

Compositional Analysis and Infrared Spectra of Styrene–Methyl Methacrylate Random Copolymers

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Synopsis

Compositional analysis of styrene–methyl methacrylate random copolymers by UV spectrophotometry at 260 nm, proton-NMR, and IR at 1730 cm^{-1} have been accomplished and agreement between these three independent methods was excellent. IR spectra of the copolymers in the region of 1100 and 1300 cm^{-1} are mainly characteristic absorption bands for the methyl methacrylate (MMA) component, but not the same for those of MMA homopolymer, that is, the IR spectra of the copolymers were not additive with those of polystyrene and PMMA. Information about the sequence distribution of copolymers of the same composition can be obtained by comparing the wavenumbers and absorption coefficients of the IR spectra in the region of $1100\text{--}1300\text{ cm}^{-1}$.

INTRODUCTION

Several analytical techniques have often been used for the determination of copolymer composition, e.g., infrared absorption spectrophotometry (IR), ultraviolet absorption spectrophotometry (UV), nuclear magnetic resonance spectrophotometry (NMR), and pyrolysis gas chromatography (PGC). When IR and UV are used for this purpose, it is normally assumed that the absorptivity (absorption coefficient) of the absorption band used for the analysis is the same in the copolymer as it is in the homopolymer. If this requirement is satisfied, a calibration curve for the copolymer analysis can be constructed using the corresponding homopolymer. A similar assumption is also required for the analysis by PGC. For example, in the case of styrene–acrylonitrile random copolymers, monomer ratios obtained by PGC were between the copolymers and physical mixtures of both homopolymers; copolymers of known composition were required to construct a calibration curve.¹ It is important, therefore, to recognize whether or not a calibration curve can be constructed using respective homopolymers.

Three techniques, proton-NMR, PGC, and carbon analysis, were compared for the compositional analyses of styrene–methyl methacrylate (MMA) and styrene–*n*-butyl methacrylate copolymers and good agreement between the three independent methods was obtained.² The ratio of IR-relative absorbance of the carbonyl band at about 1730 cm^{-1} to that of the styrene double-bond band at 1600 cm^{-1} for styrene–methyl acrylate copolymers changed linearly with the change of the copolymer composition which was obtained by proton-NMR.³

IR absorption bands of some groups in a given monomer are influenced by effects related to crystallinity and monomer sequence distribution.⁴ IR spectra in the range of 700–1000 cm^{-1} for ethylene-propylene copolymers were used to determine the monomer sequence distribution.⁵ The positions and shapes of the carbonyl bands in the IR spectra of styrene-methyl acrylate copolymers were dependent on the composition and the proportion of different methyl acrylate centered triads of the copolymers.³ Therefore, there are two types of IR absorption bands: sequence-distribution-dependent and independent. The latter can be used for the determination of copolymer composition.

In this study, the composition of styrene-MMA random copolymers P(S-MMA) has been determined using IR, UV, and proton-NMR and the correlation among these three independent data was investigated. In addition, IR spectra of P(S-MMA) have been measured and several IR absorption bands characteristic to the MMA component were found to be dependent on the composition of the copolymers.

EXPERIMENTAL

Samples. P(S-MMA) random copolymers were prepared by solution polymerization at a low degree of conversion. A mixture of the two monomers was combined with an equal volume of benzene and azobis-iso-butyronitrile (0.4 g/L) was added as an initiator. The solution was heated at 65°C under nitrogen atmosphere for 10 h. The polymerization solution was poured into a tenfold volume of methanol and the copolymer was recovered by precipitation. The copolymers were purified by reprecipitation from chloroform-methanol and dried at 55°C under reduced pressure. Yields of the copolymers were between 15 and 35%. These samples were designated as copolymers I-IX.

Besides these low-conversion copolymers, high-conversion copolymers of P(S-MMA) were also prepared by bulk polymerization.⁶ The high-conversion copolymers were fractionated into three fractions by liquid adsorption chromatography.⁶

Apparatus and Measurement. The IR absorption spectra were obtained using a Jasco Fourier-transform infrared spectrophotometer Model FT/IR-3. The IR spectra of the copolymers in the range of 400 and 3950 cm^{-1} were measured in the form of film which was cast on a KBr disk from a chloroform solution. The operating parameters were as follows: resolution, 2 cm^{-1} ; scanning number, 16; single-beam measurement; detector, TGS (triglycine sulfate). Other parameters were automatically set. The compositions of the copolymers were obtained by dissolving the copolymers in chloroform and by recording IR spectra in the regions of the carbonyl band around 1730 cm^{-1} and the C=C band around 1600 cm^{-1} . A solution cell was a NaCl window cell of 0.5-mm path length. Calibration curves were constructed with polystyrene (PS) and PMMA homopolymers.

A Jasco UV-VIS spectrophotometer Model UVIDEC-610C was used for the determination of copolymer composition by UV. The resolution of the UV instrument was set at 0.1 nm. Quartz cells of 1-cm path length were used. A calibration curve was constructed with PS homopolymer and the absorbance

at 260 nm was plotted as ordinate and PS concentration as abscissa. Chloroform was used as solvent for copolymers and PS homopolymer.

The proton-NMR spectra of the copolymers were recorded on a JEOL 60 MHz spectrometer, Model C-60H. Deuterated chloroform was used as a solvent with tetramethylsilane as an internal standard. Composition of copolymers was measured from the integrated area of the phenyl peak to the integrated total proton peak area as follows:

$$\text{Styrene (mol \%)} = \frac{8 (\text{phenyl peak area})}{5 (\text{total peak area})} \times 100$$

RESULTS AND DISCUSSION

The compositions of the copolymers I-IX obtained by three independent techniques are listed in Table I. Data from these three techniques are in good agreement except for the data obtained by the IR technique using an absorption band at 1600 cm^{-1} . The phenyl band at 1600 cm^{-1} was weak comparing with the carbonyl band at 1730 cm^{-1} and a solution of high concentration (5 wt %) was required to obtain high precision. The deviation of the data mainly arised from the instrument errors due to the low absorption coefficient. Relative standard deviation of this method was about 5%, although those of other methods were very small: UV, 0.1-0.6%; NMR, 0.3-1.5%; IR (at 1730 cm^{-1}), 0.5-0.8%.

The correlations among the data as obtained by UV, NMR, and IR (at 1730 cm^{-1}) methods were examined by plotting one vs. the other. When the X-axis was styrene content as obtained by NMR and the Y-axis was data by UV and IR (at 1730 cm^{-1}), then the respective regression lines were

$$Y = 0.999X - 0.59 \quad \text{and} \quad Y = 1.08X - 3.81$$

and the correlation coefficients were 0.999 and 0.998, respectively. Similarly, when the X-axis was styrene content as obtained by UV and the Y-axis was

TABLE I
Copolymer Composition as Obtained by Three Independent Analytical Techniques

Copolymer	Monomer feed, styrene (mol %)	Styrene (mol %)			
		UV	NMR	IR	
				1730 cm^{-1}	1600 cm^{-1}
I	90	85.5	84.2	87.0	76.8
II	80	73.4	74.7	76.4	71.2
III	70	65.7	66.3	67.4	63.4
IV	60	57.4	58.6	60.1	55.5
V	50	48.7	49.8	51.9	43.6
VI	40	42.1	43.5	42.6	35.6
VII	30	41.5	43.5	41.4	40.4
VIII	20	26.5	26.8	25.9	24.5
IX	10	15.2	14.3	11.2	6.6

data by IR (at 1730 cm^{-1}), then the regression line was

$$Y = 1.08X - 3.06$$

and the correlation coefficient was 0.998. These results show excellent agreement among the three methods. The difference between UV and NMR results was very small compared to the difference between the UV and IR (at 1730 cm^{-1}) results and between the NMR and IR results. It can be concluded that a UV absorption band at 260 nm for a styrene unit and an IR absorption band at 1730 cm^{-1} for an MMA unit are independent of the nature of neighboring monomer units in a copolymer chain.

As shown in Table I, there appears to be less styrene in the copolymers than theory predicts at the higher styrene levels and more at the lower content. This may be explained by an equation known as the copolymer composition equation. Plots of copolymer composition vs. the monomer feed can be obtained by knowing the monomer reactivity ratios of both MMA and styrene monomers, indicating more styrene in the copolymers at the lower styrene

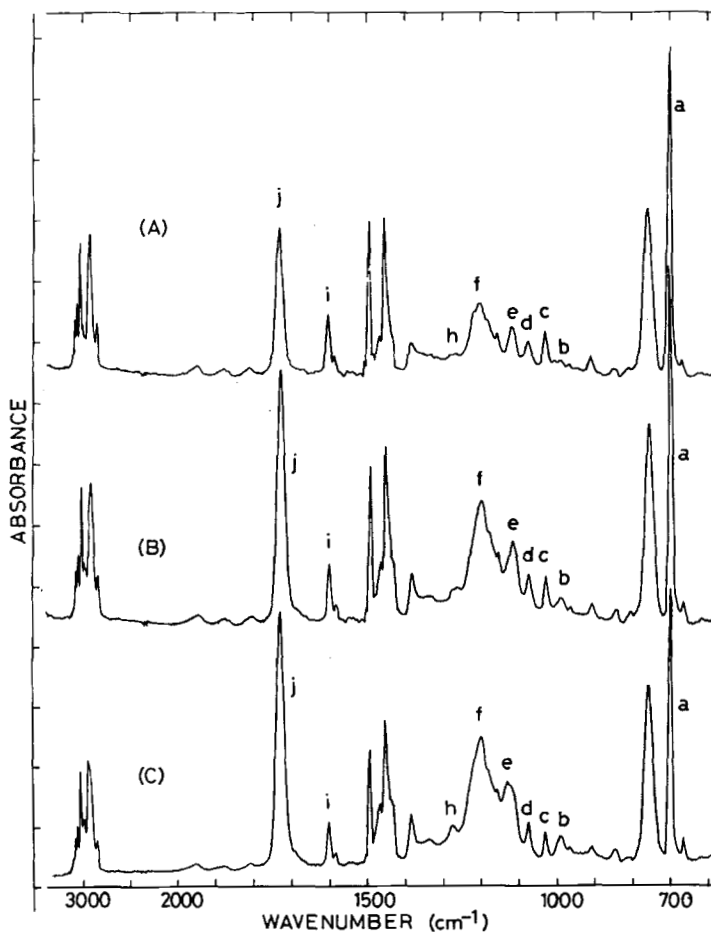


Fig. 1. Infrared spectra of P(S-MMA): (A) copolymer I, (B) copolymer II, and (C) copolymer III.

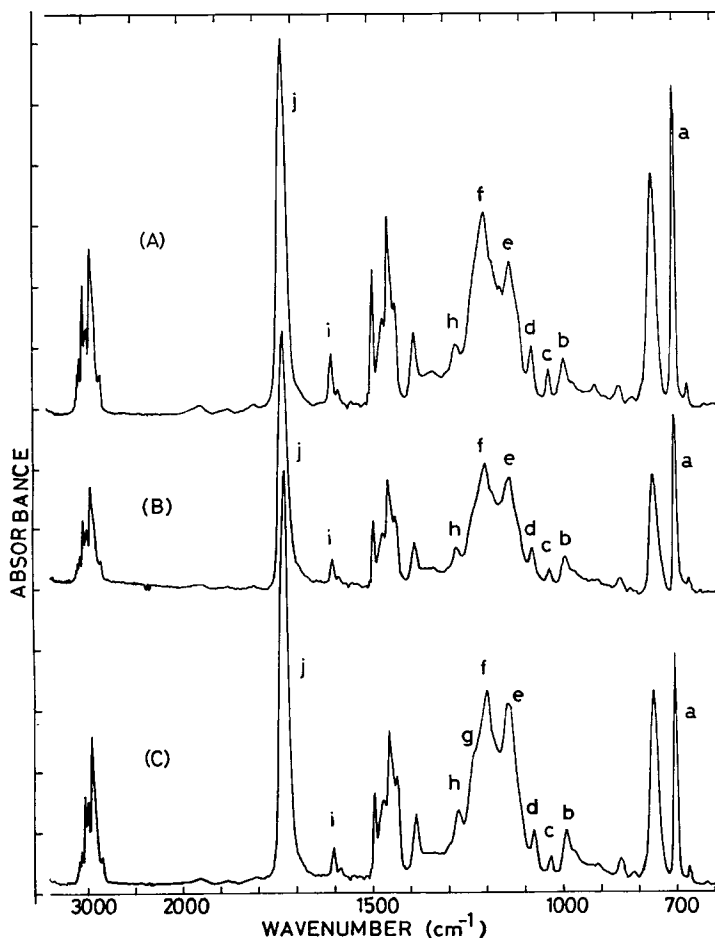


Fig. 2. Infrared spectra of P(S-MMA): (A) copolymer IV, (B) copolymer V, and (C) copolymer VI.

feed and less at the higher styrene feed. In the case of the copolymer of styrene and MMA, the experimental results conform to this equation.

Infrared spectra of P(S-MMA) random copolymers I-IX, PS and PMMA homopolymers are shown in Figures 1-4. Peaks a, c, and i are styrene characteristic bands and peaks b, d-h, and j are MMA characteristic bands, respectively. There are many very weak absorption bands arising from the styrene component in the region between 1100 and 1300 cm^{-1} , but very strong absorption bands assigned to the MMA characteristic bands are also observed in this region.

In comparison with the IR spectrum of PMMA, the trough between peaks f and g in the IR spectrum of copolymer IX became shallow. The trough became shallower with increasing styrene content in the copolymers and peak g became a shoulder of peak f in copolymer VI. In addition to this, absorbance of peak f increased. A shoulder peak g disappeared in copolymer IV.

Absorbances of peaks b and d in copolymer VI and those of peaks h and d in copolymer V were nearly equal. Wavenumber of peak e shifted to lower wavenumber with increasing styrene content in the copolymers. Peaks e

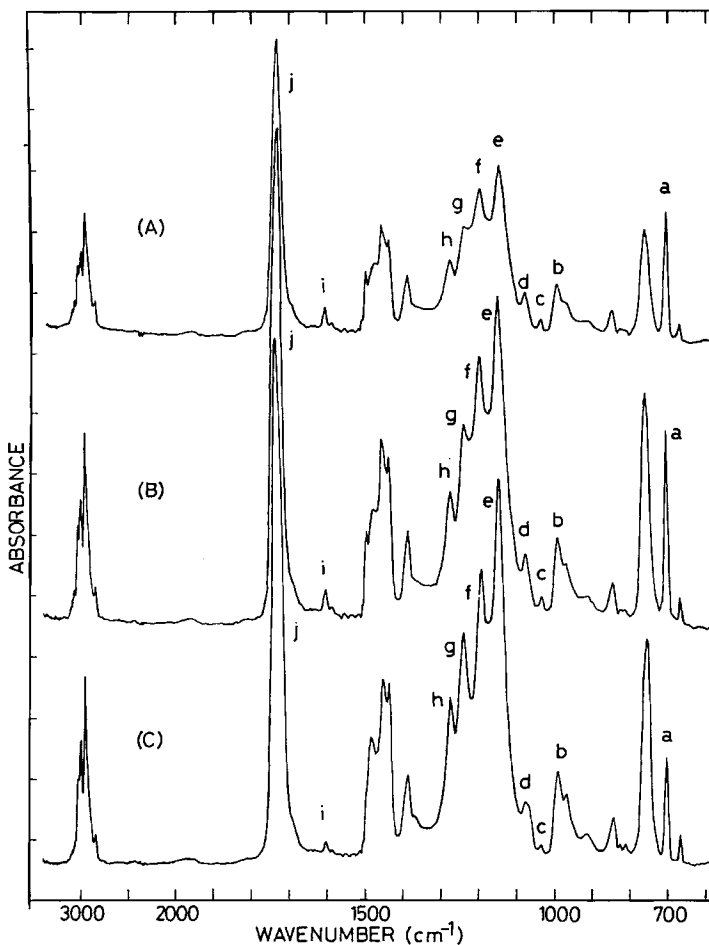


Fig. 3. Infrared spectra of P(S-MMA): (A) copolymer VII, (B) copolymer VIII, and (C) copolymer IX.

became smaller independently of peaks f-h with increasing styrene content in the copolymers and, moreover, peaks f-h were combined into one broad peak. Peaks d-h, which are assigned to the C—O absorption bands or others originated in MMA component of the copolymers, were not identical to those of PMMA itself. In other words, the spectra of the copolymers are not additive to those of the PS and PMMA homopolymers.

Relationship of wavenumber of several characteristic absorption bands, a, d-j, for styrene and MMA components with the copolymer composition is listed in Table II. Here, peak a is assigned to the C—H out of plane bending of a phenyl group for styrene component and peaks e-g to the C—O band for an ester group of MMA component. Absorption bands of a double bond of a phenyl group for styrene component and of a carbonyl group of an ester group for MMA component appeared at 1602 and 1730 cm^{-1} , respectively. Their peak positions were unchanged with copolymer composition. No correlation of the carbonyl band wavenumber with copolymer composition was observed. These results were in disagreement with that observed by Kandil and El-Gamal,³ who reported that the position and shape of the carbonyl

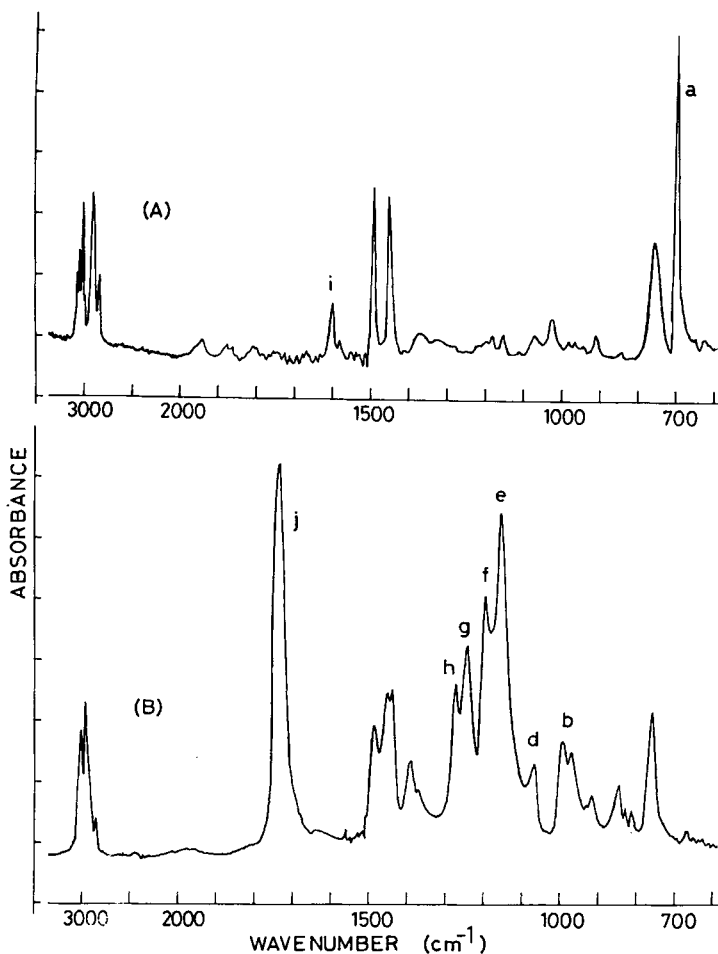


Fig. 4. Infrared spectra of (A) polystyrene and (B) PMMA.

band of styrene-methyl acrylate copolymers were dependent on the copolymer composition and on the triad sequence. However, the shift of peaks e and g to lower wavenumber with the copolymer composition was observed. As a result, peaks f and g were combined into one peak and the apparent shift of peak f to higher wavenumber was observed. Peak positions of other peaks in Table II were unchanged with the copolymer composition.

Similar results have been observed by Yanagisawa⁷ that bands at 1191 and 1148 cm^{-1} in PMMA shifted to higher and lower wavenumbers in the copolymers, respectively. He concluded that the magnitude of the shifts depends on the average sequence length of the MMA units in the copolymers. The broadening of the C—O bands in the region of 1100–1300 cm^{-1} was also observed by Haslam et al.⁸ When the amount of PS is in the range of 0–20%, the peak a moves to 702 cm^{-1} in the random copolymers from 698 cm^{-1} in PS homopolymer.

Table III shows relative absorbances of several characteristic absorption bands related to MMA component in the copolymers. Rough estimation of peak intensities of peaks b, d–h, and j in the IR spectrum of PMMA

TABLE II
Change of Wavenumber of Characteristic Band for Styrene and Methyl Methacrylate
Component with Copolymer Composition

Copolymer	Wavenumber (cm ⁻¹)							
	Peak a	Peak d	Peak e	Peak f	Peak g	Peak h	Peak i	Peak j
(PS)	698						1600	
I	699	1074	1117	1198		1273	1602	1730
II	700	1075	1119	1198		1276	1602	1730
III	700	1076	1131	1198		1273	1602	1730
IV	701	1075	1133	1198		1272	1602	1730
V	701	1076	1134	1197		1270	1602	1731
VI	701	1076	1141	1197		1270	1602	1730
VII	702	1076	1144	1196	1234	1273	1602	1730
VIII	702	1076	1145	1194	1236	1273	1602	1730
IX	703	1072	1148	1193	1240	1272	1603	1730
(PMMA)		1065	1149	1193	1242	1272		1730

homopolymer was as follows: b (m), d (w), e (s), f (s), g (s), h (m), and j (vs), where s means strong absorption, m medium, w weak, and vs very strong. If these absorption bands were independent of sequence distribution, that is, a MMA monomer unit is independent of the nature of neighboring monomer units in the copolymer chain, the relative absorbances in Table III must be the same regardless of the copolymer composition and be equal to the values of those of PMMA homopolymer. The carbonyl band at 1730 cm⁻¹ has been proved to be independent of copolymer composition and could be used for the determination of the copolymer composition. Therefore, the relative absorbances in Table III explain whether the absorption coefficients of these peaks change with the copolymer composition or not. The absorption coefficient of peak d decreased first when small amount of styrene units were attached to MMA units and then increased with increasing styrene content in the copolymer and those of peaks e and h decreased, a rate of decrease of both peaks being the same. Absorption coefficient of peak f was roughly constant over the entire copolymer composition. The overlap of absorption bands of styrene component to peak d might be considered.

TABLE III
Relative Absorbance of Characteristic Bands for MMA Component vs. Copolymer Composition

Copolymer	Relative absorbance						
	j/d	j/e	j/f	j/h	e/f	e/h	f/h
I	4.8	3.2	2.1	7.6	0.62	2.3	3.6
II	6.6	3.4	2.1	8.2	0.62	2.4	3.9
III	5.6	2.9	2.0	6.1	0.68	2.1	3.1
IV	6.5	2.6	1.9	6.1	0.73	2.3	3.4
V	5.6	2.2	2.1	6.1	0.91	2.7	3.0
VI	7.0	2.3	2.2	6.0	0.94	2.6	2.7
VII	7.6	1.7	2.1	4.0	1.16	2.3	2.0
VIII	8.1	1.5	1.9	4.0	1.22	2.6	2.1
IX	9.8	1.4	1.8	3.3	1.29	2.3	1.8
(PMMA)	7.1	1.2	1.6	2.6	1.35	2.2	1.6

TABLE IV
Relative Absorbance of Characteristic Bands for MMA Components
of High-Conversion Copolymers

Copolymer	Styrene composition (wt %)	Relative absorbance						
		j/d	j/e	j/f	j/h	e/f	e/h	f/h
H-3	32.8	7.1	1.7	1.9	4.0	1.13	2.4	2.1
Fraction 1	36.6	4.8	1.7	2.0	4.1	1.14	2.8	2.1
Fraction 2	31.7	7.7	1.8	2.0	4.1	1.13	2.3	2.0
Fraction 3	29.4	6.6	1.6	1.9	3.5	1.21	2.2	1.8
H-4	43.2	6.4	2.0	1.9	4.9	1.0	2.5	2.5
Fraction 1	46.6	5.4	2.0	1.9	4.6	0.9	2.3	2.5
Fraction 2	41.8	7.6	2.1	2.0	4.8	1.0	2.3	2.4
Fraction 3	39.6	7.6	2.0	2.0	4.8	1.0	2.4	2.4

As discussed above, the IR absorption spectra in the region of 1100 and 1300 cm^{-1} in P(S-MMA) random copolymers, which were assigned to be mainly MMA-originated absorption bands, were not additive to the IR spectra of both PS and PMMA homopolymers, and they changed in wavenumbers and absorption coefficients with composition. The copolymer samples used in this experiment were random copolymers prepared by solution polymerization under low conversion. Therefore, the sequence of styrene and MMA of these samples must be statistical. Consequently, the information about the sequence distribution of the copolymers of the same composition can be obtained by comparing the wavenumbers and absorption coefficients of the IR spectra in this region. Reproducibility of the values in Table III and the relationship between the sequence distribution and these values are now under investigation.

Table IV is the results of relative absorbances of fractions of high-conversion P(S-MMA) random copolymers. Peak d in fraction 1 was lower than that expected from its composition in sample H-3 and H-4, suggesting a greater possibility of coming from a styrene monomer unit in the neighbor of a MMA monomer unit than that expected for the statistic copolymer of the same composition.

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