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Two-Dimensional ^1H and ^{13}C NMR Spectroscopy of Styrene–Methyl Methacrylate Copolymers

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ABSTRACT: We have observed the 500 MHz proton NMR spectra of random copolymers of styrene and methyl methacrylate and the 500 MHz proton spectrum and 125 MHz carbon-13 spectrum of a 1:1 alternating copolymer of these monomers. The spectra of the alternating copolymer are much simpler owing to the restriction of possible sequences and can be very fully interpreted in terms of stereochemical configuration and chain conformation. The carbon-13 spectrum shows that the ethyl aluminum sesquichloride catalyst produces a strictly alternating structure that is entirely random with respect to stereochemical configuration. The unusual dependence of the methoxyl proton shielding on stereochemical configuration, long believed to arise from proximity to the phenyl groups of styrene units, can be directly shown by the nuclear Overhauser correlated (NOESY) 2D proton spectrum to be due to this cause. The less marked dependence of α-methyl protons arises similarly. When the NOESY proton spectrum of the main-chain methylene protons is displayed in the phase-sensitive mode, one clearly observes the geminal association of protons in the co-isotactic and co-syndiotactic diads, appearing as strong cross-peaks. In co-hetero diads, cross-peaks clearly show inter-methylene proton dipole–dipole interactions between neighboring CH_2 groups as well. These interactions are observed from the magnitudes of the cross-peaks to fall into three categories: one weak, one strong, and two intermediate-sized. This observation is shown to be consistent with the rotational isomeric state (RIS) model of Koinuma et al. if and only if approximately 20° deviations from exact staggering of the backbone conformational states are assumed. The through-space dipole–dipole proton interactions depend on the inverse sixth power of the methylene internuclear distances and thus furnish a direct and very sensitive spectroscopic test of conformational proposals. Although the 1D 500 MHz proton spectrum of the 1:1 copolymer shows no indication of spacings arising from geminal and vicinal *J*-couplings, these may be readily measured in the *J*-resolved 2D spectrum. The values of the vicinal couplings thus obtained agree very well with the predictions of the RIS model for co-meso sequences but not quite so well for co-syndio sequences.

The structure of random and alternating styrene–methyl methacrylate copolymers has been extensively studied by both proton[1-13] and carbon-13[14,15] one-dimensional NMR. A striking feature of the proton spectra is the splitting of the methoxyl resonance, which is relatively insensitive to stereochemical configuration in the methyl methacrylate homopolymer,[16] into three regions presumably reflecting the "co-tacticity" of the comonomer sequences. In particular, it has been proposed[1,6-8] that the upfield-shifted methoxyl resonances correspond to ester groups that are in close proximity to phenyl rings and experience ring-current shielding. A similar effect is seen to a lesser degree for the α-methyl resonances. These configurational effects are particularly clearly observed in the 1:1 alternating styrene–methyl methacrylate copolymer, in which the number of possible methyl methacrylate-centered triad comonomer sequences has been reduced from 10 to 3.[10,12,13]

In this paper we apply carbon-13 and proton NMR—the latter principally in the 2D mode—to the further exploration of the structure and conformation of styrene–methyl methacrylate copolymers. Principal emphasis is placed on the alternating copolymer, since the interpretation of its spectra is simpler for the reason just given.

Two-dimensional NMR techniques have been extensively applied to biological macromolecules. Two-dimensional Overhauser effect spectroscopy, termed NOESY for NOE-correlated spectroscopy, has been applied by Wüthrich, Ernst, and others to proteins,[17-23] cyclic peptides,[24,25] micelle-bound glucagon,[26] nucleic acids,[27,28] and synthetic biopolymers.[29,30] Applications to vinyl and related polymers have been more limited. Macura and Brown[31] have applied 2D *J*-resolved proton spectroscopy to poly(vinyl chloride); Mirau and Bovey[32] have applied a variety of 2D techniques to this polymer, while Gippert and Brown have reported a *J*-resolved NMR study of poly(vinyl alcohol).[33] Gerig[34] has applied ^{19}F–^1H heterocorrelated NMR to poly(*p*-fluorostyrene), while Bruch et al.[35] and Cais et al.[36] have used ^{19}F COSY (*J*-correlated spectroscopy) to study the structure of poly(vinyl fluoride) and poly(vinylidene fluoride), respectively. Bruch and Bovey[37] have applied proton NOESY to interpret the spectrum of a vinylidene chloride–isobutylene copolymer and Bruch et al.[38] have employed *J*-resolved proton spectroscopy to the study of the structure of poly(propylene oxide). Cheng and Lee[39] have studied the structure of ethylene–propylene copolymers using ^{13}C–^1H correlated 2D NMR. Chang et al.[40] have described a study of the stereochemistry of poly(vinylamine) by *J*-resolved and heterocorrelated 2D NMR. Most relevant to the present study is a proton NOESY and COSY study of isotactic and atactic poly(methyl methacrylates) by Schilling et al.[16]

Experimental Section

NMR Methods. The 2D NOESY experiments employed a $\pi/2$–t_1–$\pi/2$–τ_m–$\pi/2$–t_2 pulse sequence.[41,42] The first 90° pulse causes each proton to precess at its characteristic frequency during the evolution period t_1. The NOE depends on direct through-space dipole–dipole interaction, which manifests itself in a time of the order of the spin–lattice relaxation time, T_1. The mixing time τ_m provides such an interval, during which protons that are in sufficiently close proximity exchange incoherent magnetization through dipole–dipole relaxation. In the final 2D spectrum, cross-peaks identify the resonances of such protons. The NOE varies as the inverse sixth power of the internuclear distance and becomes negligible beyond about 4 Å.

As in all 2D experiments, the evolution time is systematically incremented and the free induction decay is detected in t_2 for a series of t_1 values. Two-dimensional Fourier transformation yields a 2D spectrum as a function of two frequencies, F_1 and F_2.

The *J*-resolved experiment separates chemical shift and scalar coupling, *J*, along the two axes of the spectrum, permitting unambiguous determination of each. The pulse sequence employed is $\pi/2$–$t_1/2$–π–$t_1/2$–t_2.[43] The 90° pulse turns the magnetization

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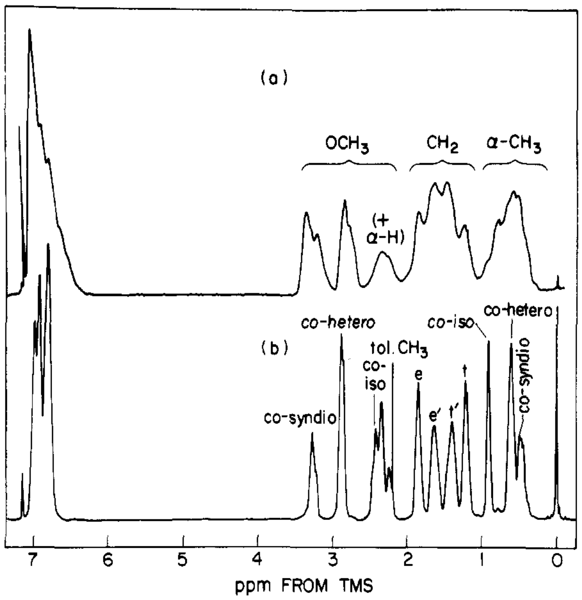


Figure 1. 500 MHz proton spectra of (a) the random and (b) alternating 50:50 styrene–methyl methacrylate copolymers, observed in 10% (w/v) hexachlorobutadiene solution at 80 °C.

vector into the xy plane, and the individual components dephase during the first interval of length $t_1/2$. The 180° pulse refocuses the spin isochromats that have dephased because of chemical shift differences but not those that have dephased because of J-coupling. The individual components of a multiplet continue to dephase during the second interval of length $t_1/2$. This results in an apparent precession frequency during t_1 that is dependent only on the magnitude of the scalar coupling constants. At the end of time t_1, the chemical shift components are completely refocused, and a spin echo is produced. The spin echo is detected as a free induction decay in the time t_2. After two-dimensional Fourier transformation of the data matrix and a "tilt"[44] of 45°, the F_2 axis reflects chemical shifts and the F_1 axis reflects the J-couplings. (A complete description of the experiment is given by Bax.[45])

NMR Measurements. The 500 MHz ^1H and 125 MHz ^{13}C NMR spectra were recorded on a JEOL GX-500 spectrometer. The polymer solutions were prepared in hexachlorobutadiene with 10% benzene-d_6 as lock and hexamethyldisiloxane (HMDS) as internal reference (0.06 ppm vs. Me_4Si for ^1H and 2.00 ppm vs. Me_4Si for ^{13}C). The solution concentrations were 10% (w/v) for the proton experiments and 20% (w/v) for the carbon experiments.

Both absolute value and phase-senstive[46] NOESY spectra were recorded. The processed data matrix consisted of 512 × 512 points covering 5000 Hz in both dimensions. The repetition time was 4 s with 16 scans collected for each of the 256 spectra. The absolute value spectra were processed with a combination of line broadening and trapezoidal multiplication in both dimensions. A 1 Hz line broadening was applied to both dimensions in the phase-sensitive spectra.

The J-resolved chemical shift dimension, F_2, covered 5000 Hz and contained 2048 points. The J-dimension, F_1, spanned 50 Hz and consisted of 128 points. The data were processed in the absolute value mode, again with a combination of line broadening and trapezoidal multiplication in both dimensions. The repetition time was 3 s with 16 scans collected for each of the 128 spectra.

Materials. The preparation of the alternating poly(styrene-*co*-methyl methacrylate) followed the protocol of Hirai et al.,[12] employing initiation with diethylaluminum sesquichloride at 0 °C without irradiation. The synthesis was performed 3 times, keeping the total monomer concentration constant at 2.5 mol·L^{-1}. The same individual monomer concentrations were used for two of the syntheses: [Sty] = 1.66 M and [MMA] = 0.83 M. The monomer concentrations were changed for the third synthesis to [Sty] = 1.37 M and [MMA] = 1.12 M to be sure that the same polymer was produced. The alternating structure was confirmed by NMR for all three syntheses. The ^1H 2D experiments were performed with the polymer synthesized with [Sty] = 1.37 M.

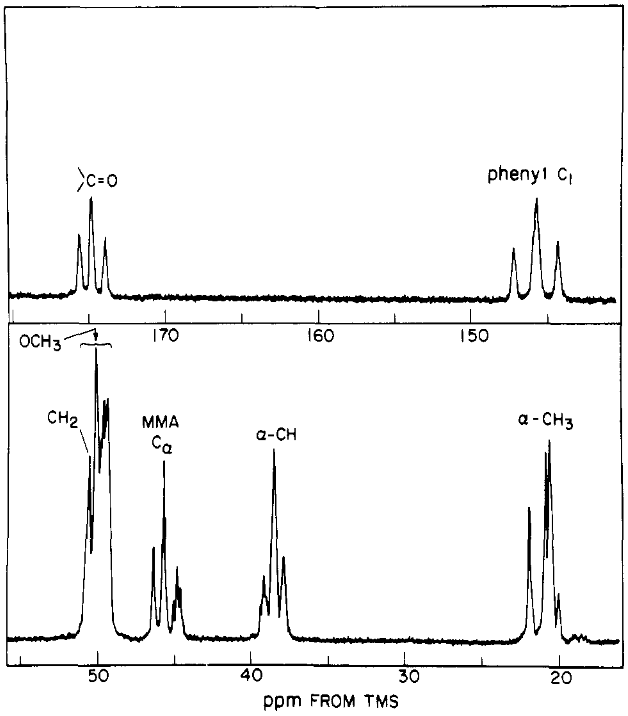


Figure 2. 125 MHz carbon-13 spectrum of the alternating styrene–methyl methacrylate copolymer, observed in 20% (w/v) hexachlorobutadiene solution at 80 °C. The aromatic resonances between 120 and 140 ppm are not shown.

Polymer from all three syntheses were combined for the carbon spectrum.

The 50:50 random copolymer was synthesized at 100 °C as described by Bovey.[1]

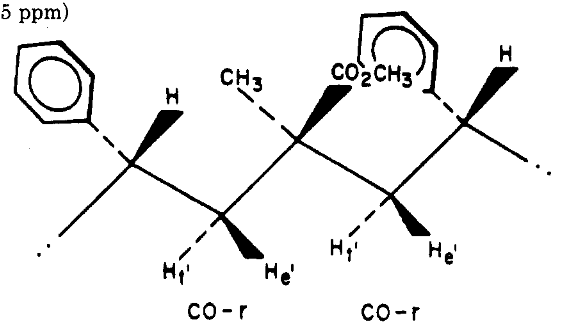
Results and Discussion

In Figure 1 are shown the 500 MHz proton spectra of random (a) and alternating (b) 50:50 styrene–methyl methacrylate copolymers. The simplification arising from restricting the number of compositional sequences is evident in (b); the broader lines of (a) result from a large number of closely spaced, unresolved chemical shifts. Spectrum (b) is similar to those previously reported[10-13] at lower frequencies except that there are no resolved spacings arising from J-coupling; as we shall see, such spacings may be seen in the 2D J-resolved spectrum, together with additional chemical shift discrimination. Spectrum (b) gives no indication of any deviation from a strictly alternating comonomer sequence. Peak assignments shown agree in general with previous reports and are discussed below.

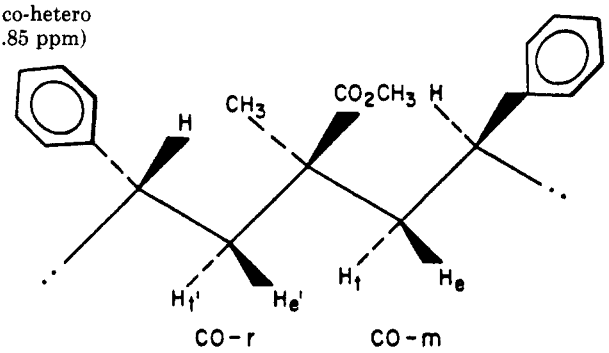
The stereochemical configuration of the alternating copolymer appears to be atactic with equal probabilities of m and r placements. This has already been reported by Katritzky[14,15] for the random copolymers by carbon-13 NMR and is indicated most directly for the alternating copolymer by the 125 MHz carbon-13 spectrum shown in Figure 2. The carbonyl (ca. 175 ppm), phenyl C_1 (ca. 145 ppm), quaternary carbon (ca. 46 ppm) and styrene α-CH resonances (ca. 38 ppm) are all 1:2:1 triplets (the last two giving indications of some pentad splitting), as one would expect for a "co-isotactic" propagation probability of 0.5. The diethylaluminum sesquichloride catalyst thus exercises rigid control over the comonomer reactivity ratios, both being zero within experimental error, but no control over stereochemistry.

In Figure 3 is shown the 500 MHz proton NOESY spectrum of the alternating copolymer, observed under the same conditions as Figure 1b. The spectrum is presented in the absolute value mode. Assignments indicated correspond to those shown for the 1D spectrum and are consistent with the cross-peaks observed between the aliphatic (upfield) and aromatic (ca. 7 ppm) portions of the spectrum. In the methoxyl proton region (ca. 2.0–3.2 ppm) the three principal resonances are assigned to co-syndio, co-hetero, and co-iso triad configurational sequences, (as earlier defined[1]) in order of increasing shielding. (A discussion of the nomenclature of the methylene protons is given later.)

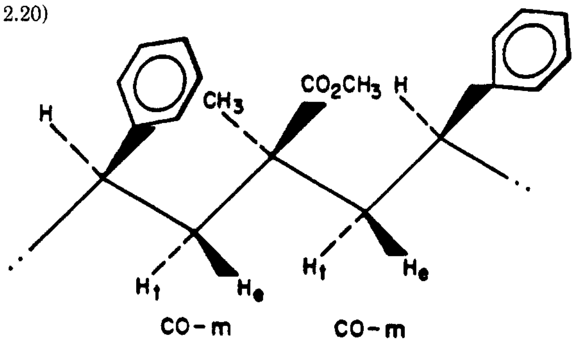
(a) co-syndio
(3.25 ppm)



(b) co-hetero
(2.85 ppm)



(c) co-iso
(ca. 2.20)



The ^{13}C and ^{1}H spectra show that these sequences occur in 1:2:1 order of probability. They are represented in a trans–trans conformation because this is believed from rotational isomeric state calculations (see next section) to predominate. The close proximity of the methoxyl protons to the faces of the phenyl groups (i.e., in their shielding zones) in co-meso diads and co-iso triads is indicated by the relatively strong cross-peak between the co-iso methoxyl peak (actually a triplet owing to pentad sensitivity) and the most shielded portion of the aromatic resonance region. The interpretation of the aromatic spectrum is not known in detail. There is a small narrow peak at 7.19 ppm arising from the C_6D_5H lock and a "star" resonance at 7.09 ppm from a small amount of residual toluene in the polymer (see Experimental Section). Because the phenyl rings are separated by methyl methacrylate units in the alternating copolymer, their ortho protons do not experience sufficient ring-current shielding to form a separate upfield peak as in polystyrene;[47] it is probable that both ortho and meta protons appear in the most shielded portion of the aromatic resonance at 6.80 ppm. Only this resonance shows cross-peaks to the methoxyl resonances. The co-iso interaction is the strongest, as expected. (Part of these cross-peaks' intensity arises from the styrene α-proton, which lies under the co-iso methoxyl resonance (see Figure 1b) and is of course in close proximity to the ortho protons.) The co-hetero methoxyl resonance shows a weaker but observable cross-peak, while the co-syndio resonance exhibits no interaction.

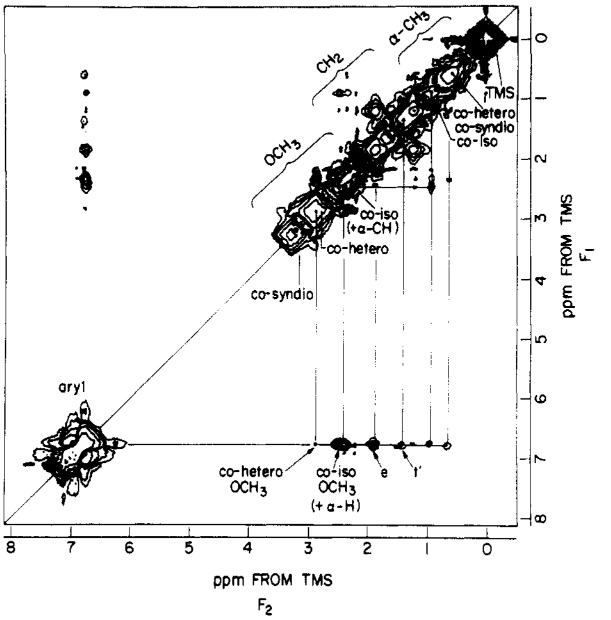


Figure 3. 500 MHz proton absolute value NOESY spectrum of the alternating copolymer at 80 °C. The mixing time was 300 ms.

The α-methyl resonances show similar shielding effects but in reverse order of chemical shift, as is to be expected, since the conformation favorable for methoxyl–phenyl interaction is unfavorable for methyl–phenyl interaction and vice versa. The shielding differentiation is about half that for the methoxyls (as previously reported by many investigators), probably because the α-methyl protons cannot extend into the maximum shielding zone of the rings. Nevertheless, cross-peaks to the aromatic region can be seen, although the co-syndio cross-peak, which ought to be the strongest, cannot be discriminated. (It should be realized that NOEs and ring-current shieldings need not necessarily show a one-to-one correspondence, owing to the special geometric requirements of the latter; a proton may be very close to the ring but on the periphery of the shielding cone or actually in the deshielding region. Conversely, because the shielding effect falls off as r^{-3} and the dipole–dipole interaction as r^{-6}, substantial shielding may still occur when the NOESY cross-peaks are too weak to observe.)

It is observed that the co-iso α-methyl resonance exhibits NOE cross-peaks to the region of the co-iso methoxyl resonance and styrene α-CH resonance, no doubt owing to interaction with the latter.

The methylene proton NOESY spectrum is shown expanded and in the phase-sensitive mode in Figure 4. This spectrum provides significant information concerning the through-space interactions—i.e., average internuclear distances—of these protons both within geminal pairs and between neighboring methylene groups. For the latter, only co-heterotactic triads (b) provide observable interactions since in the co-iso and co-syndio triads the H_e (or $H_{e'}$) and H_t (or $H_{t'}$) protons of neighboring diads have the

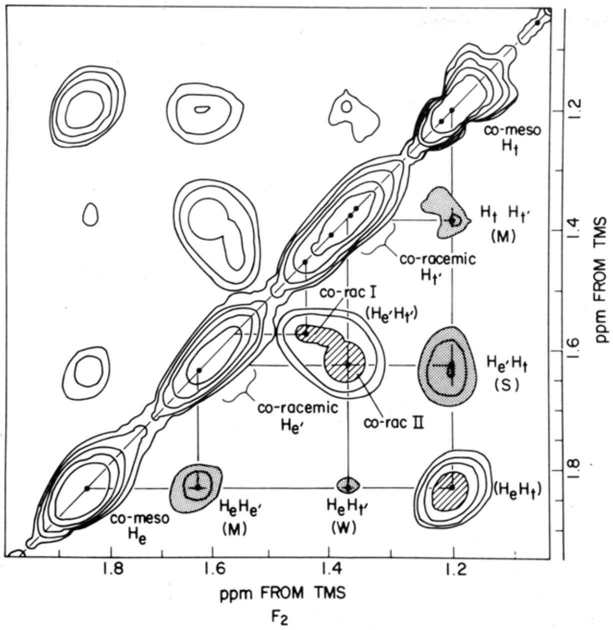


Figure 4. Expansion of the phase-sensitive proton NOESY spectrum at 500 MHz and 80 °C showing only the methylene region. Geminal interactions are indicated by hatched cross-peaks and intermethylene interactions by speckled cross-peaks. The designations S, M, and W refer to the strengths of the intermethylene proton interactions.

same chemical shift and one cannot tell intermethylene from intramethylene cross-peaks.

The methylene protons in co-meso diads are designated e and t (as shown in (c)) by an extension of the labeling of meso diads in poly(methyl methacrylate);[16] the e (erythro) proton is on the same side of the zigzag plane as the ester and phenyl groups in the trans–trans conformation, the other being designated t (for threo). As in poly(methyl methacrylate), the downfield resonance (at 1.82 ppm) is assigned to H_e and the upfield resonance (at 1.20 ppm) to H_t. The geminal association of this proton pair is demonstrated by their strong cross-peaks (designated H_e–H_t in Figure 4). Their assignments are supported by the occurrence of relatively strong cross-peaks between H_e and the phenyl protons (probably mainly ortho), with only very weak cross-peaks for H_t. These are the expected interactions for the strongly predominant (ca. 73%) trans conformation of the co-meso diad (next section). These assignments are also consistent with the magnitudes of the vicinal couplings to the styrene α-CH protons (vide infra).

The broader resonances centered at ca. 1.6 and 1.4 ppm are assigned to methylene protons of co-racemic diads (a). The scheme of proton designations is arbitrarily carried over from that of the co-meso diad with the addition of primes ((a) and (b)). The *upfield* proton now shows a cross-peak to the aromatic resonance (Figure 3) and is assigned therefore to $H_{t'}$; the $H_{e'}$ proton shows no aromatic interaction. Again, the strong cross-peaks designated $H_{e'}$–$H_{t'}$ demonstrate the geminal relationship of these protons.

Intermethylene interactions are also clearly indicated by the additional cross-peaks in Figure 4. Before examining these, it is instructive to consider the 500 MHz *J*-resolved methylene proton spectrum in Figure 5. Here, the chemical shifts in ppm of the methylene protons appear along the horizontal axis and the *J*-coupling scale (in Hertz) along the vertical axis. We see much greater resolution of spectral fine structure than appears in the 1D spectra or even in Figures 3 and 4. The co-racemic $H_{e'}$ and $H_{t'}$ resonances are now split into two sets, which we may call co-racemic I and co-racemic II. The intermethylene cross-peaks in Figure 4 show that these form the geminal pairs indicated by brackets in Figure 5. (It should be mentioned that geminal but not intermethylene correlations are also seen in the COSY proton spectrum, not shown.) Such additional chemical shift fine structure must correspond to longer configurational sequences. The eight possible configurational tetrads in an alternating copolymer may be represented in general terms as follows (it may be noted that in a homopolymer there are six possible tetrads and in a random copolymer 72):

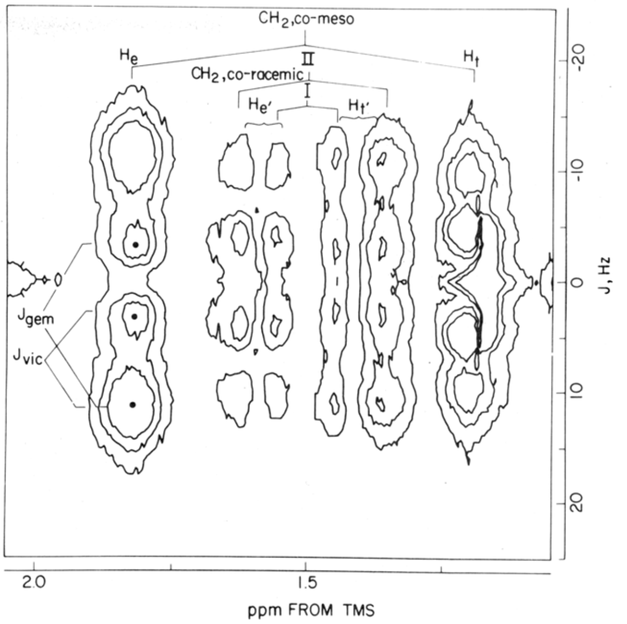
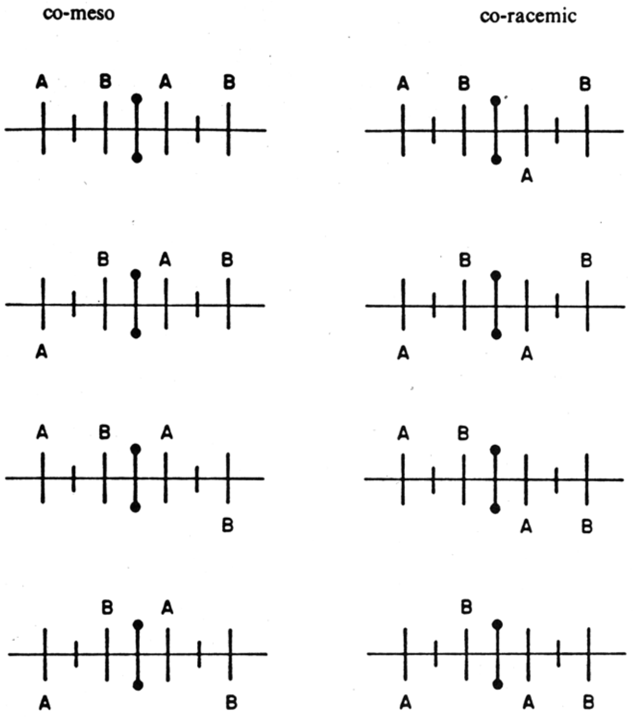


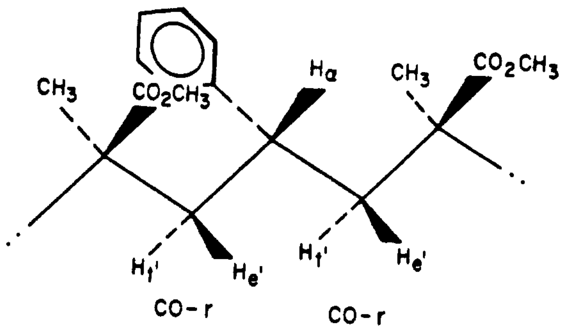
Figure 5. The *J*-resolved proton 2D spectrum at 500 MHz and 80 °C, showing the methylene proton region.



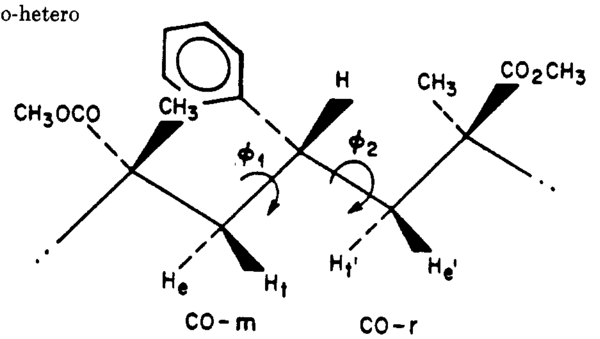
In the present configurationally random copolymer all these sequences occur with equal probability. We are resolving two groups of co-racemic tetrads but cannot at present determine which ones. The co-meso resonances are not further resolved but the broadness of their resonances is suggestive.

To describe the proton spin systems represented by this alternating copolymer, we consider the chain in terms of styrene-centered triads, analogous to the methyl methacrylate-centered triads shown previously

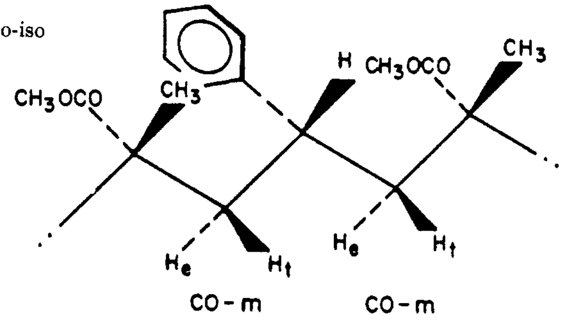
(d) co-syndio



(e) co-hetero



(f) co-iso



It will be seen that the chain may be regarded as composed of isolated five-spin systems, separated from each other by methyl methacrylate units. This is in contrast to vinyl homopolymers such as polypropylene or poly(vinyl chloride), which form essentially endless sequences of coupled spins and must be artificially treated as closed systems. In Figure 5, the smaller vertical spacing corresponds to J_{vic} and the larger spacing to J_{gem}, as indicated on the spectrum. Vertical profiles (not shown) through the center of each chemical shift position enable one to obtain the couplings shown in Table I (J_{gem} is assumed to be negative). As will be shown in the next section, the vicinal couplings in co-meso diads are in excellent accord with values expected on the basis of rotational isomeric state calculations of conformational preferences. The values for co-racemic diads, especially the apparent sensitivity to longer sequences, are less clearly understood at present.

Intermethylene NOE cross-peaks in Figure 4 appear to fall into three categories: one strong, two medium, and one weak. Accepting the chemical shift assignments discussed above, we may identify these as follows: $H_{e'}$–H_t, strong; H_e–$H_{e'}$, $H_{t'}$–H_t, medium; H_e–$H_{t'}$, weak. It will be shown in the next section that these interactions are in accord with expectation, based on the calculated average inverse sixth powers of the methylene interproton distances.

Table I
Proton *J*-Couplings (Hz) in Alternating 1:1 Styrene–Methyl Methacrylate Copolymers, Obtained From the Methylene Resonances

		J_{vic}	
sequence	J_{gem}	H_e(downfield)	H_t(upfield)
co-meso	−14.8	8.6	4.7
		J_{vic}	
sequence	J_{gem}	$H_{e'}$(downfield)	$H_{t'}$(upfield)
co-racemic I	−14.8	5.9	8.1
co-racemic II	−14.7	6.3	7.7

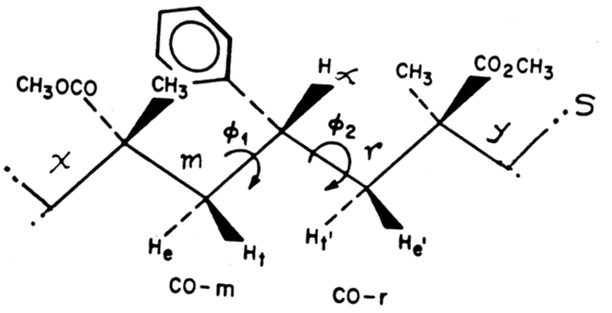
Conformational Characterization of the 1:1 Alternating Styrene–Methyl Methacrylate Copolymer. Koinuma et al.[13] have developed a conformational model for the 1:1 alternating copolymer by combining portions of the conformational descriptions derived for the styrene, methyl acrylate, and methyl methacrylate homopolymers by Yoon et al.[48,49] and Sundararajan and Flory.[50,51] We have employed their rotational isomeric states (RIS) model to calculate the conformational probabilities of the backbone bonds flanking the methine carbon of the central styrene unit in a co-hetero triad (see structure (e)). The conformations of these bonds directly influence both the three-bond vicinal couplings between methylene and methine protons and the distances between methylene protons (H_t, H_e, $H_{t'}$, and $H_{e'}$) separated by four bonds.

Longer range stereosequence effects were also included by considering all possible pentad sequences containing a co-hetero styrene-centered triad. Matrix-multiplication techniques[52] were used to obtain the bond conformation probabilities, which are listed in Table II. If we adopt the reasonable vicinal coupling constants of 11 and 2 Hz for the trans (*t*) and gauche (*g*) arrangements of methylene and methine protons,[53] then from the conformation probabilities in Table II we expect $^3J_{H_eH_\alpha}$ = 8.5–8.6 Hz; $^3J_{H_tH_\alpha}$ = 4.4–4.5 Hz; $^3J_{H_{e'}H_\alpha}$ = 3.6–3.8 Hz; $^3J_{H_{t'}H_\alpha}$ = 9.2–9.4 Hz. The vicinal couplings thus calculated for H_e and H_t are in excellent agreement with those observed (see Figure 5 and Table I), while those observed for $H_{e'}$ and $H_{t'}$ are less well reproduced. In particular, the apparent experimental dependence on co-syndio-centered sequences longer than triads is not predicted.

In Table III the calculated distances r_{HH} between methylene protons H_e, H_t and $H_{e'}$, $H_{t'}$ in the co-hetero styrene-centered triad (structure (e)) are presented for each of the three possible conformations of the main-chain bonds that separate them. The (t,t), (t,g^+), and (g^-,t) conformations are represented in Figure 6. When these r_{HH} values are raised to the −6 power and averaged over the conformations according to the calculated conformational probabilities presented in Table II, the entries in the next-to-lowest row of Table III are obtained. These values should be proportional to the strengths of the intermethylene proton–proton cross-peaks seen in Figue 4, and this is indeed observed.

The agreement between the predicted and observed pattern of NOESY cross-peaks for the co-hetero triad of the alternating copolymer confirms the validity of the Koinuma conformational model.[13] It is particularly noteworthy that this agreement requires the assumption of ca. 20° displacements from the perfectly staggered rotational states as predicted for the backbone bonds in polystyrene by Yoon et al.[48,54] If perfectly staggered $t(0°)g^{\pm}(\pm120°)$ states are assumed in calculating the in-

Table II
Bond Conformational Probabilities $P(\phi_1)$, $P(\phi_2)$[a] for



		$P(\phi_1)$		$P(\phi_2)$		$P(\phi_1\phi_2)$		
x	y	t	g^-	t	g^+	tt	tg^+	g^-t
m	m, r	0.73	0.27	0.80	0.20	0.53	0.20	0.27
r	m, r	0.72	0.28	0.82	0.18	0.54	0.18	0.28

[a] Only a single gauche (g) rotational state is allowed about each backbone bond ($\phi_1 = g^-$ and $\phi_2 = g^+$) because of severe steric contstraints in the alternative gauche state.

Table III
Intermethylene H–H Distances (r_{HH}) Calculated for the Co-Hetero Styrene-Centered Triad (Structure (e))

	r_{HH}, Å			
ϕ_1, ϕ_2	H_e–$H_{t'}$	H_e–$H_{e'}$	H_t–$H_{t'}$	$H_{e'}$–H_t
t,t (−20°, 20°)	2.89	3.10	3.10	2.20
t,g^+ (−20°, 100°)	3.74	2.63	3.68	2.59
g^-,t (−100°, 20°)	3.74	3.68	2.63	2.59
$\langle\phi_1, \phi_2\rangle$	0.0010[a]	0.0016[a]	0.0016[a]	0.0063[a]
	(0.0027)[b]	(0.0016)[b]	(0.0020)[b]	(0.0030)[b]

[a] r_{HH}^{-6} averaged over all three (ϕ_1, ϕ_2) conformations. [b] Same as a except ϕ_1, ϕ_2 = 0, ±120° in the $t,g^\pm$ states.

termethylene proton distances, one obtains the results in the bottom row (in parentheses) in Table III; i.e., all interactions are approximately the same. It is clear from Figure 4 that this is not the case.

Conclusions. The greater simplicity of the proton NMR spectrum of a 1:1 alternating copolymer of styrene and methyl methacrylate, as compared to that of a 1:1 random copolymer, enables one to draw significant conclusions concerning the conformational preferences of this polymer in solution. The unusual dependence of the methoxyl proton shielding on stereochemical configuration, long believed to arise from proximity to the phenyl groups of styrene units, can be directly shown by the 500 MHz NOESY spectrum to be due to this cause. The less marked dependence of α-CH_3 protons arises similarly. When the NOESY proton spectrum of the main-chain methylene protons is displayed in the phase-sensitive mode, one clearly observes the geminal association of protons in the co-isotactic and co-syndiotactic diads, appearing as strong cross-peaks. In co-hetero triads, cross-peaks clearly show intermethylene proton dipole–dipole interactions between neighboring CH_2 groups as well. These interactions fall into three categories, as judged from the magnitudes of the cross-peaks: one weak interaction, one strong interaction, and two intermediate-sized interactions. We have shown that this is to be expected from the rotational isomeric state model of Koinuma et al.,[13] if the approximately 20° deviations from exact staggering of the backbone conformational states in polystyrene, as assumed by Yoon et al.,[48] are taken to apply to the copolymer as well. If, on the other hand, exact staggering is assumed, all intermethylene proton interactions are predicted to be about equal, contradicting experiment. Since the through-space dipole–diple proton interactions depend on the inverse sixth power of the internuclear distances r_{HH}, this furnishes a direct and very sensitive spectroscopic test of conformational proposals.

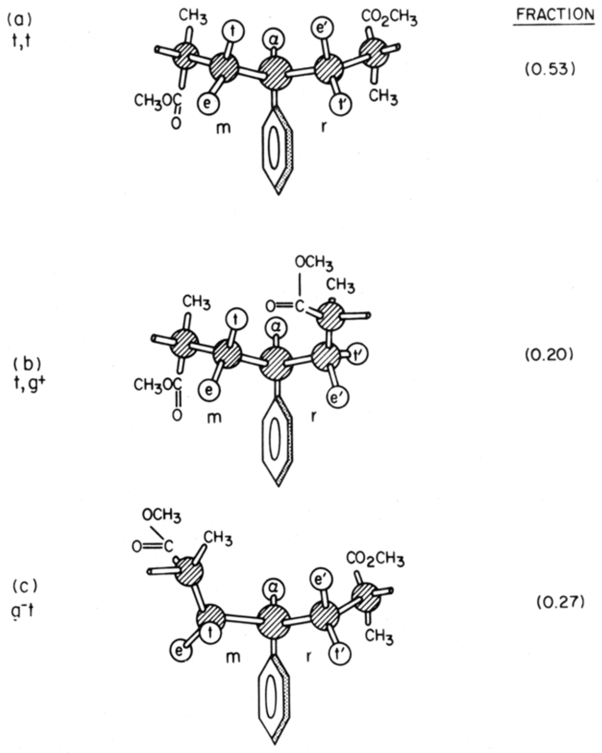


Figure 6. Ball-and-stick models of the styrene-centered MMA-Sty-MMA co-hetero triad, showing the tt, tg^+, and g^-t conformations, with 20° deviations from exact staggering.

Although the 1D 500 MHz proton spectrum of the 1:1 copolymer shows no indication of spacings arising from geminal and vicinal J-couplings, these may be readily measured in the J-resolved spectrum. The values of the vicinal couplings thus obtained agree very well with the predictions of the Koinuma model for co-meso sequences but not quite so well for co-syndio sequences.

Registry No. (Styrene)·(methyl methacrylate) (copolymer), 25034-86-0.

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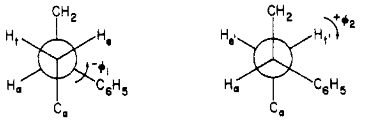
(54) As an example, in the *t,t* conformation (Figure 6a) ϕ_1, ϕ_2 = –20°, 20° because this causes relief from the steric interactions of the phenyl ring and the methyl methacrylate C_α, as can be seen in the Newman projections



Correlation between ^{13}C NMR Chemical Shifts and Conformation of Polymers. 5. Solution and Solid-State Spectra of Poly[(*S*)-3,7-dimethyl-1-octene]

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ABSTRACT: Isotactic poly[(*S*)-3,7-dimethyl-1-octene] (poly[(*S*)-3,7DM1O]) is examined by ^{13}C NMR in solution and in the solid state. The correlation between ^{13}C NMR chemical shifts and conformation of the polymer is studied by calculations based on an empirical scheme that takes into account conformational effects. Comparison between the solid-state spectra of poly[(*S*)-3,7DM1O] and poly[(*S*)-3-methyl-1-pentene] has made it possible to assign a fourfold chain helical conformation to the main chain of poly[(*S*)-3,7DM1O]. The analysis of the observed and computed ^{13}C chemical shifts of the side chain of poly[(*S*)-3,7DM1O] and its model compound 2,6-dimethylheptane has shown that the side chain of poly[(*S*)-3,7DM1O] has a considerable conformational freedom also in the solid state.

High-resolution ^{13}C NMR spectra of solid-state polymers obtained with the magic-angle spinning technique can provide information on the conformation of crystalline or amorphous polymers and on the conformational dependence of the chemical shifts, although the situation may be complicated by crystal packing effects.[1-4] Recently, on the basis of observed solid-state ^{13}C NMR chemical shifts and of conformational considerations we were able to

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