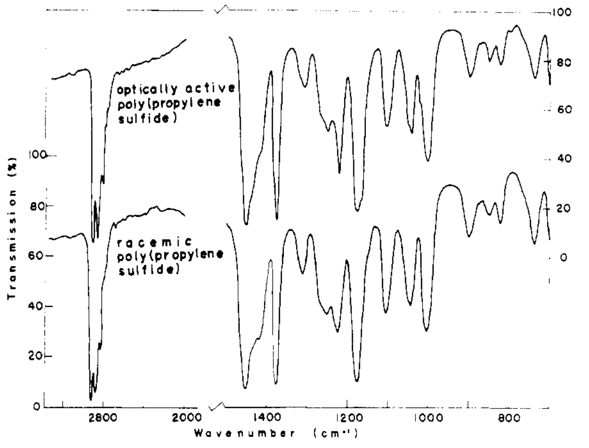

Figure 7. Infrared spectra of the optically active poly(propylene sulfide) and the racemic poly(propylene sulfide).

molecular chains. This relation between the "up" *S*-polymer chain and the "down" *R*-polymer chain is illustrated in Figure 3b and c. Consequently the lattice projection along the *c* axis of the assumed statistical model is identical with that of the optically active polymer. Accordingly the structure factors of the *hk*0 reflections are the same as those of the optically active polymer, but the structure factors of the *hkl* ($l \neq 0$) reflections are observably different from the optically active case and in very poor agreement with the observed data.

From these results, it seems most reasonable to conclude that crystalline racemic poly(propylene sulfide) consists of crystallites composed of *R*-polymer chains only and of *S*-polymer chains only.

It would be interesting to establish whether optically active crystallites exist also in the case of racemic poly(propylene oxide).

Nuclear Magnetic Resonance Studies on the Microstructure of Ethylene Copolymers. III. Solvent Effects on Proton Resonance Spectra of Ethylene–Vinyl Acetate Copolymers[1,2]

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ABSTRACT: Effects of solvent on the proton nmr spectra of ethylene–vinyl acetate (E–VA) copolymers have been investigated. In solutions of benzene and alkylbenzenes the solvent molecules selectively associate with the acetate methyl groups of E–VA dyads. The heats and entropies of complex formation were obtained by analyzing the temperature dependence of the observed spectra. It was found that presence of polar substituent in the aromatic solvent molecules (*e.g.*, halobenzenes and pyridine) precludes the formation of polymer–solvent complex. Moreover, these complexes seem to have a steric dependence since bulky alkylbenzenes impede their formation. For E–VA copolymers containing more than 62.5 mol % of ethylene, the methylene protons of the alkanelike sequences give rise to two resonance peaks in aromatic solution spectra. These peaks can be assigned to the methylene groups of the two types of intramolecular structure, "polymeric" and "monomeric," similar to those observed in the spectra of oligomeric polyethylene. The "polymeric" structure probably arises from intramolecular chain folding.

The utility of solvent effects in high-resolution nmr spectroscopy of polymers has been well recognized. In a systematic study of the solvent effects, Ramey and Messick[3] have demonstrated that proton resonances of the pendant groups in a variety of homopolymers can be resolved into the peaks corresponding to the various stereochemical sequence placements. For some oligomers of polyethylene, it was also possible to identify the two types of intramolecular structure, *i.e.*, "polymeric" and "monomeric" species, from the 1-chloronaphthalene solution spectra.[4] In our earlier work, we utilized the ester proton resonance spectra in appropriate solvents for characterizations of monomer sequence distributions in ethylene–vinyl formate (E–VF) and ethylene–vinyl acetate (E–VA) copolymerizations.[1,2]

Recently, the nmr technique has been applied to investigate the polymer–solvent interactions in solution. By examining the benzene solution spectra of poly(methyl methacrylate) (PMMA) at various temperatures, Nagai and Nishioka were able to deduce the π-complex formation between benzene molecules and the monomer units of the polymer.[5] In addition, the extent of the complexes formed was found to depend on the stereochemical configurations of the monomer units in PMMA.[6]

In this study, proton nmr spectra of E–VA copolymers dissolved in a number of solvents were obtained. From the benzene and alkylbenzene solution spectra, we have deduced the existence of π-complex formation between the copolymer segments and the solvent molecules. Indications of the intramolecular structures in the ethylene sequences of E–VA polymers, similar to

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(1) Part I: T. K. Wu, *J. Phys. Chem.*, 73, 1801 (1969).

(2) Part II: T. K. Wu, to be published.

(3) K. C. Ramey and J. Messick, *J. Polym. Sci., Part A-2*, **4**, 155 (1966).

(4) K.-J. Liu, *ibid., Part A-2*, **5**, 1209 (1967).

(5) M. Nagai and A. Nishioka, *ibid., Part A-1*, **6**, 1655 (1968).

(6) K.-J. Liu, *ibid., Part A-1*, **5**, 1199 (1967).

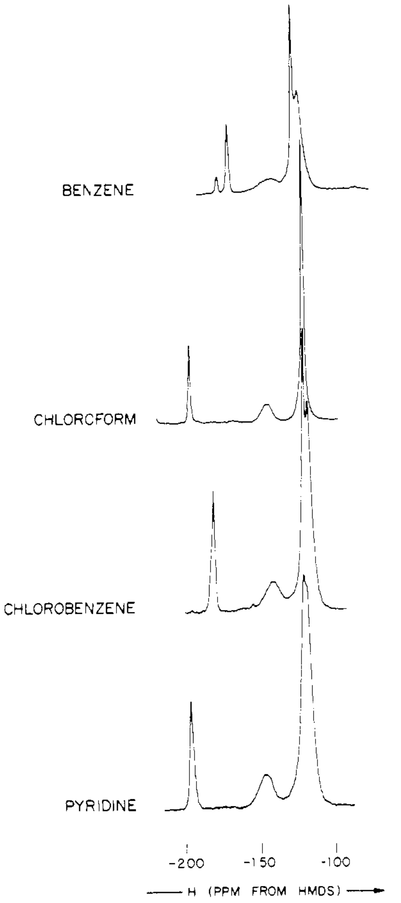

Figure 1. 220-MHz spectra of a E–VA copolymer (mole fraction f_{VA} = 0.190) dissolved in several solvents.

those observed in polyethylene oligomers, were also obtained.

Experimental Section

Synthesis of E–VA copolymers and analysis of the copolymer spectra have been described previously.[2] In this study, the nmr sample solutions were prepared to contain 10, 7.5, 5.0, and 2.5 wt % of the copolymer. A small amount of hexamethyldisiloxane (HMDS) was added as internal reference. Proton nmr spectra were recorded on Varian A-60 and HR 220 nmr spectrometers equipped with variable-temperature probes. The spectra were calibrated by the audiomodulation technique, and the average deviations of resonance peak position measurements, over five or more traces, were usually within ±0.1 Hz.

Effects of sample concentrations on chemical shifts of the various protons in E–VA copolymers were also examined. Usually, dilution of sample solution from 10 to 2.5 wt % gives rise to a chemical shift difference of less than ±0.01 ppm. The chemical shift values of the least concentrated solutions were used.

Results and Discussion

I. Acetate Methyl Proton Resonance Spectra. In part II of this series we reported the results of a preliminary study of the solvent effects on proton resonance spectra of E–VA copolymers.[2] It was found that resolution of the acetate methyl proton resonances is strongly dependent on the nature of the solvents. The doubled acetate methyl proton peaks, which appear at about −1.7 ppm from HMDS in the benzene solution spectrum, can be assigned to the comonomer dyads of VA–VA and E–VA at low and high field, respectively. On the other hand, these methyl protons give rise to only one resonance line in solutions of polar solvents such as chlorohydrocarbons, halobenzenes, and pyridine.[2] In this study, we have found that the acetate methyl resonances of E–VA polymers can also be resolved into two lines in alkylbenzene solutions. Figure 1 depicts the spectra of an E–VA copolymer dissolved in several solvents. The chemical shift data of the acetate methyl protons are presented in Table I.

TABLE I
ACETATE METHYL PROTON CHEMICAL SHIFTS OF ETHYLENE–VINYL ACETATE COPOLYMERS

Solvent[a]	Dielectric constant[b]	Chemical shifts, ppm from HMDS
Chloroform	4.806	−1.957
1,1,2-Trichloroethylene	3.42	−1.893
p-Dioxane	2.208	−1.885
Pyridine	12.3	−1.950
o-Dichlorobenzene	9.93	−1.890
Chlorobenzene	5.621	−1.815
Benzene	2.274	−1.758, −1.688

[a] The spectra of E–VA copolymers were obtained at 37°.
[b] Dielectric constants were taken from "Handbook of Chemistry and Physics," R. C. Weast, Ed., The Chemical Rubber Publishing Co., Cleveland, Ohio, 1968.

In order to gain some insight into the nature of the solvent effects, we have obtained the spectra of E–VA polymers dissolved in benzene and alkylbenzenes at several temperatures. Table II summarizes the effects of solvents and temperature on the acetate methyl proton resonances and the corresponding benzene solution spectra are shown in Figure 2.

A number of observations of these data are noteworthy. (1) The resonance peak positions of the acetate methyl protons in VA–VA dyads remain virtually constant over a wide range of solution temperatures (~100°). (2) The corresponding peak positions of E–VA dyads are dependent on the solution temperature and displaced to lower magnetic field with increasing temperature. (3) At similar temperature, the effects of solvents on the separations of the doubled acetate methyl proton peaks decrease from benzene> toluene, *o*-xylene > *m*- and *p*-xylenes, cumene > mesitylene, *t*-butylbenzene. These observations suggest that solvent molecules preferentially interact with the acetate methyl groups of E–VA dyads, and that these inter-

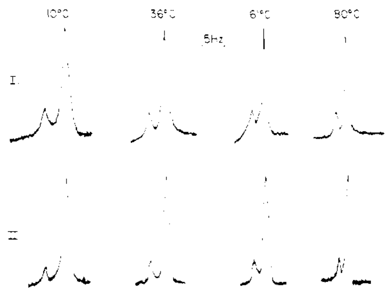

Figure 2. 60-MHz benzene solution spectra of acetate methyl protons of two E–VA copolymers (f_{VA}: I = 0.190, II = 0.105) at several temperatures.

Table II
Solvent and Temperature Effects on Acetate Methyl Proton Chemical Shifts of Ethylene–Vinyl Acetate Copolymers

	Temp, °C	Chemical shifts, Hz at 60 MHz from HMDS VA–VA	E–VA
Benzene	6	−105.4	−99.8
	12.5	−105.4	−100.2
	21.5	−105.5	−100.6
	36	−105.5	−101.3
	53.5	−105.5	−102.0
	61.5	−105.4	−102.1
	70.5	−105.4	−102.3
	80	−105.4	−102.6
Toluene	−17	−105.8	−99.7
	−7.5	−105.7	−100.2
	4	−105.9	−100.9
	19	−105.8	−101.6
	37	−105.9	−102.3
	50.5	−105.7	−102.6
	72	−105.8	−103.2
	92	−105.8	−103.7
	122	−105.8	−104.1
o-xylene	−6	−105.5	−100.1
	10	−105.6	−100.9
	36	−105.6	−102.1
	80	−105.7	−103.3
	92	−105.6	−103.5
m-Xylene	4	−106.0	−101.6
	19	−106.0	−102.3
	36	−106.0	−102.8
	50.5	−106.0	−103.3
	72	−106.1	−103.9
p-Xylene	4	−106.3	−101.9
	19	−106.3	−102.6
	60	−106.4	−103.8
	80	−106.2	−104.0
	102	−106.3	−104.6
Cumene	−17	−105.0	−99.7
	35	−104.8	−101.7
	61	−105.0	−102.5
	80	−105.0	−103.0
	100	−104.9	−103.1
Mesitylene	10	−106.6	−102.9
	37	−106.5	−103.8
	50.5	−106.4	−103.9
	72	−106.5	−104.5
	96	−106.4	−104.7
t-Butylbenzene	−18	−104.4	−99.5
	0	−104.3	−100.3
	19	−104.3	−101.0
	37	−104.5	−101.7
	61	−104.5	−102.3

actions are influenced by the steric features of the solvent molecules.

From the temperature effects on nmr spectra of PMMA, Nagai and Nishioka[5] have deduced π-complex formation of the monomer units in polymer with benzene solvent by utilizing the Abraham theory,[7] *viz.*

$$\exp(-\Delta S/R)\exp(\Delta H/RT) = (\delta_c/\delta) - 1 \qquad (1)$$

where ΔH and ΔS are, respectively, the enthalpy and entropy of complex formation, R is the gas constant, δ_c is the chemical shift of the solute proton in the complex, and δ is the shift of the solute proton observed at solution temperature T (°K). By making the assumption that each monomer unit of PMMA associates with one molecule of benzene, they derived the values for ΔH, ΔS and δ_c with the use of eq 1.[5]

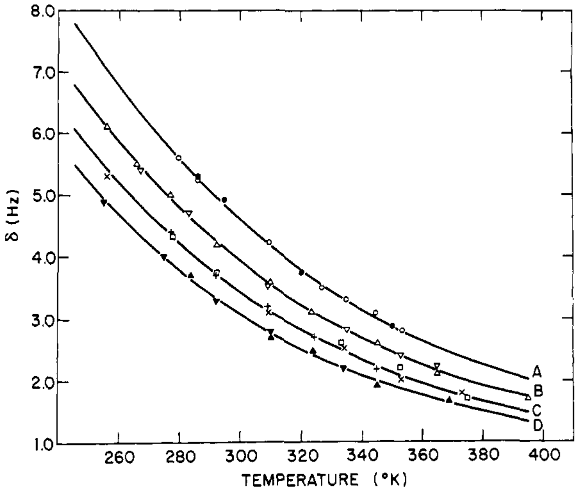

Figure 3. Effects of temperature on benzene and alkylbenzene solution spectra of acetate methyl protons of E–VA copolymers, δ = separation between the two acetate methyl proton peaks in hertz (at 60 MHz): A, benzene solvent and copolymer compositions of f_{VA} = 0.190 for ● and f_{VA} = 0.105 for ○; B–D, copolymer composition f_{VA} = 0.190. Solvents: △ = toluene, ▽ = *o*-xylene, + = *m*-xylene, □ = *p*-xylene, × = cumene, ▲ = mesitylene, and ▼ = *t*-butylbenzene.

Figure 3A depicts the separation of the two acetate methyl proton resonance peaks of two E–VA copolymers dissolved in benzene as a function of temperature. These points were best fitted by eq 1 with the following values: $\Delta H = -2.7$ kcal/mol, $\Delta S = -10.2$ eu, and $\delta_c = 13.0$ Hz (at 60 MHz). In carrying out the fitting procedure, we have made two assumptions: (1) each acetate methyl group of E–VA dyads associates with one benzene molecule; (2) the peak position of these methyl protons is displaced to lower magnetic field with decreasing degree of complexation and eventually coincides with the peak due to acetate methyl protons of VA–VA dyads with no complex formation. The fact that these results can be satisfactorily interpreted by the Abraham theory suggests complex formation between copolymer solute and the solvent molecules. Moreover, since a single set of thermodynamic parameters and δ_c was found to fit the acetate methyl proton spectra of these copolymers with different compositions, it follows that complex formation arises from association of the copolymer segments, *i.e.*, acetate methyl groups of E–VA dyads, with benzene molecules.

In Figure 3B–D, the chemical shift data of these methyl protons obtained in alkylbenzenes are graphically presented, along with the best fitted lines obtained by using eq 1. The derived thermodynamic parameters and δ_c's are summarized in Table III. It is noteworthy that ΔH and ΔS values tend to vary systematically and suggest less complex formation with increasing methyl substitution or substituent bulkiness of the benzene solvents. Therefore, the extent of association of alkylbenzene molecules with E–VA dyads in the copolymer

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(7) R. J. Abraham, *Mol. Phys.*, 4, 369 (1961).

TABLE III
THERMODYNAMIC PARAMETERS AND δ_c VALUES OF COMPLEX FORMATION

Solvent	ΔH^a	ΔS^b	$\delta_c{}^c$
Benzene	−2.70	−10.2	13.0
Toluene, *o*-xylene	−2.70	−10.3	11.5
m-Xylene, *p*-xylene, cumene	−2.65	−10.4	11.0
Mesitylene, *t*-butylbenzene	−2.60	−10.4	10.4

[a] Heat of formation in kilocalories per mole (errors = ±0.5). [b] Entropy of formation in entropy units (errors = ±1). [c] Chemical shifts (in hertz at 60 MHz) of acetate methyl protons of E–VA dyads in the complex.

is dependent on the molecular size of the solvent. In addition, since alkylbenzenes are very nearly nonpolar, δ_c values should represent the solvent shifts of the acetate methyl protons, which arises primarily from the diamagnetic shieldings of the magnetically anisotropic benzene molecules.[7,8] The observation that δ_c is reduced significantly with increasing size of the solvent molecule provides further support to our foregoing conclusion of the steric dependence in π-complex formation.

π-Complex formation of E–VA polymers with benzene and alkylbenzenes is different from that of some low molecular weight compounds in the following two aspects:[8] (1) formation of complex is dependent on the steric features of the solvent molecules; (2) no appreciable amount of complex can be found in polar aromatic solvents such as halobenzenes and pyridine. The steric dependence of complex formation is not unexpected, since the solutes of the present systems are, in fact, macromolecules. Moreover, the fact that benzene solvents selectively associate with acetate methyl groups of E–VA dyads in copolymer implies the stringent steric requirements for π-complex formation.

The polar aromatic solvent effects on acetate methyl proton spectra may be examined in terms of the reaction field shielding effects due to the polar solvent medium.[9] In order to account for the single acetate methyl proton resonance peak observed, it must be assumed that the shielding of these protons in E–VA dyads due to the reaction field of the solvent is different from that of the protons in VA–VA dyads, and these effects must coincidentally compensate for the shielding due to π-complex formation. Alternatively, the observation of the aligned solute–solvent dipole pairs for some low molecular weight compounds[10] may be applicable to our systems. It is conceivable that dipole alignments between copolymer segments and solvent molecules might diminish the π-complex formation. Since the two above-mentioned types of solvent shielding mechanisms are dependent on the polarity of the solvents, it is interesting to note that the chemical shift data of acetate methyl protons in aromatic solvents in Table I can indeed be roughly correlated with the dielectric constants of the solvents.

TABLE IV
METHYLENE PROTON CHEMICAL SHIFTS OF ETHYLENE–VINYL ACETATE COPOLYMER

Solvent	Chemical shifts,[a] ppm from HMDS $-\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2}-$	 $-\mathrm{CH}(\mathrm{OCOCH_3})\mathit{CH_2}\mathrm{CH_2}-$
Chloroform	−1.186	−1.43
Trichloroethylene	−1.185	−1.42
p-Dioxane	−1.213	−1.45
o-Dichlorobenzene	−1.127, −1.159	−1.40
Chlorobenzene	−1.163, −1.195	−1.40
Pyridine	−1.181, −1.204	−1.46
Benzene	−1.200, −1.240	−1.38

[a] The spectra were obtained at 37°. Chemical shifts of the protons of interest are italicized.

II. Methylene Proton Resonance Spectra. In Figure 1, the methylene proton resonances of E–VA copolymers can be found at −1.2 and −1.5 ppm from HMDS, which correspond to the methylene groups in the sequence placement of $-\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2}-$ and $-\mathrm{CH_2}\mathit{CH_2}\mathrm{CH}(\mathrm{OCOCH_3})-$, respectively. (The protons of interest are italicized.) Owing to the low VA contents of the copolymers investigated, the methylene proton resonances of $-\mathrm{CH}(\mathrm{OCOCH_3})\mathit{CH_2}\mathrm{CH}(\mathrm{OCOCH_3})-$ cannot be clearly observed at −1.7 ppm. However, careful examination of the spectra presented in this figure reveals that the resonance peak due to the alkanelike methylene groups (at −1.2 ppm) is further resolved into two lines in the spectra of E–VA polymers dissolved in aromatic solvents. Pertinent chemical shift data for these protons are in Table IV.

From the 1-chloronaphthalene solution spectra of polyethylene oligomers, Liu has found that the methylene protons of these molecules with more than 16 carbon atoms give rise to two resonance peaks, which he assigned to the internal methylene groups in the "polymeric" sequences of ordered structure and the disordered "monomeric" species.[4] Moreover, Bovey and Tiers[11] reported that the doubled phenyl proton peaks which appear in the spectrum of polystyrene were not observed in the spectra of the low molecular weight oligomers with degrees of polymerization equal to or less than 5.

Figure 4 depicts the benzene solution spectra of several E–VA copolymers in the methylene region. It is noteworthy that the positions of the various proton peaks remain virtually constant, while the intensities of the doubled methylene proton peaks due to the alkanelike sequences vary systematically with copolymer compositions. Moreover, the spectral features of these two peaks, which consist of a sharp resonance peak at lower magnetic field and a broad peak at higher field, are remarkably similar to those observed for polyethylene oligomers.[4] Liu has attributed the sharp methylene peak to the equivalent internal methylene groups in the "polymeric" sequence in a paraffin

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(8) P. Laszlo in "Progress in Nuclear Magnetic Resonance," Vol. 3, J. W. Emseley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, Ltd., Oxford, England, 1967, Chapter 6.

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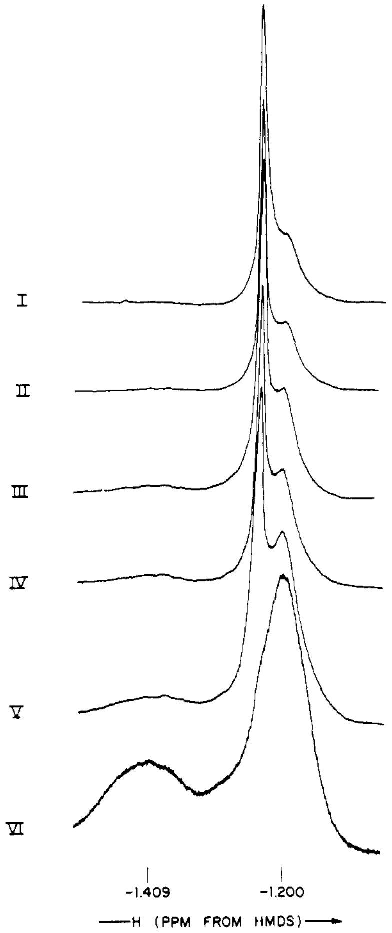

Figure 4. 220-MHz benzene solution spectra in the methylene proton region of several E–VA copolymers. Mole fractions: f_E of I = 0.930, II = 0.902, III = 0.888, IV = 0.867, V = 0.809, VI = 0.625.

molecule (with more than 16 carbon atoms), which might be situated in an ordered structure through intramolecular chain folding. The broad upfield resonance was thought to arise from the disordered "monomeric" methylene groups interacting nonequivalently with the aromatic solvent molecules.[4]

Since both polar and nonpolar aromatic solvents give rise to doubled resonance peaks for methylene protons of the alkanelike sequences in E–VA copolymers, the effects of solvents must be different from those of benzene and alkylbenzenes on acetate methyl proton spectra *via* π-complex formation.

In order to examine the feasibility of Liu's theory in interpreting the methylene proton spectra of E–VA copolymers, we have calculated the fractions of ethylene units in blocks of eight or more ethylene units. The equation for such calculation can be written as

$$G(n) = f_E[1 + (n - 1)(1 - P_{EE})]P_{EE}^{n-1} \quad (2)$$

TABLE V

DISTRIBUTIONS OF ETHYLENE SEQUENCES IN ETHYLENE–VINYL ACETATE COPOLYMERS

f_E[a]	$G(8)_{calcd}$[b]	$G(8)_{obsd}$[b]
0.625	0.084	0
0.809	0.429	0.34
0.867	0.598	0.41
0.888	0.688	0.50
0.902	0.738	0.56
0.930	0.831	0.61

[a] f_E is the mole fraction of ethylene in E–VA copolymers. [b] $G(8)_{calcd}$ is the fraction of ethylene in blocks of eight or more units of ethylene. $G(8)_{obsd}$ values were obtained by peak area measurements from the benzene solution spectra.

where $G(n)$ is the fraction of polymer existing in blocks of n ethylene units or longer, P_{EE} represents the probability that an ethylene monomer will add to a growing E–VA polymer radical ending in ethylene, f_E is the mole fraction of ethylene in the copolymer.[12]

For statistically random E–VA copolymerization,[2] P_{EE} is equal to f_E, and eq 2 can be simplified to

$$G(8) = f_E^{\,8}\,[1 + 7(1 - f_E)] \quad (3)$$

The calculated $G(8)$'s for E–VA copolymers are presented in Table V. The corresponding fractions of ethylene units in "polymeric" sequences derived from the alkanelike methylene proton spectra are also included. It is interesting to note that the observed values are, in all cases, smaller than the calculated values for $G(8)$. This is in agreement with Liu's observation that the "polymeric" methylene groups in $C_{18}H_{38}$ and $C_{28}H_{58}$ account for 33 and 50% of the total methylene groups, respectively. Moreover, for an E–VA copolymer of f_E = 0.625 the calculated $G(8)$ is very small (~0.08). Indeed, no appreciable resonance peak due to the "polymeric" methylene protons can be observed in the benzene solution spectrum (see Figure 4). Therefore, we conclude that the long ethylene sequences of E–VA copolymers dissolved in aromatic solvents exist in two types of structure: "polymeric" and "monomeric," which are similar to those observed for oligomeric polyethylene. The "polymeric" structure probably arises from chain folding of the long methylene sequences containing eight or more ethylene units.[4,13]

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