

Spectroscopic Determination of Copolymer Composition in High Isocyanate Content Polymers*

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Synopsis

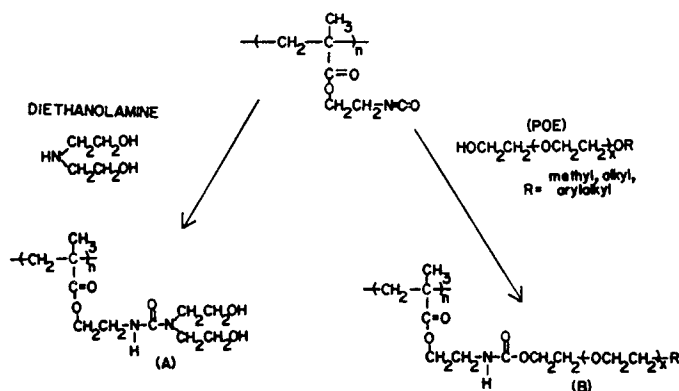
Copolymer compositions high in aliphatic isocyanate content cannot be determined by typical titration methods due to crosslinking during polymer workup. A quantitative method involving ultraviolet analysis of an isocyanate/absorbing amine adduct is presented. Agreement between the ultraviolet (UV) method and elemental analysis, in both composition data and reactivity ratios (r_1r_2 , which are calculated from data obtained by the UV method) delineate a viable method of polymer analysis. Data from Fourier transform infrared (FTIR) analysis of the urea linkage is in good agreement with nitrogen analysis and the UV method, but is sufficiently biased to cause significant differences in r_1r_2 values. Bias in the infrared analysis may arise from the intra- or intermolecular interaction of C=O and N—H groups of the urea linkage. Hypochromic effects are observed in UV analysis in noncarbonylic solvents. Hypochromicity varied with copolymer composition and could be related to sequence distributions. The hypochromic effects observed were most pronounced in low amine adduct content polymers where the majority of phenyl chromophores are isolated between MMA units.

INTRODUCTION

The determination of copolymer compositions has been accomplished by a variety of methods including nuclear magnetic resonance (NMR), infrared, and ultraviolet spectroscopy, elemental analysis, and in the case of copolymers containing reactive functional groups, by titration methods. All of these methods may be considered to be "system specific" in that they are not generally applicable to all copolymer systems. Discrepancies often exist among data obtained by different methods for the same copolymer.¹

Polymers containing pendant aliphatic isocyanate functionality may be synthesized by the free radical polymerization of isocyanatoethyl methacrylate (IEM). Copolymers of IEM have found application in various areas including industrial coatings.^{2,3} Typically, IEM copolymers used in coatings applications contain small amounts of the isocyanate-containing monomer. The determination of copolymer composition in low IEM content copolymers, is easily approximated by isocyanate titration methods,^{4,5} which involve precipitation and drying of the copolymer to remove residual —N=C=O containing monomer. Titration methods for the determination of isocyanate

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Scheme 1. (A) IEM-containing polymer reacted with diethanolamine to form a water-soluble polyol. (B) IEM-containing polymer reacted with a monohydroxy-functional poly(oxyethylene).

content are not suitable for high IEM content copolymers; the latter are prone to crosslinking during the precipitation and drying steps.

Hydrophobically modified water-soluble polymers of specific molecular architectures have found use in latex coatings as thickening agents.⁶ Water-soluble, nonionic, copolymers may be obtained by the reaction of pendant isocyanate groups in copolymers of IEM with reagents that impart hydrophilic properties to the polymer (Scheme 1); such copolymers serve as model compounds for nonionic "associative thickener" type waterborne coatings rheology modifiers. In the latter macromolecular models, ionic groups (i.e., carboxylate, sulfonate, quarternary amine, etc.) are undesirable. Although very hydrophilic, ionic groups impart water sensitivity to the coating.

To achieve water solubility through the introduction of hydrophilic groups [(i.e., hydroxyl, poly(oxyethylene))] via the pendant -N=C=O groups, high IEM content is required. In copolymers of IEM and methyl methacrylate (MMA) in which the -N=C=O groups have been reacted with diethanolamine, at least 50 mol% of IEM must be present to achieve water solubility (Table I).

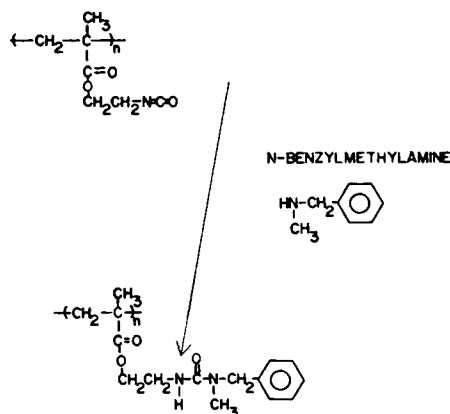
Many examples of the use of ultraviolet (UV)⁷⁻⁹ and infrared (IR)¹⁰⁻¹³ spectroscopy for the determination of copolymer composition exist. This paper describes an ultraviolet and infrared method for the determination of copolymer compositions with high IEM content. Pendant -N=C=O

TABLE I
Solubility Properties and Molecular Weight Data
IEM/MMA Copolymers Reacted with Diethanolamine

Polymer	A	B	C	D	E	F	G	H
Wt% IEM ^a	80	70	60	50	40	30	20	100
Wt% MMA ^a	20	30	40	50	60	70	80	—
H ₂ O Sol.	S	S	S	I	I	I	I	S
M _w ($\times 10^{-5}$) ^b	1.18	1.00	1.13	1.03	2.65	1.98	1.13	0.99
M _n ($\times 10^{-5}$) ^b	0.56	0.40	0.44	0.41	0.45	0.56	0.56	0.43

^aWeight percents for initial monomer charge. Polymerizations were run to > 80% conversion.

^bMolecular weight data obtained by SEC. IEM/MMA copolymers were reacted with MeOH to provide THF-soluble products for chromatography.



Scheme 2. Synthesis of UV-absorbing polymer for analysis.

groups in the copolymer are reacted with *N*-benzylmethylamine prior to analysis, thereby alleviating the possibility of crosslinking during work up. The resulting product (Scheme 2), is suitable for analysis in the UV spectral region (λ_{\max} 259.2 nm), and has two IR bands (λ_{\max} 1641 cm^{-1} , Amide I and λ_{\max} 1529 cm^{-1} , Amide II) not obscured by absorbance bands of the comonomer, MMA. Amide I is a C=O stretching band and Amide II arises from N—H bending.

EXPERIMENTAL

Materials

IEM was provided by Dow Chemical and was used as received. MMA (Aldrich) was washed with dilute aqueous NaOH, followed by repeated washing with distilled water. The monomer was predried over CaCl_2 and distilled under vacuum from CaH_2 . 2,2'-Azobis(2-methylpropionitrile) (AIBN, Alfa) was recrystallized from absolute ethanol and vacuum dried. Tetrahydrofuran (QO Chemical) was distilled from CaH_2 . *N*-Benzylmethylamine (Aldrich) was distilled under vacuum; only the middle fraction was retained. The amine as well as the purified MMA monomer were stored under argon at 0°C. 2,6-Di-*tert*-butyl-4-methylphenol (Aldrich), a hindered inhibitor used in IEM/amine monomer synthesis, was used as received. Other reagents and solvents [petroleum ether (Baker), chloroform (Aldrich), *N,N*-dimethylformamide (Baker), and ethyl acetate (Aldrich)] were reagent or spectrophotometric grade and were used as received. The UV spectrometers were an IBM 9430 and a Hewlett Packard 8451A. Infrared spectra were recorded on a Mattson FTIR spectrometer.

Preparation of Polymers

Polymerizations were run to low conversion in THF at 60°C. AIBN, the initiator, was charged at 0.5% based on total monomer weight. The monomers, IEM and MMA, were charged at several molar ratios and polymerizations were conducted in capped pyrex vials in a heated oil bath. Each vial was equipped with a small magnetic stir bar and the oil bath was heated with a

magnetic stirrer-heating plate. After addition of the solvent and monomers, oxygen-free argon was introduced to the vials before they were capped. After polymerization the solutions were added slowly to a cooled, stirred THF solution of *N*-benzylmethylamine (20% molar excess based on total IEM). The polymers were repeatedly precipitated from THF solutions into petroleum ether. After the final precipitation, the polymers were vacuum filtered and vacuum dried at 35°C.

Homopolymers of the IEM-*N*-benzylmethylamine adduct were synthesized by both reaction of IEM homopolymer with *N*-benzylmethylamine and by reaction of IEM monomer with the amine, followed by polymerization of the adduct monomer. Adduct monomer was synthesized as follows: IEM was added slowly to an equimolar THF solution of the *N*-benzylmethylamine. The amine solution was cooled and stirred during IEM addition. A small amount of 2,6-di-*tert*-butyl-4-methylphenol was added to the IEM to prevent polymerization during the monomer derivatization. ¹H-NMR confirmed that the desired urea monomer was formed in the reaction: ¹H-NMR (90 MHz, CDCl₃) 7.3 (*s*, 5.0 H ring), 6.10 (*s*, 1H, *trans* Me vinyl), 5.53 (*m*, 1H, *trans* ester vinyl), 5.26 (*s*, b, 1H, N—H), 4.5 (*s*, 2H, —CH₂ benzylic), 4.23 (*t*, 2H, —O—CH₂), 3.50 (quartet, 2H, —CH₂—N—), 2.86 (*s*, 3H, —N—CH₃), 1.86 (*s*, 3H, vinyl—CH₃).

Fourier transform infrared (FTIR) spectra of the homopolymer of the IEM-amine adduct monomer were identical to the polymer formed by the reaction of amine with IEM homopolymer. SEC analysis of the copolymers indicated that the polymer formed by polymerizing the IEM-amine adduct methacrylic monomer was significantly lower in molecular weight than the IEM homopolymer reacted with the amine.

PROCEDURE AND RESULTS

Infrared Analysis

Analyses were based on calibration curves constructed from various concentrations of the homopolymer formed from the reaction of IEM homopoly-

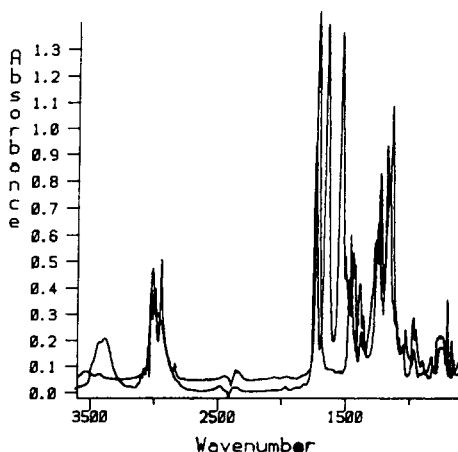


Fig. 1. FTIR spectra of IEM homopolymer reacted with *N*-benzylmethylamine (lower trace at 3500 cm⁻¹) and MMA homopolymer (upper trace at 3500 cm⁻¹).

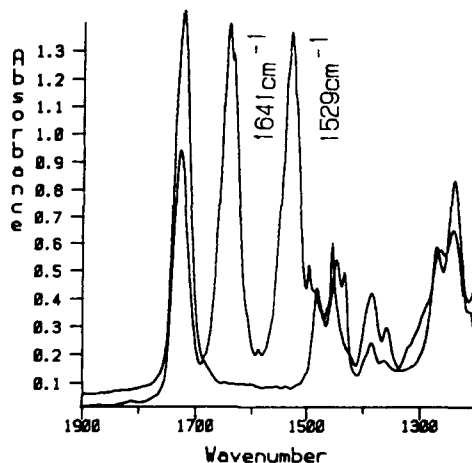


Fig. 2. FTIR spectra of IEM homopolymer reacted with *N*-benzylmethylamine and MMA homopolymer in the region of interest for analysis; Amide I at 1641 cm^{-1} and Amide II at 1529 cm^{-1} .

mer with *N*-benzylmethylamine. Homopolymers for the calibration curve and copolymers were analyzed in chloroform. Wavelengths were chosen such that one homopolymer and the copolymers showed a strong absorbance where the other homopolymer did not interfere. Calibration curves, plotted as absorbance $\cdot\text{ cm}^{-1}$ (peak area) versus concentration of homopolymer, were obtained through a series of dilutions. Copolymer samples were analyzed at $27.627\text{ g polymer/L}$. Concentration of the percent IEM-*N*-benzylmethylamine adduct present in the copolymer was calculated by linear estimate from the calibration curve.

FTIR spectra of both IEM homopolymer reacted with *N*-benzylmethylamine and MMA homopolymer are shown in Figures 1 and 2. Peak area versus concentration data used as calibration curves for the peaks centered at 1641 cm^{-1} and 1529 cm^{-1} (Amide I and Amide II) are shown in Figure 3.

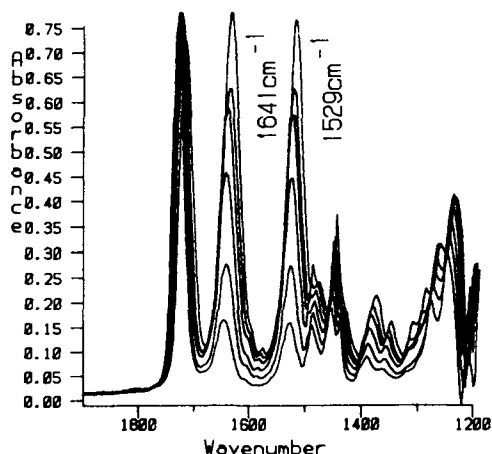


Fig. 3. FTIR spectra of copolymers of IEM with MMA in which the IEM is reacted with amine. The peaks at 1641 cm^{-1} and 1529 cm^{-1} increase as the percentage of IEM in the copolymer increases.

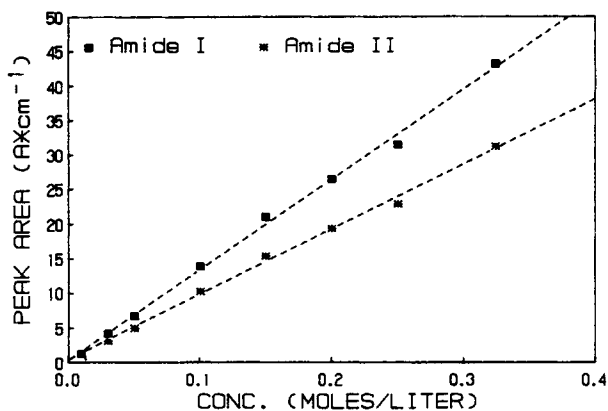


Fig. 4. FTIR calibration for the determination of copolymer composition. (■) Amide I, 1641 cm^{-1} . (*) Amide II, 1529 cm^{-1} .

TABLE II
IEM/MMA Copolymers Reacted with *N*-Benzylmethylamine
Infrared and % N Copolymer Composition Analysis

Polymer	% Conv.	Mol% IEM in feed	Mol% IEM in copolymers		
			Amide I	Amide II	N analysis
A	3.9	10	11.09	10.47	13.33
B	5.2	20	21.25	20.64	22.22
C	4.6	30	30.45	33.78	36.93
D	3.8	40	47.57	46.83	49.18
E	4.7	50	56.73	59.69	52.14
F	5.4	60	69.95	72.14	67.16

Integration intervals used were from 1680 to 1591 cm^{-1} (Amide I, centered at 1641 cm^{-1}) and from 1568 to 1499 cm^{-1} (Amide II, centered at 1529 cm^{-1}). Copolymers analyzed show increasing absorbances at Amide I and II wavelengths with increasing IEM/amine adduct content (Fig. 4). Conversion, monomer feed, and copolymer composition data based both on FTIR and nitrogen analysis are provided in Table II.

Ultraviolet Analysis

Ultraviolet analyses were similar to the IR analyses. Samples were dissolved in chloroform, ethyl acetate, or *N,N*-dimethylformamide. The concentrations of the calibration curve samples were obtained through a series of dilutions. Plots were constructed as maximum absorbance versus concentration. The copolymer composition was determined by linear estimate from the calibration curve.

The ultraviolet spectrum of IEM homopolymer reacted with *N*-benzylmethylamine contains shoulders and fine structure related to vibrational levels accompanying electronic transitions in the benzenoid ("B"-type) band (Fig. 5). A calibration curve for UV analysis is shown in Figure 6. Copolymer composition, as determined by nitrogen analysis and by ultraviolet spectroscopy is presented in Table III.

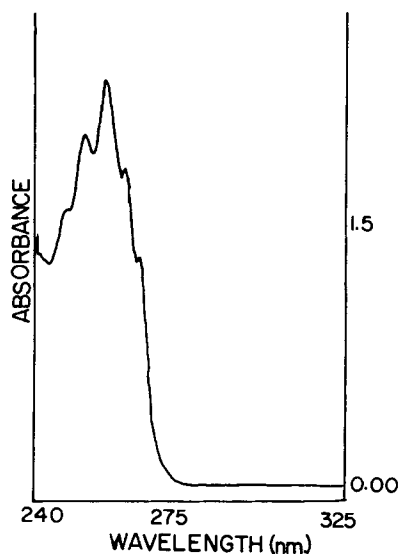


Fig. 5. UV spectrum of IEM homopolymer reacted with *N*-benzylmethylamine. Solvent: Chloroform. $\lambda_{\max} = 259.2$ nm.

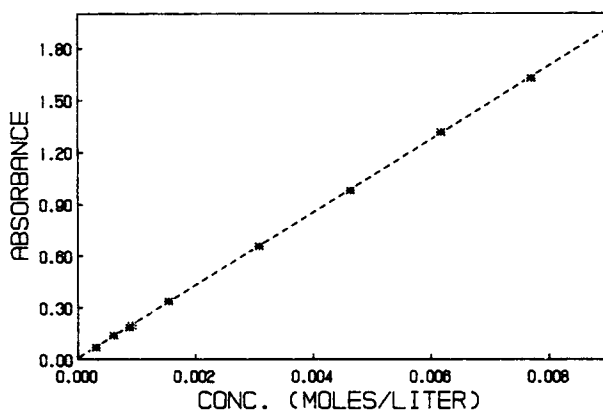


Fig. 6. UV calibration curve for the determination of copolymer composition. $\lambda_{\max} = 259.2$ nm.

TABLE III
IEM/MMA Copolymers Reacted with *N*-Benzylmethylamine,
Ultraviolet and % N Copolymer Composition Analysis

Polymer	Mol% IEM in feed	Mol% IEM in copolymers	
		UV	N analysis
A	10	15.34	13.33
V	20	20.55	22.22
C	30	37.43	36.93
D	40	49.17	49.18
E	50	51.81	52.14
F	60	65.30	67.16
G	70	69.09	72.41

DISCUSSION

A simple UV method for the determination of copolymer composition in high isocyanate content polymers is applicable to systems where simple titration methods are not viable. The agreement between the UV spectroscopic composition and nitrogen analysis composition data indicate that the UV method is of value for polymer analysis.

Ramelow and Baysal¹ review several examples of bias in polymer analysis including the observations of Lewis et al.¹⁴ that carbon, nitrogen, and chlorine analyses were not consistent with one another in their studies of copolymers of vinylidene chloride and acrylonitrile. Ritchey and Ball¹⁵ reported that Kjeldahl analyses were consistently low compared to NMR analysis in the study of styrene-co-acrylonitrile polymers. Izumi and Kitagawa¹⁶ found consistent bias between Kjeldahl and NMR analyses of acrylonitrile-methyl methacrylate copolymers and infrared analysis agreed with neither. The study of styrene-co-methyl methacrylate polymers by Gruber and Elias¹⁷ utilizing elemental analysis, IR, UV, NMR, and refractometry clearly indicated that significant biases do exist in copolymer analysis methods.

The effect of bias in polymer analysis on copolymerization reactivity ratios, as observed by Gruber and Elias, prompted an investigation of r_1r_2 values. Small differences in composition data can lead to large differences in r_1r_2 values.¹⁸ Reactivity ratio values based on composition data obtained by nitrogen analysis, UV spectroscopy, and by FTIR analysis are presented in Figures 7 and 8. Reactivity ratios were calculated by the Kelen-Tudos linearization method, the only linear method of r_1r_2 determination in which all data are weighted equally and which is insensitive to the transposition of data.¹⁹⁻²¹

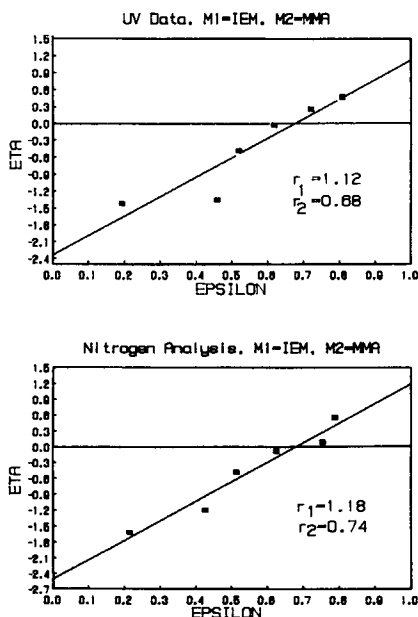


Fig. 7. Kelen-Tudos plots for the determination of copolymerization reactivity ratios. Upper: UV analysis. Lower: Nitrogen analysis.

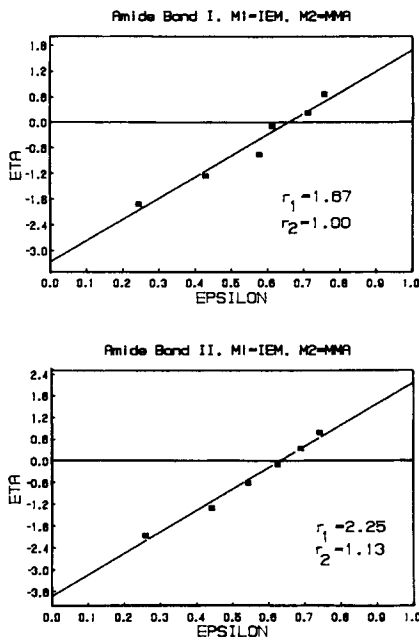


Fig. 8. Kelen-Tudos plots for the determination of copolymerization reactivity ratios. Upper: FTIR, Amide I. Lower: FTIR, Amide II.

The α value in the Kelen-Tudos equation:

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad (1)$$

was chosen so as to symmetrically distribute the experimental points between zero and one.²⁰ Reactivity ratio values were determined by a least-squares fit through the epsilon-eta points. Epsilon and eta values, the X and Y coordinates, respectively, in a Kelen-Tudos plot, are calculated parameters based on monomer feed and copolymer composition data. Although composition data based on infrared analysis are in close agreement with composition data obtained by nitrogen analysis and the UV method, differences exist in the r_1 and r_2 values obtained. Reactivity ratio values obtained by UV analysis are $r_1 = 1.12$, $r_2 = 0.68$; and by nitrogen analysis $r_1 = 1.18$, $r_2 = 0.74$. Polymerizations in this work were carried out at 60°C. Thomas² reported values of $r_1 = 1.04$, $r_2 = 0.74$ for IEM/MMA copolymerization conducted at 115°C.

As suggested by Tidwell and Mortimer,¹⁸ plots were constructed in which the ordinate is the difference between the observed and calculated composition values and the abscissa is the initial monomer feed composition (Figs. 9 and 10). The points in the plots based on the UV analysis method and on nitrogen analysis appear random. Although the response plot based on infrared analysis of Amide band I shows no particular trends, the response curve for Amide band II data shows a definite trend indicative of a bias in the analysis. Amide I, arising from C=O stretching, and Amide II, arising from N—H bending, are generally thought to be resolved in dilute solution and

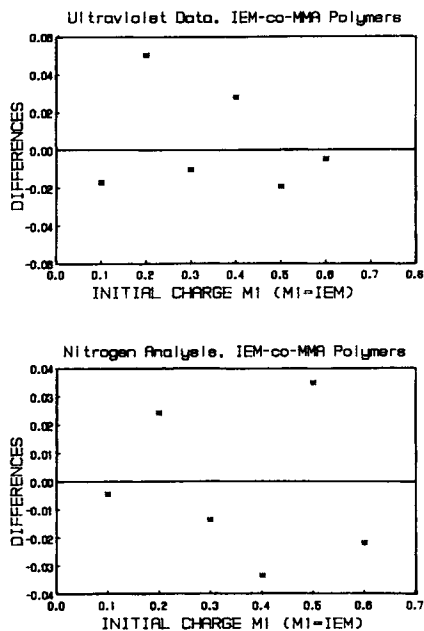


Fig. 9. Response plots. Y axes are the differences between experimentally determined copolymer compositions and compositions back calculated from reactivity ratios determined by experiment for a given initial feed. Lack of pattern in the data points indicates that the copolymerization model chosen is adequate and that there is not an obvious bias in the analytical procedure. Upper: UV data, Lower: Nitrogen analysis data.

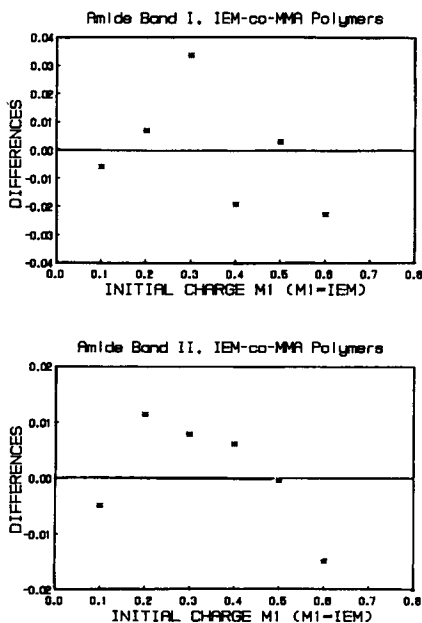


Fig. 10. Response plots. See Figure 9. Upper: FTIR, Amide I. Lower: FTIR, Amide II.

indeed, they appear to be in the spectra generated for analysis.* Furthermore, they are of approximately the "correct" intensity; Amide II being approximately two-thirds as intense as Amide I. A detailed study of the infrared spectra of dialkyl ureas does indicate, however, that in some instances, interactions between N—H and C=O groups may complicate the resolution of these absorbance bands.²²

Infrared analyses were performed in chloroform, and despite fairly good agreement with composition data obtained by other methods, r_1r_2 values based on the analysis are high. The bias in the analysis may be due to C=O/N—H interactions. As solvent selection may be used to eliminate hypochromicity in UV analysis by interfering with neighboring chromophore interactions,²⁸ it was assumed that proper solvent selection could effectively nullify such interactions and improve the FTIR analysis; however, analyses performed in solvents of varying dielectric constant (THF, 1,3-dioxolane, chloroform) yielded identical composition values for the same copolymer.

Hypochromicity, a reduction in the molar absorptivity (extinction coefficient) of a given chromophore has been observed in a variety of macromolecular systems. In polynucleotides, a reduction in the molar absorptivity is thought to result from the interaction between one particular excited state of a given chromophore and different higher electronic states of neighboring chromophores.²³ The first satisfactory theory of hypochromism was given by Tinoco²⁴ and by Rhodes²⁵ and was later treated by Devoe.²⁶ Although hypochromicity is infrequently addressed in studies of common synthetic polymers, Russo and others²⁷⁻²⁹ have thoroughly investigated hypochromic effects in styrene (STY)-MMA copolymers. As the STY-MMA systems are similar to the absorbing adduct-MMA systems studied here, a description of experimental observations on STY-MMA copolymers follows.

Styrene-Methyl Methacrylate Copolymers

Russo and others²⁷⁻²⁹ studied STY-MMA copolymers in which sequence distribution was varied by employing different synthetic techniques. Mechanical mixtures of styrene and methyl methacrylate homopolymers, block copolymers, statistical copolymers, and an alternating STY-MMA copolymer, produced by alkyl aluminum halide complexation,³⁰ were analyzed spectrophotometrically. Hypochromicity in STY-MMA copolymers was attributed to interactions between the carbonyl groups of MMA and the phenyl rings of styrene.

Mixtures of STY and MMA homopolymers as well as block copolymers showed no hypochromicity. In the statistical copolymers, hypochromicity was most pronounced in copolymers containing about 50 mol% styrene. Of the various copolymer types studied, hypochromic effects, in a given solvent, reached a maximum in the alternating STY-MMA copolymer. Sequence distribution differences were invoked to explain the observations; hypochromicity increases as the percentage of styrene (phenyl chromophores) isolated

*Spectra of copolymers to be published in the next edition of "Atlas der Polymer-und Kunststoff-Analyse" (Carl Hanser Verlag-Verlag Chemie, Munchen-Weinheim) D. O. Hummel, Editor.

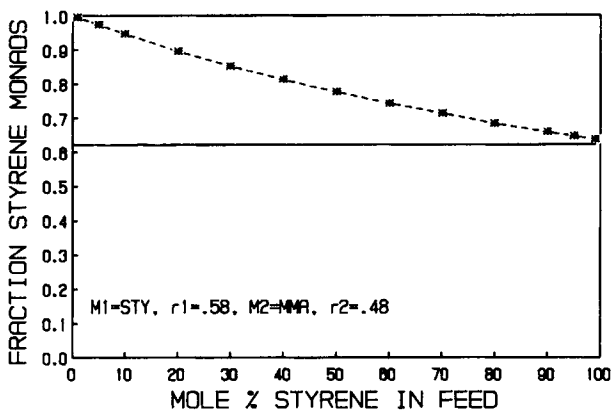


Fig. 11. Fraction of styrene in STY-MMA copolymer present as isolated styrene units as a function of the styrene content in the initial monomer charge. As calculated, sequence distribution values become undefined at 100 mol% styrene.

between MMA units increases. Isolated styrene units do not exist in the mechanical mixtures or block polymers, exist to a greater extent in the statistical copolymers, and exclusively exist in the alternating copolymer.

Hypochromicity decreased with increasing solvent dielectric constant²⁷ and could be eliminated through the use of carbonyl-containing (ester) solvents.²⁸ STY-MMA polymers in noncarbonylic solvents showed hypochromicity only over discrete ranges of composition.^{27,28} At a copolymer of composition 50 : 50 STY : MMA, about 77.5% of the styrene in the copolymer is present as monads, styrene units with MMA on both sides of it in the polymer chain. Hypochromicity was found to be maximum over a composition range usually containing this 50 : 50 STY : MMA polymer. It should be noted that from reactivity ratios, an azeotropic composition of 55.3% STY : 44.7% MMA is predicted. Furthermore, STY-MMA copolymerization proceeds with a tendency toward alternation; it is not truly random. Even at styrene feeds as high as 99% (the highest value for which sequence distribution calculations are meaningful), the alternating tendency in polymerization is evidenced by the formation of about 63.5% styrene monads. The fraction of styrene monads in a low conversion (< 5%) batch polymerization is illustrated in Figure 11. The data presented were calculated from accepted literature values for r_1 and r_2 .³¹

IEM Absorbing Amine Adduct-MMA Copolymers

Hypochromicity, defined here as a reduction in the molar absorptivity of the phenyl chromophore (259.2 nm) in a copolymer, relative to that of the IEM/amine adduct homopolymer, causing a deviation from linearity in a plot of adduct content versus absorbance, was observed in MMA-IEM/amine adduct polymers used in this study. Hypochromic nonlinear deviations could be eliminated by the use of carbonylic solvents. Molar absorptivity varied with copolymer composition in solvents in which hypochromic effects were observed (Fig 12). The largest percent hypochromicity occurred in low adduct content polymers in noncarbonylic solvents (Table IV). Copolymers of low IEM/amine adduct content, containing a large fraction of adduct chromophores isolated between MMA units, exhibited the maximum hypochromicity.

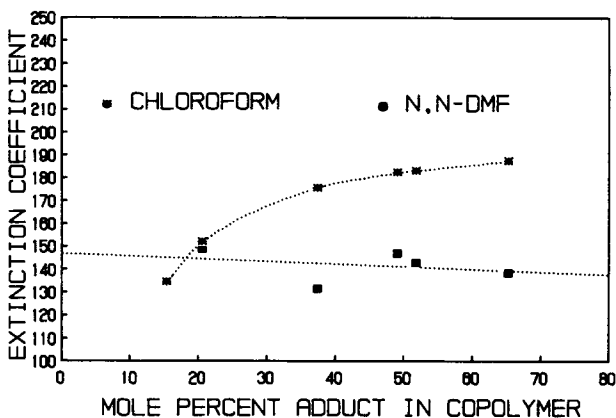


Fig. 12. Extinction coefficient vs. copolymer composition. Nonlinear deviations are eliminated in the carbonylic solvent, *N,N*-dimethylformamide (■) while they are pronounced in chloroform (*). Hypochromicity reaches a maximum at low adduct concentration where the majority of the chromophoric units are isolated between MMA.

A copolymer of 10:90 IEM:MMA (mol%) contains about 90% of the total amount of IEM as units isolated between MMA units. At a 80:20 IEM:MMA feed ratio, 55% of the IEM in the copolymers is present as monads (Fig. 13).

Hypochromic behavior in the IEM/adduct-MMA polymers is analogous to that observed in the STY-MMA systems, but the maximum hypochromicity occurs at a different composition due to the differences in the reactivity ratios of the monomer pairs; for STY-MMA reactivity ratios are³¹ M1 = STY, $r_1 = 0.58$; M2 = MMA, $r_2 = 0.48$; $r_1 r_2 = 0.28$; for IEM-MMA reactivity ratios are² M1 = IEM, $r_1 = 1.04$; M2 = MMA, $r_2 = 0.74$; $r_1 r_2 = 0.77$. At a copolymer composition of 10:90 IEM:MMA, the percentage of phenyl chromophore units isolated between MMA units is close to its maximum as is the hypochromicity observed. Hypochromic effects across broad composition ranges, as opposed to the relatively narrow composition ranges in STY-MMA polymers, are likely due to the presence of a greater number of interacting groups. In addition to the ester groups of MMA and IEM, urea carbonyl groups are present in these copolymers.

TABLE IV
Percent Hypochromicity as a Function of Copolymer Composition and Solvent Type

Polymer	Mol% IEM	Percent hypochromicity	
		Chloroform	Ethyl acetate
A	15.34	30.68	.24
B	20.55	21.58	.59
C	37.43	9.43	1.08
D	49.17	6.00	1.21
E	51.81	5.45	1.23
F	65.30	3.33	1.32
G	69.09	2.89	1.34

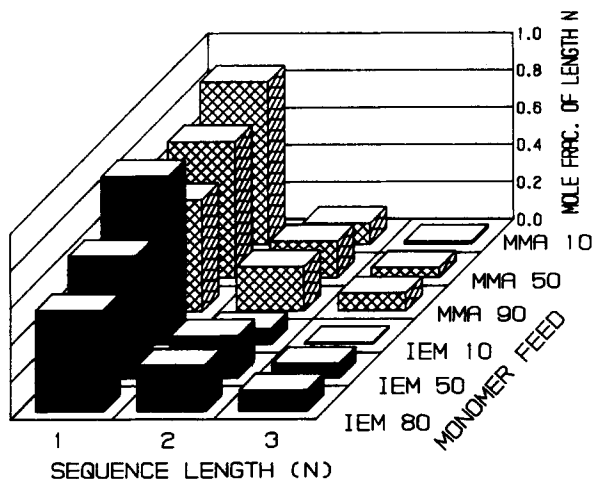


Fig. 13. Fraction of monads, diads, triads as a function of monomer feeds in IEM-MMA copolymerization. Based on $r_1(\text{IEM}) = 1.04$, $r_2(\text{MMA}) = 0.74$.²

CONCLUSIONS

A method for the determination of copolymer composition in high isocyanate content polymers, which are not readily analyzed by classical titration methods, is presented. Copolymers of isocyanate-containing monomers like IEM² and *m*-TMI³ or similar structures (i.e., the reaction product of hydroxyethyl methacrylate (HEMA) with unsymmetrical diisocyanates to yield an $-\text{N}=\text{C}=\text{O}$ containing monomer) have found use as crosslinking systems in coatings. The determination of copolymer composition in systems such as these is of prime importance in delineating structure-property relationships. Further, modifications of the type of analysis described here have been employed in other systems. The determination of copolymer composition in acrylamide polymers through the incorporation of an absorbing moiety followed by spectrophotometric analysis has been reported.³²

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