

Resonance 5 at 1.8 ppm can be identified by its unique coupling pattern. This resonance is not coupled upfield to resonances 6 or 7; it is only coupled to resonances in the downfield region. This can only correspond to methylene resonances between adjacent methyl acrylate units in head-to-tail MM diads. The coupling to the downfield region represents coupling to the methine protons on either side of the central methylene protons. It should be noted that MM diads can have meso or racemic relative stereochemistry. The methylene protons in meso diads are nonequivalent, whereas methylenes in racemic diads are equivalent because of the symmetric nature of racemic diads. Therefore, the coupling patterns and chemical shifts expected for meso MM methylenes are quite different from those expected for racemic MM methylenes. Nonequivalent meso methylenes are coupled to each other, and both are coupled to neighboring methines. On the other hand, neighboring methine protons are only coupled to one resonance corresponding to racemic methylenes. Since the latter coupling pattern is the primary one observed in this polymer, made by using a free radical initiator, resonance 5 must correspond to only racemic MM methylenes. There is a very small amount of meso MM diads as evidenced by a weak cross peak, representing geminal coupling between the nonequivalent meso methylene (indicated by an × in Figure 2). The amount of meso diads is much larger in a sample of E/MA/CO containing an exceptionally high amount of methyl acrylate, and the COSY spectrum on this sample reveals all of the expected couplings for methylenes in meso diads.[25] These results are consistent with the observation by Bovey and Tiers[26] that poly(methyl methacrylate) made by a free radical initiator contains predominantly racemic diads. Similar results also were observed by Heatley and Bovey[27] for poly(isopropyl acrylate). The chemical shift of 1.8 ppm observed for resonance 5 is in excellent agreement with the shifts of 2.0 and 1.8 ppm observed for central methylenes in racemic diads of poly(methyl methacrylate) and poly(isopropyl acrylate), respectively.[14,26,27]

Now that the upfield resonances have been assigned, the coupling to these resonances can be used to assign the downfield resonances. Methylenes at the center of MM diads are coupled to the methine on either side, and these methines can be at the center of three triads: MMM, EMM, or CMM. It should be noted that in all sequences involving CM diads, it is assumed that the carbon monoxide adds adjacent to the methylene and not the methine of the methyl acrylate. There are two main reasons for this assumption. First of all, addition next to the methylene is less sterically hindered than addition next to the methine. Furthermore, an MA methine α to a carbonyl would be shifted far downfield, and no methine resonance is observed at a reasonable chemical shift for this sequence. Therefore, there is no evidence for addition of CO directly

adjacent to an MA methine. The COSY spectrum shows that resonance 5, corresponding to racemic MM methylenes, is coupled to resonances 2 and 4 at 2.8 and 2.3 ppm, respectively. Therefore, these resonances must correspond to methines at the center of MMM, EMM, and CMM triads. The methine in CMM is shifted downfield by the carbonyl in the β position, and this sequence must correspond to resonance 2. The methines in MMM and EMM have similar chemical environments and are assigned to resonance 4.

Resonance 2 is coupled to both the downfield part of resonance 4 and resonance 6 in addition to the coupling to resonance 5 discussed above. The central methine proton in CMM is coupled to only two types of protons: equivalent methylenes in racemic MM diads (resonance 5) and the two nonequivalent methylene protons α to the carbonyl as shown in Figure 3c. Since both of the nonequivalent methylene protons α to the carbonyl are shifted downfield, the coupling between resonances 2 and 4 must correspond to coupling between the MA methine and one of these nonequivalent methylenes. The location of the cross peaks between resonances 2 and 4 indicates that this α-methylene proton is shifted downfield from the EMM and MMM methine resonances previously assigned to resonance 4. The other nonequivalent α-methylene resonance in CMM sequences must also be shifted downfield and coupled to the MA methine (resonance 2), but no other cross peak is observed from resonance 2 to a downfield resonance. Furthermore, there must be strong geminal coupling between these nonequivalent α methylenes. The only cross peaks from resonance 4 (one of the α methylenes) to a downfield resonance are the cross peaks connecting resonances 2 and 4, and these are large cross peaks. These observations suggest that the other α methylene is overlapped with the methine in resonance 2, and the cross peaks connecting resonances 2 and 4 are due to both vicinal CH/CH_2 coupling and geminal coupling between the two nonequivalent methylenes. These results are confirmed by the 2D ^{13}C–^{1}H correlated spectrum discussed later.

Coupling between resonance 2 and resonances 4 and 5 accounts for all the possible coupling associated with CMM triads. Therefore, the cross peaks between resonances 2 and 6 observed in the COSY spectrum must be due to coupling in another sequence. The central methine in the sequence CME is in a similar environment to the central methine in CMM, and the methine in CME is coupled to adjacent methylene protons in ethylene. These nonequivalent methylene protons can be part of MEE, MEM, or MEC sequences, and all of these protons have been assigned to resonance 6. Therefore, resonance 2 must also contain central methines in CME triads, and the cross peaks connecting resonances 2 and 6 are due to coupling between the MA methine and neighboring E methylenes in CME triads. The MA methine in CME triads also is coupled to the nonequivalent methylenes α to the carbonyl, and these α methylenes are assigned to resonance 2 and the downfield part of resonance 4 as in the case of α methylenes in CMM sequences.

The only remaining triad sequence containing a central methine proton in EME. The methine in this sequence is in a similar environment ot EMM, and this methine is assigned to resonance 4 on the basis of chemical shift. Similarly, equivalent methylenes α to carbonyl resonances in CEE and CEM are assigned to resonance 4 on the basis of chemical shift. Therefore, the upfield part of resonance 4 contains two types of protons: (1) MA methine protons in EME, EMM, and MMM sequences and (2) methylene protons α to a carbon monoxide in CEE and CEM sequences. The cross peaks from resonance 4 to resonance 6 represent the superposition of two types of interactions: (1) coupling between MA methines and neighboring nonequivalent methylenes that are not α to a carbonyl and (2) coupling between methylenes α to a carbonyl and neighboring equivalent methylenes β to a carbonyl.

Table I
Proton Line Assignments for E/MA/CO Terpolymer

resonance	chem shift,[a] ppm	sequences	description
1	3.66	all	MA methyls in all sequences
2	2.84	CME, CMM	methine
2, 4	2.83, 2.43	CME, CMM	nonequivalent methylenes α to carbon monoxide
3	2.65	CEC	ethylene protons
4	2.34	EMM, MMM[b]	methine
4	2.31	EME	methine
4	2.41	MEC	equivalent methylenes α to carbon monoxide
4	2.37	EEC	equivalent methylenes α to carbon monoxide
5	1.79	MM	equivalent methylenes in racemic diads
6	1.54	CEE, CEM	equivalent β methylenes (labeled z in Figure 3b)
6	1.62, 1.38	EM	nonequivalent methylenes labeled y in Figure 3a
7	1.28	EEE, EEC	central ethylene methylenes and methylenes γ to carbon monoxide
7	1.26	MEE, MEM	central equivalent x methylenes γ to the carbonyl (Figure 3a)
	1.05	CE	terminal methyls
	0.90	EE	terminal methyls
	0.87	ME	terminal methyls

[a] Chemical shift listed for each resonance is the average of all listed sequences. Uncertainty on each chemical shift is ±0.02 ppm. Shifts are referenced to tetrachloroethane-d_2. [b] There are so few MMM triads that the proton assignment of this methine cannot be accurately determined. It is probably to slightly lower field than the value listed here.

By analysis of the chemical shifts and coupling patterns observed in the COSY spectrum, protons in different monomer sequences are assigned to specific resonances in the proton NMR spectrum, and these results are summarized in Table I. In addition to the large cross peaks observed between the main resonances of E/MA/CO, several weak cross peaks are observed for small upfield resonances in the region from 0.4 to 1.2 ppm. The chemical shifts of these resonances indicate that they correspond to methyl end groups on ethylene units. These methyl protons are coupled to the neighboring methylene protons in ethylene. Hence, cross peaks observed for these methyl protons are due to CH_3/CH_2 coupling, and the location of these cross peaks pinpoints the location of methylene protons adjacent to CH_3 end groups. The ethylene unit at the end of a chain can be adjacent to a carbon monoxide, methyl acrylate, or another ethylene unit. Hence, the methylene protons adjacent to methyl ends can be in three environments: CE, ME, or EE. There are three sets of cross peaks observed from methyl end groups to the corresponding methylenes at chemical shifts corresponding to resonances 4, 6, and 7. The cross peaks mapping to resonance 4 are assigned to CH_3/CH_2 coupling in CE terminal sequences since the methylenes are α to a carbonyl in this sequence. Similarly, the cross peaks mapping to resonances 6 and 7 are assigned to CH_3/CH_2 coupling in ME and EE terminal sequences, respectively. The

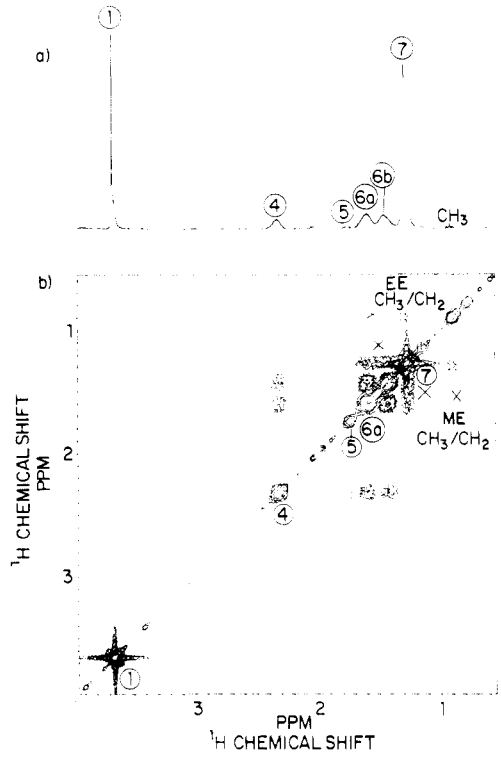


Figure 4. Normal 300-MHz proton spectrum and contour plot of 2D COSY spectrum of E/MA copolymer. An "×" represents weak peaks visible at lower contour levels.

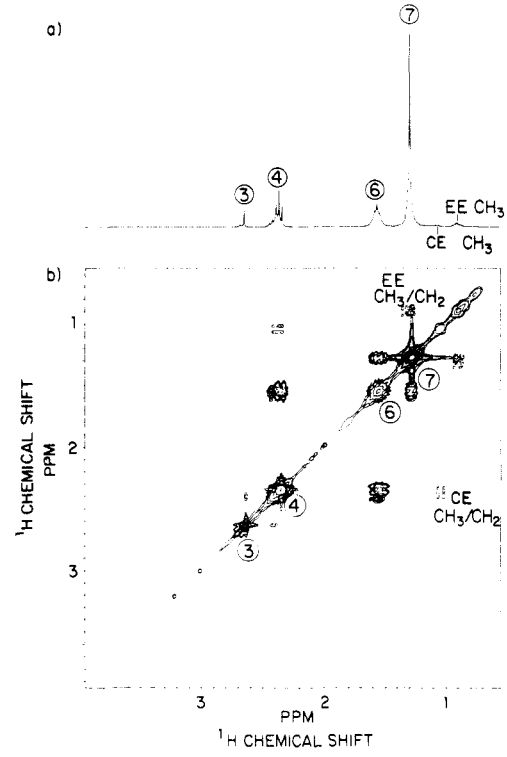


Figure 5. Normal 300-MHz proton spectrum and contour plot of 2D COSY spectrum of E/CO copolymer.

methyl end groups for CE, ME, and EE sequences are assigned to resonances at 1.05, 0.87, and 0.90 ppm, respectively, since these methyl protons are coupled to resonances 4, 6, and 7, respectively. Hence, both methylene and methyl protons in terminal ethylene units in three different environments (CE, ME, and EE) can be observed and assigned from the COSY spectrum.

In order to confirm the proton line assignments obtained for the E/MA/CO terpolymer, COSY spectra of the two copolymers, E/MA and E/CO, were obtained, and these spectra are shown in Figures 4 and 5, respectively. All of the chemical shifts and coupling patterns observed in the COSY spectra of the two copolymers are consistent with those observed in the COSY spectrum of the terpolymer. As in the terpolymer, the MA OCH_3 proton in E/MA can be assigned immediately to resonance 1 for all sequences since this resonance has a chemical shift of 3.7 ppm, shows very little fine structure in the 1D spectrum, and has no cross peaks to any other resonance in the COSY spectrum. In addition, resonance 1 is not present in the spectrum of the copolymer E/CO. Resonances 2 and 3 in the spectrum of the terpolymer are not present in the spectrum of E/MA since these resonances are due to sequences containing carbon monoxide. Resonance 2 is also not present in the spectrum of E/CO since this resonance corresponds to MA methines in CMM or CME triads. However, resonance 3, corresponding to CEC methylenes, is present in the spectrum of E/CO. Although no cross peaks were observed for this resonance in the COSY spectrum of the terpolymer, very weak cross peaks are observed between resonances 3 and 4 in the spectrum of E/CO copolymer. We believe these cross peaks represent weak four-bond coupling across the carbonyl between α-methylene protons on each side of CO in the sequence CECEE as shown in Figure 3d. One pair of α methylenes is at the center of a CEC triad and corresponds to resonance 3. The methylenes on the other side of CO are α to one CO and δ to another CO. Hence, the chemical shift of these methylenes is expected to be slightly downfield from α methylenes in EECEE sequences (resonance 4) due to the extra carbonyl. The cross peaks in the COSY spectrum map resonance 3 to the downfield part of resonance 4, in excellent agreement with the expected result for the four-bond coupling described above. Furthermore, cross peaks corresponding to four-bond coupling in a COSY spectrum have greater intensity when no geminal or vicinal coupling is present, as is the case here.[28] These cross peaks were not observed in the terpolymer COSY spectrum because of the larger number of possible sequences; this weak interaction is split into many sets of cross peaks mapping to slightly different places.

Resonance 4 in the spectrum of the terpolymer E/MA/CO contains both MA methine protons (triads EMM, EME, and MMM) and methylene protons α to a carbonyl. Consequently, this resonance is in the proton spectra of both E/MA and E/CO copolymers. In the COSY spectrum of E/MA, there are cross peaks connecting resonance 4 with resonances 5, 6a, and 6b. The cross peaks connecting resonances 4 and 5 are due to coupling between MA methine and methylene protons sandwiched between MA units in EMM and MMM triads. As in the terpolymer, only one resonance (resonance 5) is observed for central methylenes in MM diads in the copolymer E/MA, and this indicates that predominantly racemic MM diads are formed as discussed earlier. The cross peaks connecting resonances 4 with resonances 6a and 6b in the COSY spectrum of E/MA are due to coupling between MA methine and adjacent nonequivalent methylenes in the triads EMM and EME. The cross peaks connecting 6a and 6b reflect geminal coupling between these nonequivalent methylenes. As discussed earlier, these methylenes are nonequivalent because of the adjacent acrylate structure. The two pairs of cross peaks from the methine to these methylenes (4/6a and 4/6b) are not visible as separate peaks in the COSY spectrum of the terpolymer because of overlap with cross peaks connecting methylenes α to CO and methylenes β to CO in triads containing CE or CM

diads. These cross peaks connecting resonances 4 and 6 are present in the COSY spectrum of the copolymer E/CO and are due to coupling between α methylenes and equivalent β methylenes in CEE sequences. Hence, the COSY spectra of the copolymers confirm the fact that the cross peaks between resonances 4 and 6 in the COSY spectrum of E/MA/CO are caused by the combination of two distinct types of interactions. As in the terpolymer, resonance 7 corresponds to central methylenes in EEE triads in the spectra of both copolymers, and cross peaks are observed between resonances 6 and 7 in the COSY spectra of both E/MA and E/CO.

The locations of CH/CH_2 cross peaks in the COSY spectrum of E/MA copolymer can be used to pinpoint the locations of central methines in different sequences. Central methines in MMM sequences are coupled to resonance 5 only, central methines in EME sequences are coupled to resonances 6a and 6b only, and central methines in EMM sequences are coupled to all three resonances. Resonance 5 has cross peaks that map to a resonance slightly downfield from the resonance coupled to resonances 6a and 6b. This indicates that the MMM methine is slightly downfield from the EME methine, and the EMM methine is in between MMM and EME. These shifts make sense since additional carbonyls are expected to cause a slight downfield shift of the methine proton.

The methyl end groups on terminal ethylene units observed in the spectrum of E/MA/CO also are observed in the spectra of the copolymers. Methyl and groups are coupled to neighboring methylenes, which can be adjacent to carbon monoxide, methyl acrylate, or ethylene in the terpolymer. In the E/MA copolymer, methylenes in terminal ethylene units can be adjacent to methyl acrylate or ethylene only, and two pairs of cross peaks to terminal methyls are observed in the COSY spectrum of E/MA. The resonance at 0.87 ppm is coupled to resonance 6 and is assigned to ME terminal methyls. The resonance at 0.90 ppm is coupled to resonance 7 and must correspond to EE terminal methyl protons. Similarly, in E/CO, two types of terminal methyls are possible: CE and EE. The cross peaks connecting the methyl resonance at 1.05 ppm with resonance 4 are due to methyl/methylene coupling in CE terminal sequences, and the cross peaks connecting the methyl resonance at 0.90 ppm with resonance 7 are due to CH_3/CH_2 coupling in EE chain ends.

Now that the proton line assignments have been made for E/MA/CO, these assignments can be used to make the ^{13}C NMR line assignments from the 2D carbon-13/proton correlated spectrum. However, the ^{13}C NMR spectrum, shown in Figure 6, contains many lines of similar intensity in the region from 5 to 60 ppm, and it is extremely difficult to distinguish methine, methylene, and methyl carbon signals on the basis of chemical shift or relative intensity. Since there is overlap of methylene and methine resonances in the proton spectrum of E/MA/CO, it is necessary to be able to distinguish methine and methylene carbon signals in order to make ^{13}C line assignments from the 2D $^{13}C/^{1}H$ correlated spectrum. This can be accomplished by performing distortionless enhancement by polarization transfer (DEPT) spectroscopy to determine the multiplicity of all carbon signals.

The DEPT spectrum of E/MA/CO obtained with a 45° proton pulse, shown in Figure 7a, contains all protonated carbon signals, whereas the DEPT spectrum obtained with a 90° proton pulse, shown in Figure 7b, contains only methine carbon signals. In the DEPT spectrum obtained with a 135° proton pulse, shown in Figure 7c, methine and methyl carbon signals are positive, while methylene signals

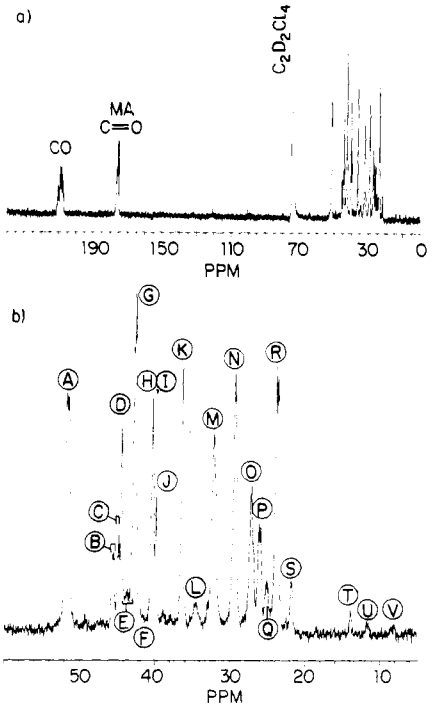


Figure 6. 75-MHz ^{13}C NMR spectrum of a 5% solution of E/MA/CO terpolymer in tetrachloroethane-d_2 at 100 °C. Proton decoupling was gated off during the relaxation delay and gated on during data acquisition to suppress the nuclear Overhauser effect (NOE). A total of 4000 transients were recorded with a 90° pulse and a 30-s relaxation delay. (a) Entire ^{13}C spectrum showing the CO and MA carbonyl resonances at 208 and 176 ppm, respectively. (b) Expansion of aliphatic region (5–60 ppm).

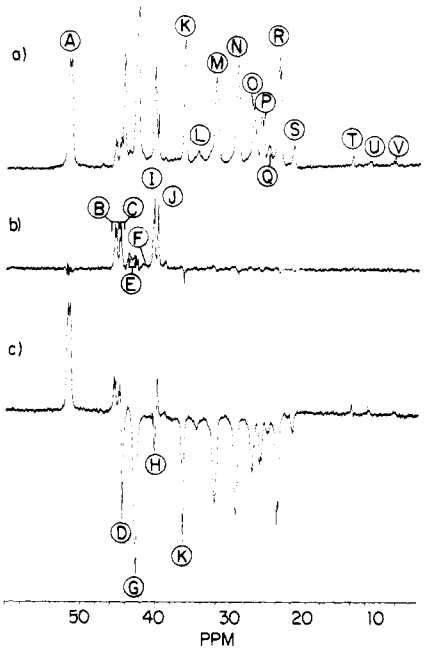


Figure 7. Distortionless enhancement by polarization transfer (DEPT) spectra of E/MA/CO terpolymer. (a) 45° proton read pulse. All protonated carbon signals are positive. (b) 90° proton read pulse. Only methine carbon signals are observed. (c) 135° proton read pulse. Methine and methyl carbon signals are positive, and methylene carbon signals are negative.

are negative. These three DEPT spectra clearly show that carbon resonances labeled A, T, U, and V correspond to methyl carbons, and resonances labeled B, C, E, F, I, and J correspond to methine carbons. All other resonances

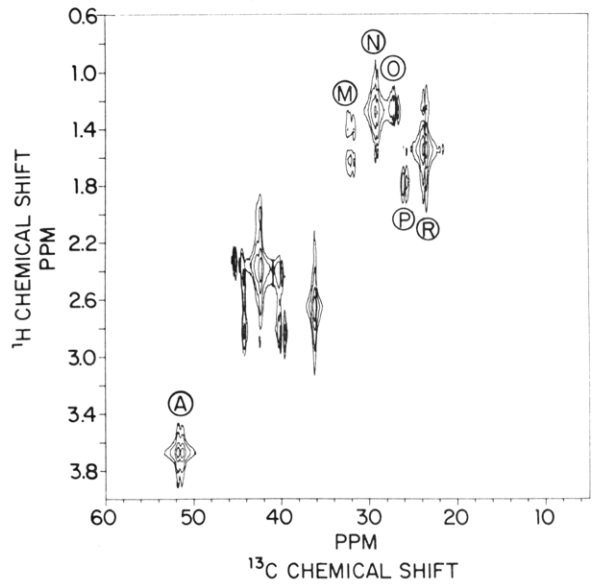


Figure 8. Contour plot of 2D ^{13}C–^{1}H correlated spectrum of E/MA/CO terpolymer. The x axis corresponds to the ^{13}C chemical shift, and the y axis corresponds to the ^{1}H chemical shift. These data were processed by using a sine-bell shifted by $\pi/4$ in both dimensions.

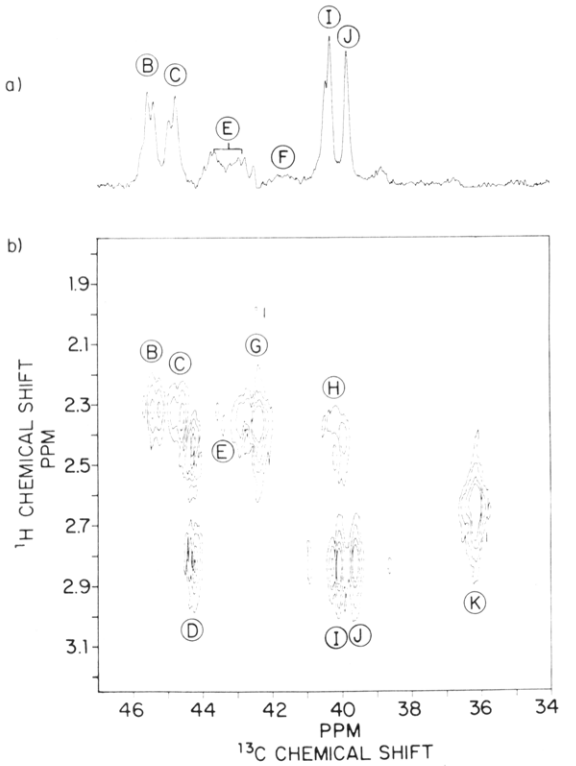


Figure 9. (a) Expanded region of methine only DEPT spectrum. (b) Contour plot of expanded region of the 2D ^{13}C–^{1}H correlated spectrum of E/MA/CO terpolymer. The data were reprocessed by using a sine-bell filtering function with no phase shift in both dimensions in order to improve the resolution in this region.

correspond to methylene carbons. Therefore, the multiplicity of all carbon signals is determined unambiguously from the DEPT spectra.

Now that the multiplicity of each of the carbon signals is known, carbon-13 line assignments can be made from the 2D ^{13}C–^{1}H spectrum shown in Figure 8. Carbon resonance A (52 ppm) maps to proton resonance 1, so resonance A is assigned to MA OCH_3. Some fine structure due to sequence effects is observed in the ^{13}C spectrum, but this fine structure cannot be assigned unambiguously.

In the upfield region, carbon resonances N and O both map to proton resonance 7, which corresponds to EEE central methylenes along with EEM x methylenes and EEC γ methylenes (see Figure 3). Although the indicated methylenes have the same proton chemical shift, the corresponding carbon signals of x methylenes in EEM and γ methylenes in EEC sequences are shifted upfield from EEE methylenes due to the presence of the $COOCH_3$ and carbonyl groups, respectively, in the γ position. The γ acrylate group in EEM is predicted to shift x methylenes upfield by ~2 ppm on the basis of chemical shift additivity rules,[29] but the γ carbonyl should have smaller effect on γ methylenes in EEC sequences. Therefore, resonance N is assigned to both EEE central methylenes and EEC γ methylenes, and resonance O is assigned to x methylenes in EEM sequences.

Resonances M and R both map to proton resonance 6, which corresponds to two types of protons: equivalent EM methylenes (y in Figure 3a) and nonequivalent EEC or MEC β methylenes (z in Figure 3b). These resonances can be uniquely assigned despite overlap in the ^{1}H spectrum. Resonance M has two peaks corresponding to nonequivalent methylene protons, whereas resonance R has only one peak corresponding to equivalent methylene protons. Therefore, resonance M is assigned to nonequivalent y methylenes in EM diads, and resonance R is assigned to equivalent β methylenes in EEC and MEC triads. The location along the proton axis of the peaks in the 2D ^{13}C–^{1}H correlated spectrum corresponding to resonance M pinpoints the location of the two nonequivalent y methylenes in EM diads. Similarly, the location of the peak for resonance R pinpoints the location of EEC and MEC equivalent β-methylene protons. The chemical shifts observed for these methylenes in the 2D ^{13}C–^{1}H correlated spectrum is in good agreement with the shifts observed in the COSY spectrum.

Resonance P shows a single peak in the 2D ^{13}C–^{1}H correlated spectrum, and the proton chemical shift corresponds to resonance 5. Hence, resonance P is assigned to equivalent methylenes in racemic MM diads. It should be noted that both the proton and carbon-13 assignments for racemic diads truly correspond to isolated diads of methyl acrylate. It appears that there are no long runs of methyl acrylate (tetrads or longer) based on the lack of any significant amount of MMM triads in both E/MA/CO and E/MA copolymers. Hence, resonances 5 and P are best described as central methylenes in XMMX tetrads, where X is not methyl acrylate. This will be justified in the next section when the assignments of EME, EMM, and MMM methines are discussed. The digital resolution and sensitivity of the 2D spectrum are not sufficient to detect unique peaks for resonances L, Q, and S, and these methylene resonances cannot be assigned from the 2D spectra alone. These resonances will be discussed further after consideration of the ^{13}C spectra of the copolymers, E/MA and E/CO.

The downfield region is best seen in an expansion of the 2D ^{13}C–^{1}H correlated spectrum (reprocessed with a sine-bell window function in both dimensions to enhance resolution) shown in Figure 9. The top trace in Figure 9 is the corresponding expanded region of the DEPT spectrum containing only methine carbons. Methine resonances B, C, E, and F all map to proton resonance 4. Therefore, these resonances must correspond to central methines in EME, EMM, and MMM triads. Chemical shift considerations indicate that MMM is upfield from EMM, which is upfield from EME because of the extra γ effects associated with adjacent methyl acrylate units. We cannot

make definitive assignments due to the complex nature of the observed fine structure, but some tentative assignments can be made on the basis of chemical shift additivity rules and the observed relative intensities of the lines. Since an adjacent methyl acrylate unit has an additional $COOCH_3$ group in the α position to the central methine, each adjacent methyl acrylate is expected to shift the central methine upfield by ~2 ppm.[29] The resonance corresponding to MMM central methines should be small because MMM sequences are anticipated to be unlikely due to steric crowding caused by the bulky acrylate groups. Furthermore, EME sequences are anticipated to be more likely than EMM sequences since more ethylene than methyl acrylate is available to react. On the basis of the above considerations, the small signal F is assigned to MMM methines, the two peaks labeled E are assigned to EMM methines, and both peaks B and C are assigned to EME methines. The chemical shift difference between each of the triads is ~2 ppm as expected. Also, the assignment of resonance F to MMM methines agrees well with the chemical shift of 42 ppm given by Randall for poly(methyl acrylate).[30]

Additional support for these ^{13}C assignments is given by the proton chemical shifts associated with the cross peaks in the ^{13}C–^{1}H correlated spectrum. Peaks B and C map to a proton resonance that is slightly upfield from that mapped to by resonance E. Since we know from the COSY spectrum of E/MA copolymer that EME methines are upfield from EMM methines in the proton spectrum, these observations support the ^{13}C assignments of resonances B and C to EME methines and resonance E to EMM methines. It should be noted that if the unit next to the ethylene is carbon monoxide in EME and EMM sequences, the additional γ carbonyl will shift the central methine signal slightly upfield (~0.5 ppm), and this accounts for the additional fine structure observed for EMM and EME methine signals (resonances B, C, and E).

Methylene resonances G and H map to equivalent protons in resonance 4. There must correspond to CEE and CEM methylenes α to carbon monoxide. The CEM α methylene is expected to be upfield from CEE because of the extra γ effect, so resonances G and H are assigned to CEE and CEM α methylenes, respectively.

Methylene resonance D has peaks mapping to two nonequivalent protons corresponding to resonance 2 and the downfield part of resonance 4. This must correspond to the nonequivalent α methylenes in CME and CMM sequences. The proton chemical shifts observed in the 2D ^{13}C–^{1}H correlated spectrum confirm the observations in the COSY spectrum. In these sequences, one of the α-methylene protons is overlapped with the MA methine in the proton spectrum. The central methines in CME and CMM triads must correspond to carbon methine signals I and J since these resonances map to proton resonance 2. As before, I and J are assigned to CME and CMM respectively on the basis of chemical shift. The remaining carbon, methylene resonance K, maps to proton resonance 3 and is assigned to both CEC methylenes.

The relative intensities of the peaks corresponding to EME, EMM, MMM, and CME, and CMM methines indicate that only a very small fraction of the total methyl acrylate is at the center of MMM triads in both E/MA/CO and E/MA copolymers. Since MMM triad sequences are so unlikely, MMMM tetrad sequences must be even more unlikely. Therefore, we can assume that the amount of MMMM tetrads is negligible. This means that MM diads are isolated as discussed earlier and cannot be part of MMMM tetrads.

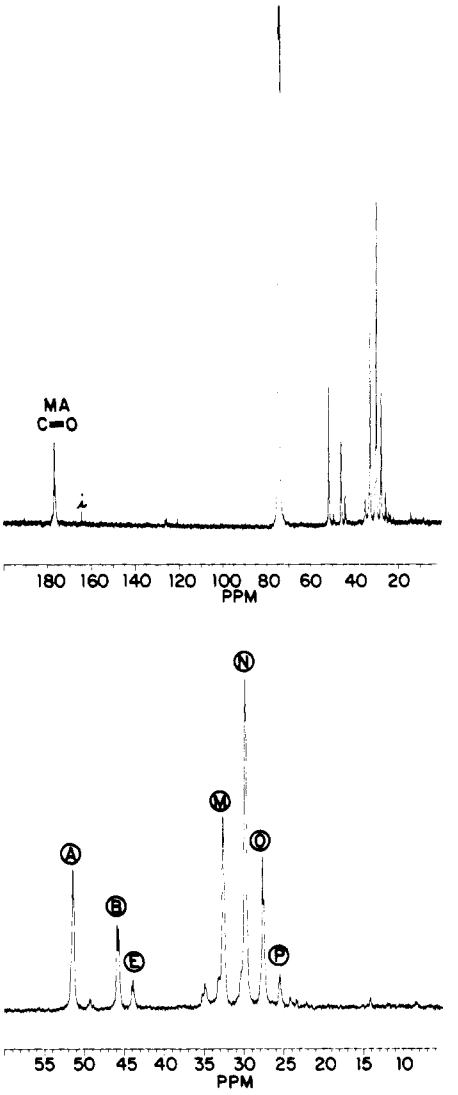


Figure 10. 75-MHz ^{13}C spectrum of a 10% solution of E/MA copolymer in tetrachloroethane-d_2 at 100 °C. Proton decoupling was gated off during the relaxation delay and on during acquisition to suppress the NOE. A total of 2377 transients were recorded with a 90° pulse and a 30-s relaxation delay. Top trace shows overall spectrum; bottom trace shows expansion of aliphatic region (5–60 ppm).

Methyl resonances T, U, and V are too weak to be detected in the 2D ^{13}C–^{1}H correlated spectrum. These resonances must correspond to the three types of terminal methyls observed in the proton spectrum. Resonance T has a chemical shift of 14 ppm, which is in good agreement with the chemical shift observed for terminal methyls in linear polyethylene[31] and is assigned to EE terminal methyls. Terminal ME methyls are shifted upfield by the carbonyl, and these methyls are assigned to resonance U. Resonance V is assigned to CE terminal methyls since a β carbon monoxide causes a considerable upfield shift in other sequences. All of the ^{13}C line assignments are summarized in Table II.

The assignments given in Table II are confirmed by the ^{13}C spectra of the copolymers E/MA and E/CO, which are shown in Figures 10 and 11, respectively. As expected, the MA methyl signal is a sharp singlet at ~52 ppm (resonance A) in the spectrum of E/MA and is not observed in the spectrum of E/CO. The central methine signals in EME and EMM triads are observed only in E/MA copolymer (resonances B and E), but no signal for MMM triads is observed in the copolymer due to the low probability of

Table II
Carbon-13 Line Assignments for E/MA/CO Terpolymer

resonance	chem shift,[a] ppm	sequences	description
A	51.6	all	MA methyls in all sequences
B, C	45.4, 44.8	EME	central methine
D	44.3	CME, CMM	nonequivalent methylenes α to carbon monoxide
E	43.2	EMM	central methine
F	41.5	MMM	central methine
G	42.4	EEC	α methylenes
H	40.1	MEC	methylenes α to carbon monoxide
I	40.2	CME	central methine
J	39.7	CMM	central methine
K	36.2	CEC	both central methylenes
L	34.6	MEM	methylenes α to acrylate (see text)
M	32.1	EM	y methylenes (see Figure 3a)
N	29.3	EEE, EEC	central ethylene methylenes and methylenes γ to carbon monoxide
O	27.1	MEM, MEE	central equivalent x methylenes γ to the carbonyl (Figure 3a)
P	25.9	EMME[b]	central methylenes in racemic MM diads
Q	25.1	CMME[b]	central methylenes in racemic MM diads
R	23.7	CEE	methylenes β to carbon monoxide
S	21.8	CEM	methylenes β to carbon monoxide
T	14.0	EE	terminal methyl
U	11.6	ME	terminal methyl
V	8.3	CE	terminal methyl

[a] Chemical shift listed for each resonance is the average of all listed sequences relative to tetrachloroethane-d_2. Uncertainty on each chemical shift is ±0.2 ppm. [b] There is probably a very small amount of EMMM and CMMM tetrads, but we cannot assign these structures since they are present at such low levels.

occurrence anticipated for this sequence. Although some fine structure due to some sensitivity to longer sequences is observed for these methines, the large splitting seen in the terpolymer is not present in E/MA copolymer. This confirms the notion that this large splitting is due to the possible presence of carbon monoxide as the monomer adjacent to ethylene in these sequences.

Resonances D, H, I, and J are not observed in either E/MA or E/CO copolymers, and this supports the assignments of these resonances to sequences involving both methyl acrylate and carbon monoxide to E/MA/CO terpolymer. Resonance G, which is assigned to EEC α methylenes, is observed in E/CO but not E/MA as expected. Similarly, resonance K is observed in E/CO copolymer, and this confirms the assignment of this peak to CEC methylenes. Resonance M corresponds to y-type methylenes (see Figure 3a) in EM sequences, and this peak is observed in E/MA but not E/CO copolymer as expected.

In the ^{13}C spectrum of the terpolymer, resonance N is assigned to EEE central methylenes and EEC γ methylenes, whereas resonance O is assigned to x-type methylenes (see Figure 3b) in MEE and MEM sequences. These assignments are verified by the copolymer spectra. The spectrum of E/MA contains single peaks for both N and O that correspond to only EEE methylenes (resonance N) and x-type methylenes in MEM and MEE sequences (resonance O). By contrast, the spectrum of E/CO does not contain resonance O and contains two peaks for resonance N that correspond to EEE central methylenes and

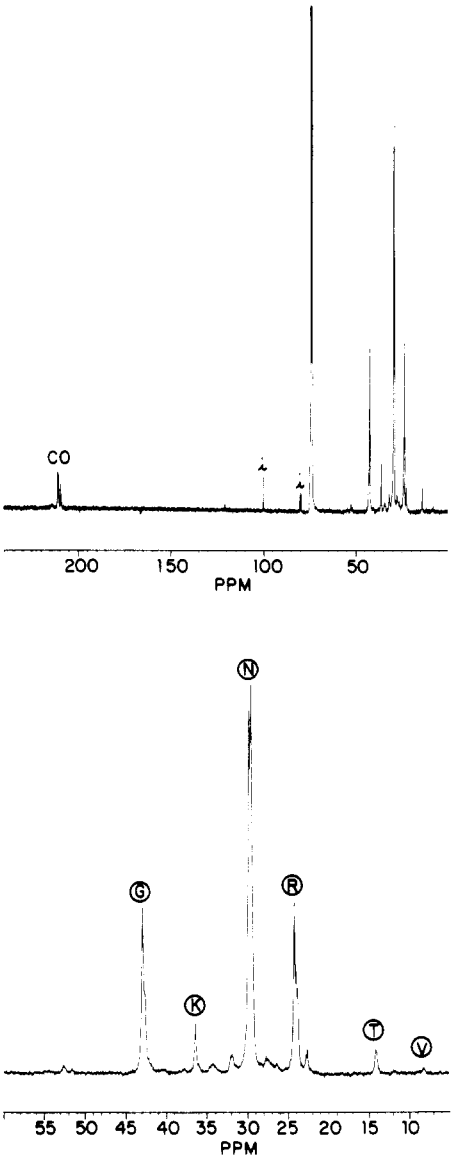
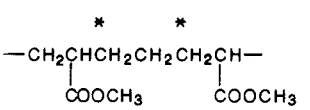


Figure 11. 75-MHz ^{13}C spectrum of a 10% solution of E/CO copolymer in tetrachloroethane-d_2 at 100 °C. The NOE was suppressed, and 1616 transients were recorded with a 90° pulse and a 30-s relaxation delay. Top trace shows overall spectrum; bottom trace shows expansion of aliphatic region (5–60 ppm).

EEC γ methylenes (shifted slightly upfield). EEC β methylenes are assigned to resonance R, and this assignment is verified since this peak is only in the spectrum of E/CO. Resonance P is only in the spectrum of E/MA as expected since this corresponds to central methylenes in racemic MM diads.

The assignments made for the terpolymer E/MA/CO are verified from the copolymer spectra, but there are three resonances, L, Q, and S, that cannot be assigned from the terpolymer spectra alone. Tentative assignments can be made for these resonances from the ^{13}C spectra of the two copolymers. Resonance L at ~35 ppm is observed only in the spectrum of E/MA copolymer (not labeled in Figure 10). This resonance must correspond to a sequence containing only ethylene and methyl acrylate. We tentatively assign this resonance to the indicated methylenes in MEM sequences as shown below:



This structure also is consistent with cross peaks connecting resonances at 1.12 and 1.50 (indicated by × in Figure 4) since coupling is present between indicated methylenes and central methylenes in the above sequence.

Resonances Q and S are not observed in the spectrum of either E/CO or E/MA copolymers. These resonances must correspond to sequences containing both methyl acrylate and carbon monoxide. Resonance Q is slightly upfield from resonance P, which can be caused by an extra carbonyl in the γ position. Hence, resonance Q is tentatively assigned to methylenes between MM diads in CMM sequences as shown in Figure 3c. Similarly, resonance S is tentatively assigned to β methylenes in CEM sequences (ethylene adjacent to methylene of methyl acrylate) since these methylenes have an additional $COOCH_3$ group in the γ position.

We have only assigned the major different resonances in the spectrum of this terpolymer. There are many minor sequences that we have not considered. In particular, we have not considered sequences involving inverted units of methyl acrylate. We also have not considered branching. In the spectra of both E/MA and E/CO copolymers there are numerous small peaks due to branching on both ethylene and methyl acrylate. The E/MA/CO terpolymer probably contains peaks due to branching, but these peaks are buried under other resonances. Likewise, peaks due to other minor sequences are probably buried under other larger peaks, and we will not attempt to assign these minor sequences in the spectra of E/MA/CO terpolymer.

Conclusions

The unique coupling patterns and chemical shifts observed for many sequences enabled the proton monomer sequence assignments to be made unambiguously at the triad level from the 2D COSY spectrum of this complex terpolymer, E/MA/CO. In addition, end groups corresponding to terminal EE, ME, and CE were observed and assigned in the COSY spectrum. The coupling patterns observed in the COSY spectra of both E/MA and E/MA/CO indicate that predominantly racemic MM diads are formed in these polymers. This is in excellent agreement with previous results on other acrylate-containing polymers made by free radical initiators.

The ^{13}C line assignments were made from the combination of DEPT and 2D ^{13}C–^{1}H correlated spectroscopy despite the complexity of the conventional ^{13}C spectrum. DEPT spectroscopy allowed the multiplicity of each resonance to be determined unambiguously. Hence, ^{13}C assignments were made easily from the 2D ^{13}C–^{1}H correlated spectrum even in situations where overlap of methine and methylene signals occurs in the proton spectrum. Furthermore, equivalent and nonequivalent methylenes were distinguished in the 2D ^{13}C–^{1}H correlated spectrum, and this allowed ^{13}C assignments to be made despite spectral overlap of proton resonances. Proton chemical shifts were determined more accurately from the ^{13}C–^{1}H correlated spectrum because of the greater dispersion in the ^{13}C spectrum. All ^{1}H and ^{13}C assignments were confirmed by looking at the ^{13}C spectra of the copolymers E/MA and E/CO.

The combination of several techniques proved more powerful than any one alone in assigning the ^{1}H and ^{13}C spectra of this complex terpolymer. Despite spectral overlap, detailed line assignments were made in both the ^{1}H and ^{13}C spectra. These techniques show tremendous potential for interpretation to NMR spectra of similar polymers.

Acknowledgment. We thank Dr. J. R. Harrell, E. I. du Pont de Nemours and Co., for synthesis of the E/MA/CO terpolymer.

Registry No. (E)(MA) (copolymer), 25103-74-6; (E)(CO) (copolymer), 25052-62-4; (E)(MA)(CO) (copolymer), 73764-12-2.

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