1H-NMR Study of Structure and Tacticity in *p-t*-Butylstyrene/Methyl Methacrylate Copolymers

J. J. UEBEL* and F. J. DINAN, *Research Laboratories, Eastman Kodak Company, Rochester, New York 14650 and Department of Chemistry, Canisius College, Buffalo, New York 14208*

Synopsis

Copolymers prepared by the bulk copolymerization of *p-t*-butylstyrene (S) and methyl methacrylate (M) were analyzed by 1H-NMR. The spectra showed fine structure in the δ 2.2–3.6 region similar to that reported for styrene/methyl methacrylate copolymers. Reactivity ratios for S-M copolymers determined by classical composition measurements differed markedly from the same ratios determined by NMR when it was assumed that NMR peak-triad assignments could be made by analogy with published styrene/methyl methacrylate assignments. A new set of peak-triad assignments was proposed that reconciles this difficulty and gives good agreement between triad fractions measured by NMR and those calculated from theory.

INTRODUCTION

1H-NMR spectroscopy has been used extensively to study the structure of vinyl copolymers.[1] Generally, this technique gives useful information regarding the sequencing, tacticity, and composition of these materials. Styrene/methyl methacrylate copolymers have been the subject of a number of studies.[2–7] Recently, the 1H-NMR spectra of styrene/methyl methacrylate copolymers were studied at 100 MHz.[7] These NMR spectra had six peaks in the δ 2.0–3.6 region due to methoxy protons. The chemical shifts of these peaks were explained in terms of shielding by neighboring phenyl rings, and the peak areas were reported to be consistent with statistical calculations based on triad sequence probabilities.

In this study we examined the copolymerization of methyl methacrylate (M) and *p-t*-butylstyrene (S). We found the 1H-NMR spectra of these copolymers to be strikingly similar to those reported for the corresponding methyl methacrylate/styrene copolymers, but our interpretation of the spectral data differs significantly from that reported[7] for methyl methacrylate/styrene copolymers.

EXPERIMENTAL

Reagent-grade methyl methacrylate and Dow Chemical *p-t*-butylstyrene (95% para, 5% meta) were distilled before use. Copolymerizations were conducted in bulk, and the solutions were purged with nitrogen before the reaction was initiated. The reactions were run at 60°C on a 10-g scale and were initiated with

* To whom correspondence should be addressed (Kodak).

CCC 0360-6376/83/061773-11$02.10

50 mg of 2,2'-azobis(2-methylpropionitrile) dissolved in 0.5 mL of acetone. Monomer conversions were 4–6%. The copolymers were precipitated with methanol and then dissolved in warm dioxane. Reprecipitation with methanol and drying *in vacuo* at 80°C gave monomer-free copolymer. Copolymer composition was determined from percent carbon and directly determined percent oxygen data obtained on a Perkin–Elmer 240B elemental analyzer. The analyzer was calibrated with standard samples before and after the determination of each set of experimental samples to ensure maximum accuracy. Statistical analysis of standard samples established a 90% confidence limit of ±0.14% of content.

The ^{1}H-NMR spectra were determined on a JEOL model FX-270 spectrometer (270 MHz, sample temperature 100°C) or on the Carnegie–Mellon spectrometer (600.6 MHz, room temperature). Samples were prepared as ca. 5% solutions in $CDCl_2CDCl_2$ with tetramethylsilane as an internal standard.

Areas were measured with a Hewlett-Packard 85 computer in conjunction with an electrostatic graphics pad and a standard area measurement program. Appropriate subtractions based upon experimentally determined copolymer composition were made to correct for polymer backbone (methine) absorption in the δ 2.2 region.

The components of peak I were resolved and quantitatively estimated on a Du Pont model 310 curve resolver.

RESULTS AND DISCUSSION

The 270-MHz ^{1}H-NMR spectrum of the δ 2.0–3.6 region of a *p-t-*butylstyrene/methyl methacrylate (S-M) copolymer is shown in Figure 1; the six methoxy resonances of this copolymer composition are readily observed in this spectrum. Generally, spectra obtained from various S-M copolymers are similar to published spectra for the corresponding styrene/methyl methacrylate copolymers.[7]
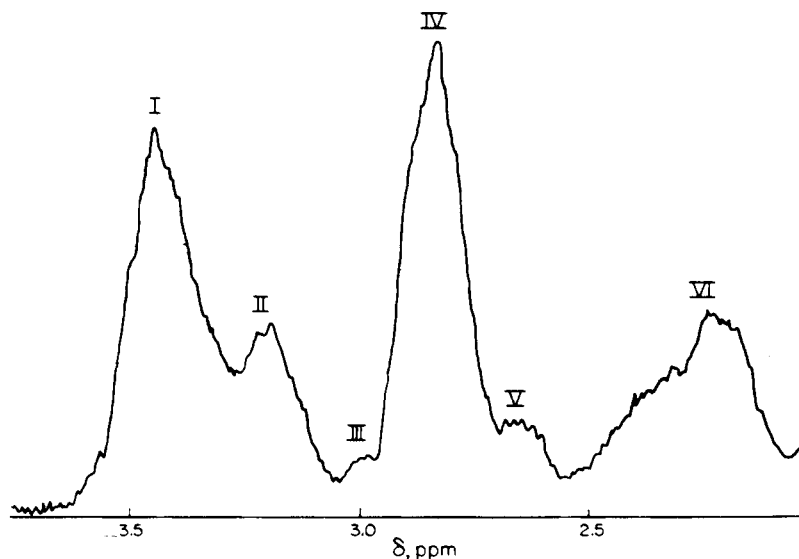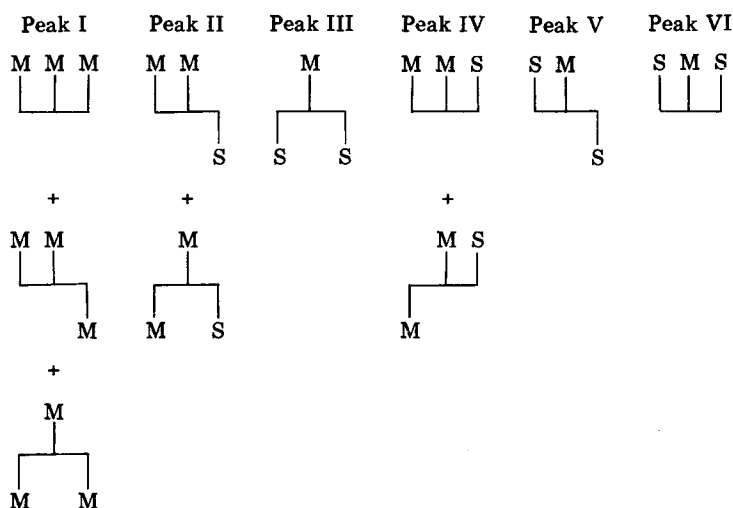

Fig. 1. 270-MHz ^{1}H-NMR spectrum of 0.5*M p-t*-butylstyrene, 0.5*M* methyl methacrylate in $CDCl_2CDCl_2$ at 100°C.

Peak I   Peak II   Peak III   Peak IV   Peak V   Peak VI

M M M   M M   M   M M S   S M   S M S

S   S   S   S

+   +   +

M M   M   M S

M   M   S   M

+

M

M   M

M methyl methacrylate, S p-t-butylstyrene.

Scheme 1. Assignments of Peaks I–VI to Methoxy-Centered Triads
By Analogy to Styrene/Methyl Methacrylate Assignments.[4,5,7]

Scheme 1 shows the methoxy-centered triad assignments which, by analogy
with styrene/methyl methacrylate copolymers, would be consistent with liter-
ature proposals.[4,5,7] The mole fractions of each of the components of the various
copolymer compositions were calculated from percent carbon and percent oxygen
data determined by elemental analysis. Composition measurements made in
this fashion, although more precise, generally agreed with those made by elec-
tronic integration of aromatic and aliphatic peak areas in the ^{1}H-NMR spectra.
Reactivity ratios derived from these data by the Kelen–Tüdös method[8] (Fig. 2)
are $r_M = 0.44$ and $r_S = 0.50$. These figures are similar to those reported for co-
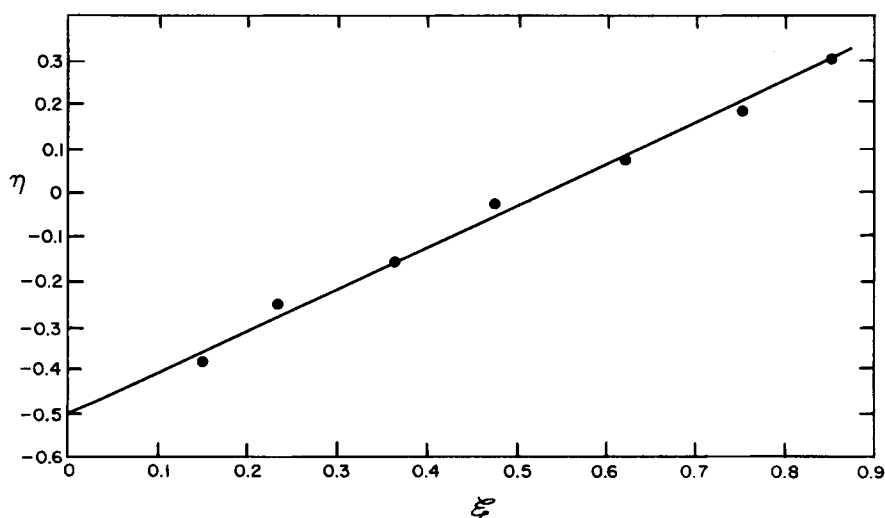polymerization of styrene ($r = 0.45$) and methyl methacrylate ($r = 0.47$).[7]

Fig. 2. Kelen–Tüdös plot for the determination of p-t-butylstyrene/methyl methacrylate reactivity
ratios; $r_M = 0.44$, $r_S = 0.50$ (see ref. 8 for an explanation of η and ξ).

On the basis of the terminal-copolymerization model,[8] the theoretical fractions of the three triad types, MMM, MMS, and SMS, in any given copolymer composition can be calculated from eqs. (1)–(5):

$$P_{11} = (1 + m_2/r_1 m_1)^{-1} \tag{1}$$

$$P_{11}^2 = f_{111} \tag{2}$$

$$P_{12} = (1 + r_1 m_1/m_2)^{-1} \tag{3}$$

$$P_{12}^2 = f_{212} \tag{4}$$

$$f_{112} = 2P_{12}(1 - P_{12}) \tag{5}$$

where P_{11} is the conditional probability of finding adjacent monomer-1 units and P_{12} is the conditional probability of finding a monomer-2 unit adjacent to a monomer-1 unit in the polymer chain; m_1 and m_2 are mole fractions of the two monomers in the feed; r_1 (r_M in this study) is the reactivity ratio that characterizes monomer 1; and f_{111}, f_{112}, and f_{212} are the fractions of the three triad types, MMM, MMS, and SMS, respectively.

As described elsewhere,[9] eqs. (1) and (2) can be combined and rearranged to give

$$\left(\frac{1}{f_{111}}\right)^{1/2} = 1 + \frac{1}{r_1}\frac{m_2}{m_1} \tag{6}$$

From this relationship, f_{111} can be plotted against the feed ratio, as shown in Figure 3, to give a line of slope r^{-1}.

If, by analogy with the styrene/methyl methacrylate system,[7] peak I is assumed to be due exclusively to the MMM (i.e., 111) triad, then a plot of the peak I area against the feed ratio should give a measure of r_M. However, the reactivity ratio obtained by this procedure (Fig. 3, $r_M = 1.2$) is significantly different from that obtained by copolymer composition measurements. This difference is too large
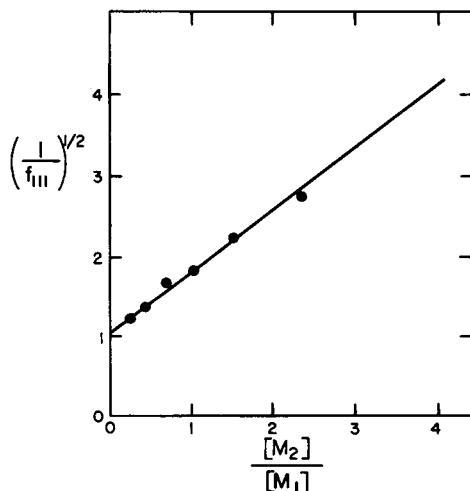

Fig. 3. Plot of normalized MMM (111) triad area f_{111} vs. monomer feed ratio according to eq. (6), assuming peak I corresponds to MMM triad; slope $r_M^{-1} = 1.2^{-1}$; intercept 1.0.

to be attributable to errors in area measurement or any other experimental parameters.

It has also been shown[9] that eqs. (3) and (4) can be combined and rearranged to give

$$\left(\frac{1}{f_{212}}\right)^{1/2} = 1 + r_1 \frac{m_1}{m_2} \tag{7}$$

This relationship allows r_M to be determined from the 212 (SMS) triad information obtained from the NMR spectra.

Application of eq. (7) to the SMS data obtained from the p-t-butylstyrene/methyl methacrylate ^{1}H-NMR spectra gave the plot shown in Figure 4. The intercept of this plot (1.3) deviates significantly from the ideal value of 1.0; however, the slope of the experimental line gives $r_M = 0.50$. This value is not identical with that obtained from copolymer composition measurements, but it is substantially closer than the value based on peak I area measurements.

Both theory and experience[9] suggest that the reactivity ratios determined by 111 plots [eq. (6)] and 212 plots [eq. (7)] should agree with each other and with the value determined by classical copolymer composition measurements. The disagreement suggested the possibility of incorrect triad assignments.

Recently, another method was published[10] for the determination of copolymer reactivity ratios from NMR spectral data, independent of that used earlier. This method, as it applies to the determination of r_1, is summarized in eqs. (8) and (9):

$$\overline{N}_1 = (f_{212} + \tfrac{1}{2}f_{112})^{-1} \tag{8}$$

$$\overline{N}_1 = 1 + r_1 M_1/M_2 \tag{9}$$

where $\overline{N}_1$ is the number-average sequence length for monomer 1 (M in this case), and f_{212} and f_{112} represent the normalized SMS and MMS triad fractions, respectively. Figure 5 illustrates the application of eq. (9) to ^{1}H-NMR spectral
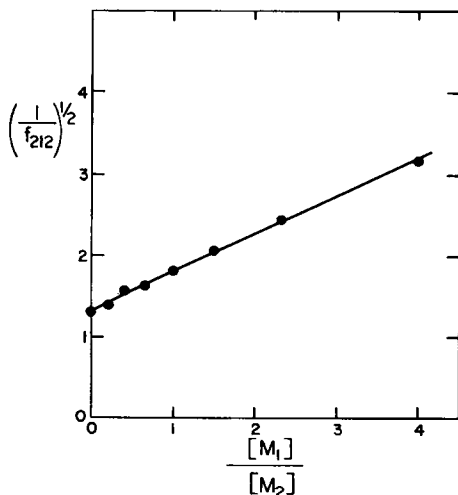

Fig. 4. Plot of normalized SMS (212) triad area f_{212} vs. monomer feed ratio according to eq. (7), assuming peaks III, V, and VI correspond to SMS triads; slope $r_M = 0.50$; intercept 1.3.
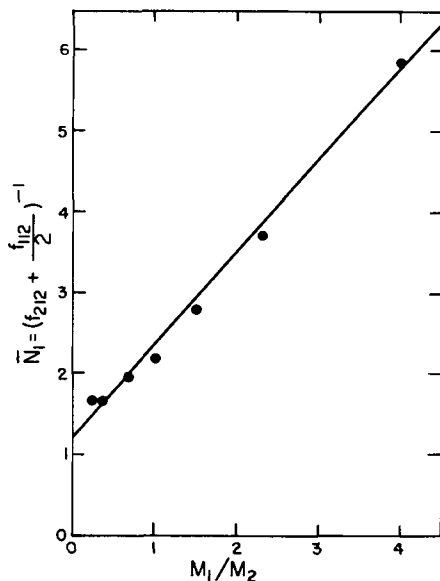
Fig. 5. Plot of the number-average sequence length $\overline{N}_1$ for monomer 1 (M) vs. monomer feed ratio, according to eq. (9), assuming peaks II and IV correspond to MMS (112) triads and peaks III, V, and VI correspond to SMS (212) triads; slope $r_M = 1.1$.

data obtained from the p-t-butylstyrene/methyl methacrylate copolymer. The fractions were determined from triad-to-peak assignments analogous to those reported for styrene/methyl methacrylate (Scheme 1).[7] The slope of this experimental line gives $r_M = 1.1$, a figure in accord with that obtained in the plot in which peak I is assumed to be due exclusively to MMM triads (Fig. 3) and differing markedly from the value obtained by copolymer analysis ($r_M = 0.44$) and the value ($r_M = 0.50$) based exclusively on SMS triad data (Fig. 4).

These disparities suggested that one or more of the triad-peak assignments made for the p-t-butylstyrene/methyl methacrylate spectra by analogy with styrene/methyl methacrylate might be incorrect. To check this possibility, 600-MHz ^{1}H-NMR spectra of several copolymer compositions were determined.

These spectra generally show the anticipated increased spectral dispersion obtainable at higher magnetic field strengths. Significantly, at this resolution peak I is split into two readily discerned but not fully resolved components (Fig. 6). The downfield component apparently is due to MMM triads, since its relative size increases at high methyl methacrylate feed ratios and decreases as the amount of p-t-butylstyrene in the feed is increased. Conversely, the upfield component is apparently due to an S-containing triad, since its area is relatively low at high M feed ratios and increases as the concentration of S in the copolymer feed is increased (Fig. 6). The concentration of this second component can be estimated quantitatively if the r_M value determined by the copolymer composition method is assumed to be correct.

To accomplish this, we measured the total copolymer methoxy area (peaks I–VI) and determined the fraction represented by peak I. If the normalized fraction of MMM triads [calculated from eqs. (1) and (2)] is substracted from
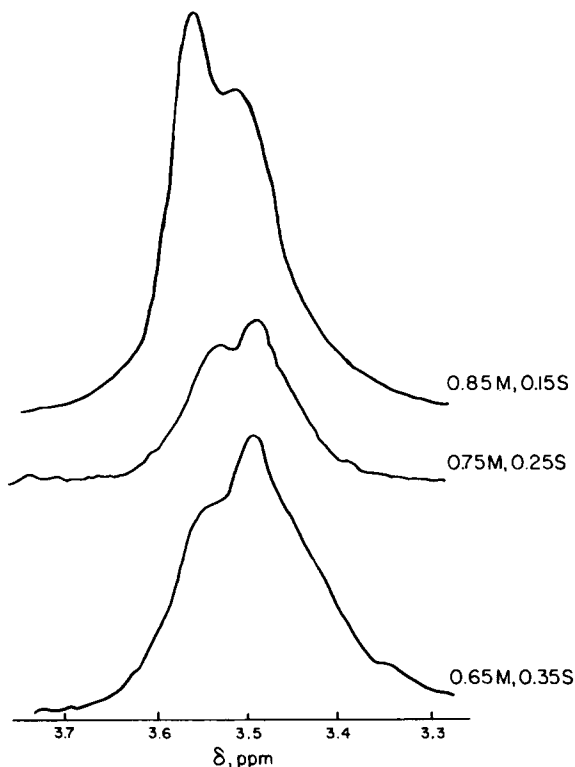
Fig. 6. ^{1}H-NMR spectra of p-t-butylstyrene/methyl methacrylate copolymers determined at 600 MHz.

the peak I fraction, the remainder, designated as Δ, is a quantitative measure of the second of the two components of peak I. This relationship is shown in eq. (10):

$$\Delta = f_I - f_{MMM} \tag{10}$$

where f_I is the normalized fraction of the total methoxy area due to peak I and f_{MMM} is the normalized fraction of MMM triads calculated from eqs. (1) and (2) with r_M assumed to be 0.44, the value obtained from copolymer composition data.

Assignment of the component Δ to a specific triad composition was facilitated by comparison of the theoretical triad distributions, calculated from eqs. (1)–(5), with the experimentally observed peak fractions. The theoretical and experimental triad distributions agreed well when Δ was assumed to be an MMS triad. Table I shows the values of Δ determined for various copolymer compositions and the resulting triad distributions if Δ is assumed to be due to an MMS triad.

The magnitude of the peak I component, Δ, was also estimated by curve resolution, assuming peak I to be composed of two Lorentzian peaks. The values determined for Δ by this technique were within 10% of those calculated from eq. (10).

Assignment of Δ as an MMS triad also requires consideration of its tacticity.

TABLE I
Determination of Δ and Experimental versus Theoretical Triad Distributions with Δ Assumed to be MMS

F_M[a]	f_I[b]	f_{MMM}[c]	Δ[d]	f_{MMS}		f_{SMS}	
				Experimental[e]	Theoretical[f]	Experimental[g]	Theoretical[h]
0.2	0.08	0.01	0.07	0.24	0.18	0.75	0.81
0.3	0.14	0.03	0.11	0.33	0.27	0.64	0.71
0.4	0.19	0.05	0.14	0.36	0.35	0.58	0.60
0.5	0.31	0.09	0.22	0.44	0.42	0.47	0.48
0.6	0.33	0.16	0.17	0.45	0.48	0.39	0.36
0.7	0.47	0.26	0.21	0.49	0.50	0.25	0.24
0.8	0.61	0.41	0.20	0.44	0.46	0.15	0.13

[a] Mole fraction methyl methacrylate in the feed.
[b] Experimentally measured peak I area fraction.
[c] Calculated from eqs. (1) and (2) ($r_M = 0.44$).
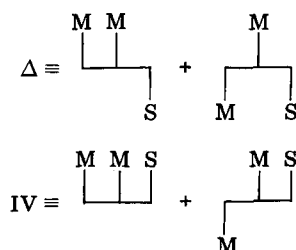[d] Calculated from eq. (10).
[e] Sum of peak IV + Δ.
[f] Calculated from eq. (5).
[g] Sum of peaks II, III, V, and VI.
[h] Calculated from eqs. (3) and (4).

Since Δ occurs at significantly lower field than the other MMS triad assigned to peak IV, it seems reasonable to assume, based on the anticipated aromatic ring shielding,[11] that Δ and IV have the following stereochemical relationship:

These two MMS components should then be related by the tacticity parameter σ, a measure of the probability that alternating M and S units will take the same configuration.[4] Thus the components Δ and IV are related by σ, and the ratio of these components is a measure of σ. Calculated σ values are summarized in Table II. The calculated average σ value, 0.61 ± 0.10, is reasonably constant

TABLE II
Sigma Values Derived from Ratio of Peaks IV and Δ

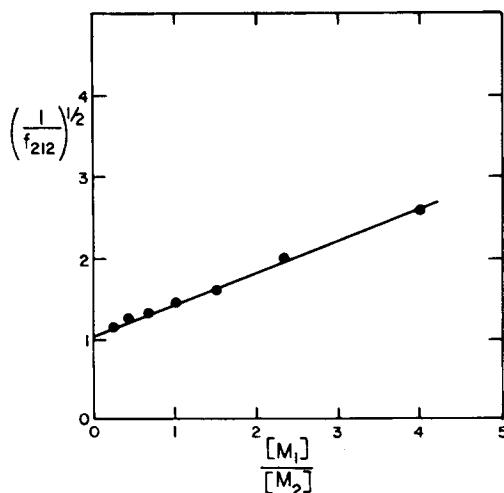| F_M	f_{IV}	Δ	$\sigma = f_{IV}/(f_{IV} + \Delta)$
0.2	0.17	0.07	0.71
0.3	0.23	0.11	0.68
0.4	0.23	0.14	0.62
0.5	0.23	0.22	0.51
0.6	0.28	0.17	0.62
0.7	0.28	0.21	0.57
0.8	0.24	0.20	0.54
		Average	0.61 ± 0.10

Fig. 7. Plot of normalized SMS (212) triad area f_{212} vs. monomer feed ratio according to eq. (7), assuming peaks II, III, V, and VI belong to SMS triads; slope $r_M = 0.45$.

over a wide range of feed ratios. Note that σ is most likely to be in error at low F_M values, where peak I has a small area and overlaps peak II, making Δ more uncertain. Nevertheless, the σ value thus derived is similar to those reported for styrene/methyl methacrylate and various *para*-substituted styrene/methyl methacrylate copolymers.[12,13]

The assignment of Δ as an MMS triad containing no coisotactic S—M bonds necessitates a reassignment of peak II, since this peak, in styrene/methyl
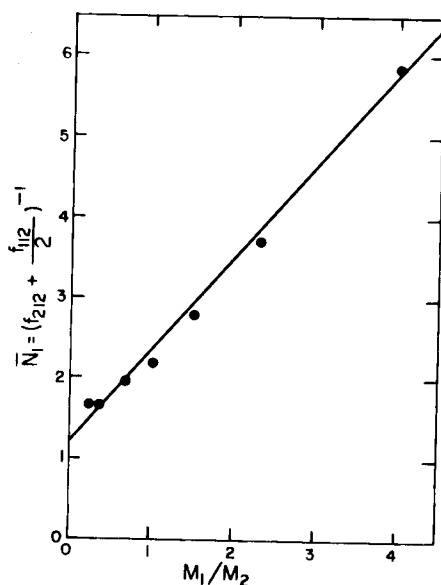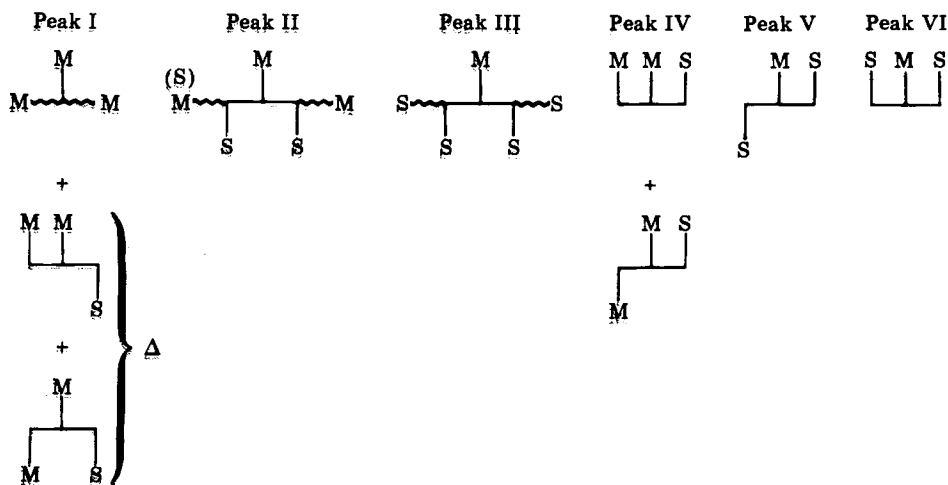

Fig. 8. Plot of number-average sequence length $\overline{N}$ vs. monomer feed ratio according to eq. (9), assuming peaks IV and Δ correspond to MMS (112) triads and peaks II, III, V, and VI correspond to SMS (212) triads; slope $r_M = 0.41$.

Peak I   Peak II   Peak III   Peak IV   Peak V   Peak VI

Scheme 2. Triads and/or Pentads Assigned to Peaks in the ¹H-NMR Spectrum of p-t-Butylstyrene/Methyl Methacrylate Copolymers.

methacrylate copolymers, had been assigned to the triad now attributed to Δ. Peaks II and III are assigned to pentads in which the central SMS triads have the same tacticity and the observed chemical shift difference is due to pentad influences. Scheme 2 summarizes the triads and/or pentads assigned to each of the peaks in the ¹H-NMR spectra of S–M copolymers.

A key point showing that the assignments in Scheme 2 are correct is that all of the previously discussed NMR-based graphical methods, when used in conjunction with the new peak assignments, give values of r_M that agree closely with the value determined by the classical copolymer composition method of Kelen–Tüdös. The pertinent revised plots are shown in Figures 7 and 8.

Although we have not explicitly discussed the application of these findings to the analogous styrene/methyl methacrylate copolymers, it is obvious that they should also be considered with regard to that system; we are now doing this.

References

1. F. A. Bovey, High Resolution NMR of Macromolecules, Academic, London, 1972.
2. F. A. Bovey, J. Polym. Sci., 62, 197 (1965).
3. H. J. Harwood and W. M. Ritchey, J. Polym. Sci. Part B, 3, 419 (1965).
4. K. Ito and Y. Yamashita, J. Polym. Sci. Part B, 3, 625 (1965).
5. K. Ito and Y. Yamashita, J. Polym. Sci. Part B, 6, 227 (1968).
6. H. Horai, T. Tanabe, and H. Koinuma, J. Polym. Sci. Polym. Chem. Ed., 18, 203 (1980).
7. J. San Román, E. L. Madruga, and M. A. Del Puerto, Angew. Makromol. Chem., 78, 129 (1979).
8. T. Kelen and F. Tüdös, J. Macromol. Sci., 9, 1 (1975).
9. J. J. Uebel and F. J. Dinan, J. Polym. Sci. Polym. Chem. Ed., 21, 917 (1983).
10. (a) A. Rudin, K. F. O'Driscoll, and M. S. Rumack, Polymer, 22, 740 (1981); (b) K. F. O'Driscoll, J. Polym. Sci. Polym. Chem. Ed., 18, 2747 (1980).

11. T. Tanabe, H. Koinuma, and H. Hirai, *Makromol. Chem.*, **182**, 3237 (1981).

12. K. Ito, S. Iwase, K. Umehara, and Y. Yamashita, *J. Macromol. Sci. Chem. Part A-1*, **5**, 891 (1967).

13. H. J. Harwood, A. K. Shah, R. E. Bockrath, and W. M. Ritchey, *Appl. Polym. Symp.*, **8**, 227 (1969).