Monomer Reactivity Ratios in UV-Initiated Free-Radical Copolymerization Reactions

ULKU S. RAMELOW* and QING HUA QIU

Department of Chemistry, McNeese State University, Lake Charles, Louisiana 70609-0455

SYNOPSIS

The homopolymers of styrene (S) and vinyl acetate (VA) and their copolymers were prepared in bulk by ultraviolet (UV)-radiation-initiated free-radical polymerization with azobis-isobutyronitrile (AIBN) as an initiator. The reactivity ratios for these copolymerizations were determined by analyzing the monomer content in the copolymers by UV spectroscopy. The same method was extended to other copolymers of styrene such as styrene–methyl methacrylate and styrene–ethyl acrylate. A new analysis method was developed to measure reactivity ratios. For this purpose, UV light was used as a photochemical initiator and UV absorption spectroscopy was used for the determination of the instantaneous composition of copolymers. Nuclear magnetic resonance (NMR) was used to calculate percent conversion.
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INTRODUCTION

There are a number of methods of estimating monomer reactivity ratios in copolymerization. For this purpose, infrared (IR) spectroscopy, nuclear magnetic resonance (NMR), and ultraviolet (UV) absorption spectroscopy are used. None of them is generally applicable. UV spectroscopy is an attractive choice when the following conditions can be met: The backbone units must not have overlapping absorbance; the solution can be prepared in nonopaque solvents; and there must be no major shifts in spectral intensity or position of one backbone unit due to the presence of another.
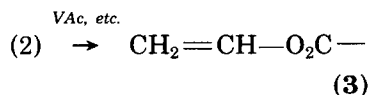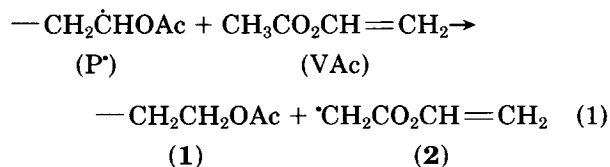
There are several methods of estimating monomer reactivity ratios in copolymerization such as linearization based on differential copolymer equations (the Kelen–Tudos method[1] and the Fineman–Ross method[2]); the intersection method, based on a transformed integrated Mayo–Lewis copolymer equation[3] and improved by computer calculations[4]; the curve-fitting method based on a differential copolymer equation,[5] which was improved by nonlinear least squares[6]; and the curve-fitting/intersection method based on the integrated copolymer equation[7,8] and improved by consideration of measurement errors in both variables.[9]
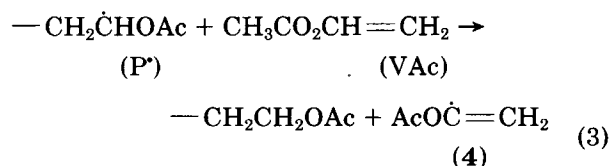
By the use of good experimental run planning procedures, estimation methods, and experimental practices, it is possible to obtain $r_1 r_2$ values which are both precise and accurate. Almost none of the copolymerization data in the literature has been generated under conditions which satisfy simultaneously all these criteria. Tidwell and Mortimer[10] stated, "Hence we are led to conclude that the original question raised whose data can one believe? cannot be answered from the existing literature." Bamford et al.[11] demonstrated the variation of reactivity ratios by changing the dielectric constant of the reaction medium. All the early methods are inadequate,[12,13] whereas new computer programs for minimizing errors lead to the maximum reliable information about monomer reactivity ratios.[11,14]

Chain transfer to the monomer is of great significance in the free-radical polymerization of vinyl acetate (VA) because it ordinarily stops the growth of most of the polymer chains and, thus, controls their molecular weight.[15,16] The mechanism of this transfer process is therefore of much interest. There is a reasonable transfer pathway involving H abstraction from the methyl group of VA by the propagating macromolecule radical P˙:


$$—CH_2\dot{C}HOAc + CH_3CO_2CH=CH_2\rightarrow$$
$$\text{(P·)} \qquad\qquad \text{(VAc)}$$

$$—CH_2CH_2OAc + \text{·}CH_2CO_2CH=CH_2 \quad (1)$$
$$\text{(1)} \qquad\qquad \text{(2)}$$

VAc, etc.
$$(2) \quad\rightarrow\quad CH_2=CH—O_2C—$$
$$\text{(3)}$$

$$—CH_2CH_2CH(OAc)CH_2CH(OAc)CH_2— \quad (2)$$

The propagating radical **2** adds to another VA molecule by head-to-tail propagation; then, it should generate a chain end (**3**). For many years, this reaction given in eq. (1) was considered to be the predominant transfer step. In the early 1980s, this theory was challenged by Litt and Chang[17] who studied the bulk and emulsion polymerization of deuterated monomers and calculated that almost all of the transfer involved the abstraction of a vinyl H atom:

$$—CH_2\dot{C}HOAc + CH_3CO_2CH=CH_2 \rightarrow$$
$$\text{(P·)} \qquad\qquad . \quad \text{(VAc)}$$

$$—CH_2CH_2OAc + Ac O\dot{C}=CH_2$$
$$\text{(4)} \qquad\qquad (3)$$

The monomer radical (**4**) formed would be expected to react with additional monomer to give a chain end (**5**), as given in eq. (4):

$$AcO\dot{C}=CH_2 + VAc \rightarrow$$
$$\text{(4)}$$

$$CH_2=C(OAc)CH_2CH(OAc)CH_2CH(OAc)CH_2—$$
$$\text{(5)}$$

$$(4)$$
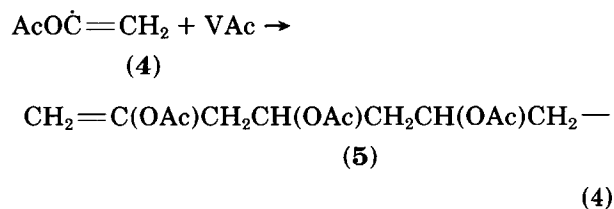
Vinyl C—H bonds are so strong that they ordinarily are not attacked by C-centered radicals. Thus, the above reactions have been most fascinating. These reactions were investigated and proven by using ^{13}C-NMR in order to determine the structure of the long chain ends of the polymer.[16,18]

Starnes et al. polymerized VA monomer at high temperature in the presence of AIBN catalyst.[16] In this work, the free-radical polymerization of vinyl acetate and styrene and their mixtures was performed by using UV light and AIBN as an initiator.

The proper mechanism for free-radical copolymerization of styrene and vinyl acetate initiated by UV light is given by the following equations:

$$I \xrightarrow[\text{UV (254 nm)}]{k_i} 2\ R\text{·}$$

$$R\text{·} + (VA) \rightarrow (VA)\text{·}$$

$$R\text{·} + S \rightarrow S\text{·}$$
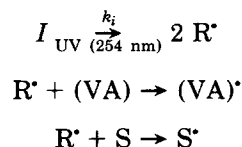
Initial $(VA\text{·})$ free radicals $(—CH_2—\dot{C}H—OAc)$ form a propagating radical:

$$—CH_2—\underset{\underset{OAc}{|}}{CH}—CH_2—\underset{\underset{OAc}{|}}{\dot{C}H}$$
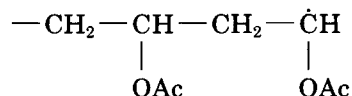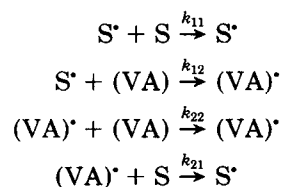
by reacting with its monomer, also with a possibility of forming $CH_2=\dot{C}OAc$ radicals which can be formed by H-atom abstraction from its monomeric molecule,[16,17] then giving a chain end as shown in eq. (4). Both propagating radicals for styrene and vinyl acetate must be more stable than their initial radicals; otherwise, they will go into degradation. Initial $(S\text{·})$ free radicals
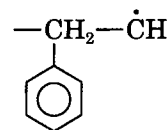
form the propagating radical
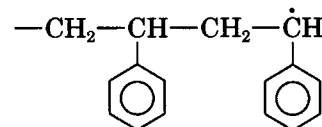
Styrene and vinyl acetate initial radicals formed give the following reactions:

$$S\text{·} + S \xrightarrow{k_{11}} S\text{·}$$

$$S\text{·} + (VA) \xrightarrow{k_{12}} (VA)\text{·}$$

$$(VA)\text{·} + (VA) \xrightarrow{k_{22}} (VA)\text{·}$$

$$(VA)\text{·} + S \xrightarrow{k_{21}} S\text{·}$$

where r_1 and r_2 are the reactivity ratios and defined as

$$r_1 = k_{11}/k_{12} \qquad r_2 = k_{22}/k_{21}$$

The mechanism is assumed to be the same for the other copolymerization reactions given in this work.

By using the rate of creation of radicals and the rate of consumption of the monomers, the following copolymer equation was obtained (Alfrey–Mayo equation):[18,19]

$$\frac{d[S]}{d[VA]} = \frac{(k_{11}/k_{12} \times [S]/[VA] + 1)}{(k_{22}/k_{21} \times [VA]/[S] + 1)}$$

This equation can be modified by defining $h = d[S]/d[VA]$ as the mole ratio of monomer 1 to monomer 2 in the copolymer; $H = [S]/[VA]$, the same ratio in the monomer feed; $r_1 = k_{11}/k_{12}$, the ratio of reactivity of monomer 1 toward itself to the reactivity of monomer 2; and also $r_2 = k_{22}/k_{21}$. Therefore,

$$h = (r_1 \times H + 1)/(r_2/H + 1),$$

or, by the arrangement,

$$H(1 - h)/h = r_2 - r_1(H^2/h) \tag{5}$$

Equation (5) is obtained, which will be used to measure the reactivity ratios in this study.[2] According to eq. (5), if $H(1 - h)/h$ values are plotted vs. H^2/h, from the intercept and slope, r_2 and r_1 values can be calculated, respectively.

EXPERIMENTAL AND DISCUSSION

Materials

Styrene was obtained from the Aldrich Chemical Co. The 4-*tert*-butylcatechol (4-TBC) inhibitor was removed by washing three times with 10% NaOH solution, then several times with deionized water, dried over anhydrous sodium sulfate, and distilled at 30 Torr between 32 and 35°C.

Vinyl acetate (VA) was a product of Eastman Kodak Co. and distilled at 30 Torr at 30–40°C. Methyl methacrylate and ethyl acrylate were also products of the Aldrich Chemical Co. Their inhibitors were removed with the same method given above and methyl methacrylate was distilled at 30 Torr between 40 and 43°C. Ethyl acrylate was distilled at 30 Torr between 35 and 40°C.

The 2-2'-azobisisobutyronitrile (AIBN) catalyst was a product of Polyscience and was purified from methanol before use as follows: A solution was prepared in methanol and cooled. The crystals were collected on a fritted glass filter and dried under vacuum at room temperature. All solvents were reagent grade and used without further purification.

For UV-irradiation, a Philips HPR 125 W mercury vapor UV lamp was used with a maximum wavelength of 254 nm. UV spectra were taken with a Perkin-Elmer Lambda 3B UV/visible spectrophotometer equipped with a P-E 3600 data station and P-E 660 printer. NMR spectra were taken with a

Perkin-Elmer R-12 double-resonance accessory continuous wave (CW) spectrometer.

Molecular weights of poly(vinyl acetate) samples were determined at 25°C by using an Ubbelohde viscometer and acetone as solvent. All samples were degassed and irradiated in quartz tubes of 12 cm height and 2.8 cm diameter.

Preparation of Homopolymers and Copolymers

Monomers were mixed in different volume ratios in a quartz tube and about 1% (by weight) AIBN catalyst was added to each tube. Tubes were sealed with rubber septa and connected to the manifold of the vacuum system with syringe needles and degassed to 10^{-4} to 10^{-5} mmHg pressure for 5–6 h. Degassed tubes were irradiated for 2–3 h by UV-rays under a mercury vapor UV lamp at 254 nm. The tubes were irradiated in a horizontal position at a distance of 20 cm from the light source.

All monomers and copolymer mixtures were degassed to 10^{-5} mmHg pressure and irradiated by UV rays for 2–3 h. After completing the required irradiation time, styrene and methyl methacrylate homopolymers were dissolved in chloroform and precipitated in methanol. Ethyl acrylate homopolymer was dissolved in THF and precipitated in petroleum ether and washed with acetone and water. Styrene-ethyl acrylate copolymers were obtained in the same way. VA homopolymer was dissolved in THF and precipitated in ethanol. Styrene–VA copolymers were also prepared in the same way as was the VA homopolymer. All homopolymers and copolymers were filtered and dried at room temperature in a vacuum oven to constant weights.

Preparation of Copolymers for Analysis

For UV analysis, about 0.01–0.05 g copolymer samples were dissolved in 10 mL chloroform solution and spectra were taken in a 1 cm cell. A wavelength was sought at which the homopolymer and its copolymer showed a characteristic peak and the other homopolymer did not absorb. By preparing a solution of various known concentrations, spectra were taken for each copolymer as well as for its corresponding homopolymer. One of the homopolymers was chosen as a reference for analysis. A calibration curve was obtained by plotting the absorbance at a specific wavelength against the known concentration of one of the homopolymers. The absorbance of a copolymer sample at this particular wavelength was determined and the corresponding monomer amount was calculated from the calibration curve. Corre-

Table I Styrene–Vinyl Acetate Copolymer Analysis (A)

S-VA Copolymer No.	Volume Ratio in Feed (S/VA)	[S] in Feed (mol/L Chl. × 10^3)	[VA] in feed (mol/L Chl. × 10^3)	Mol % [S] in Feed (f_1)
1	3/7	2.61	7.59	25.6
2	4/6	3.49	6.51	34.9
3	5/5	4.36	5.42	44.6
4	6/4	5.24	4.34	54.7
5	7/3	6.11	3.25	65.2

S: styrene, density = 0.909 g/mL, MW = 104.19. VA: vinyl acetate, density = 0.934 g/mL, MW = 86.09. Chl.: Chloroform.

sponding percentages of the monomer in the copolymer were calculated.

Copolymer Analysis of Styrene–Vinyl Acetate

The monomer mixtures were prepared in the given volume ratios as shown in Table I. The mixture was incorporated with 1% initiator AIBN and degassed at 10^{-5} mmHg, then irradiated with UV light for 2 h. The copolymer was dissolved in THF and precipitated in ethanol. The copolymer samples were prepared at about 0.0015 g in 10 mL chloroform. The absorption band at 252 nm was used for the analysis of styrene content in the copolymer. Figure 1 shows the UV absorption of poly(vinyl acetate). It does not have any absorption band at either 252 or 257 nm, the wavelengths where styrene absorbs. Figure 2 shows the UV absorption spectrum of polystyrene. The absorption bands at 252 and 257 nm were examined (Table II). A calibration curve drawn for polystyrene at 252 nm was chosen as a reference (Fig. 3).

Styrene–VA copolymers can easily be examined for their styrene content at 252 nm. Figure 4(a)–(e)

shows the UV absorption spectra of styrene–VA copolymers. By using the calibration curve (Fig. 3), the styrene content and mol % of styrene in the copolymer were determined. The results are given in Table III.

Molar ratios in the feed (H) and in the copolymer (h) were calculated. $H(1 - h)$ and H^2/h values were tabulated. The r_1 and r_2 values for styrene and VA calculated by using Figure 5 were found to be 2.74 and 0.10, respectively.

UV spectroscopic analysis of styrene–methyl methacrylate and styrene–ethyl acrylate were done by using the same procedure, and r_1 and r_2 values were calculated by the same method. The mol % of styrene in copolymers calculated by using UV spectroscopy was plotted against the mol percentages of styrene in monomer feed for three different copolymer samples. Figure 6 shows such a relationship.

NMR Study of Styrene–Vinyl Acetate Copolymers

The percent conversion of poly(vinyl acetate) was determined by using NMR spectroscopy. Figure 7 shows the NMR spectrum of VA monomer. The
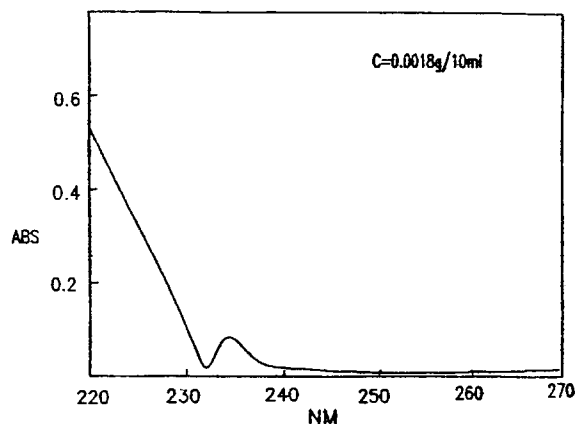
Figure 1 UV absorption spectrum of poly(vinyl acetate). C = 0.0018 g/10 mL chloroform.
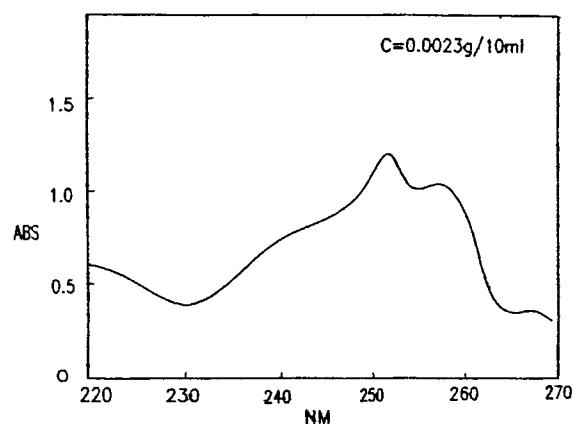
Figure 2 UV absorption spectrum of polystyrene. C = 0.0023 g/10 mL chloroform.

Table II   Calibration Curves of Polystyrene by UV Spectroscopy

[PS] g/10 mL Chloroform $\times$ 10^3	Absorbance at 252 nm
0.0	0.000
1.1	0.500
1.4	0.840
2.3	1.225
3.4	1.623

|	Absorbance at 257.5 nm
0.0	0.000
1.2	0.325
2.5	0.817
3.4	0.890
4.2	1.305
5.4	1.505

peak at (A) shows the $=CH_2$ functional group in VA. Since polymer conversion is directly proportional to the $=CH_2$ bond opening, the decrease in the integral peak height is proportional to the degree of polymerization. The height of integral lines corresponding to the peak at (A) was measured for each irradiated sample. The samples were removed with a syringe from the irradiation tube for every 10 min interval of irradiation time and the NMR signal was taken immediately without adding any solvent. Percent conversion is calculated from the height of each integral line (for peak at A) for the irradiated VA by comparing the height for the monomeric VA at 0 min irradiation as follows:

$$\text{Percent conversion} = (H_0 - H_i)/H_0 \times 100$$

where H_0 is the height of the integral line at zero time irradiation, and H_i, the height of integral line at irradiation time t.

Figure 8 shows the percent conversion vs. irradiation time for VA samples. After 30 min, polymerization shows a sudden acceleration, and within 40 min, the conversion reaches as high as 85% (Table IV).

The molecular weights of the irradiated VA samples were also calculated. After a selected irradiation time, about 2 mL samples were taken out with a syringe, dissolved in THF, and precipitated in ethanol and a little amount of acetone and water. The polymers were dried in a vacuum oven at room temperature. Molecular weights were determined by using an Ubbelohde viscometer at 25°C. Acetone
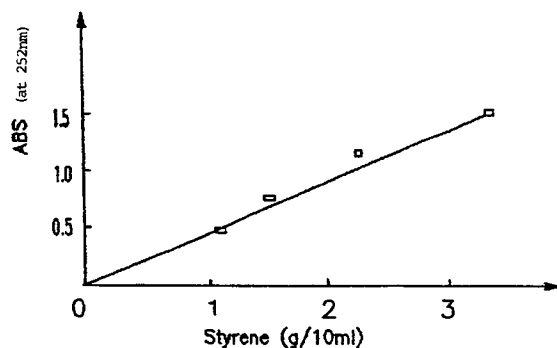
**Figure 3**   Calibration curve for the UV absorption of polystyrene at 252 nm.

was used as a solvent. The Mark–Houwink–Sakurada equation[20]:

$$[\eta]_{int} = KM^a \quad \text{with}$$

$$K = 2.14 \times 10^{-2} \text{ mL/g and } a = 0.68$$

was used for molecular weight determinations.

Up to 30 min of irradiation, the molecular weight reaches to 50,000–77,000. Between 45 and 75 min, molecular weight reaches 130,000. Above 90 min, it is above 150,000. After 30 min of irradiation, the sample became viscous. After 45 min of irradiation, the acceleration and sudden jump in molecular weight is explained by the reaction proceeding with another rate constant. This is also proved by obtaining two straight lines when $\ln([VA_0]/[VA])$
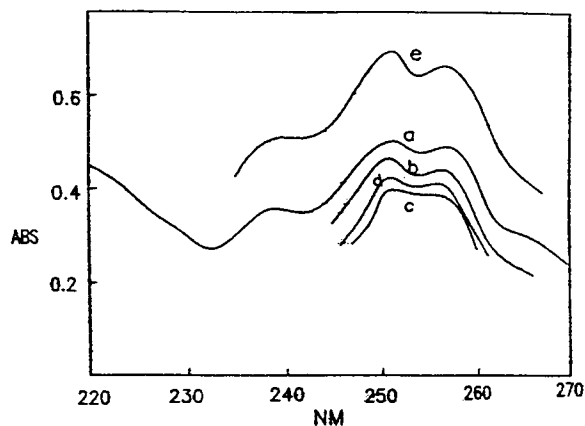
Figure 4   UV absorbance spectra of styrene–VA copolymers: (a) [S]/[VA] volume ratio 3/7, 0.0014 g copolymer/10 mL chloroform; (b) [S]/[VA] volume ratio 4/6, 0.0012 g copolymer/10 mL chloroform; (c) [S]/[VA] volume ratio 5/5, 0.0011 g copolymer/10 mL chloroform; (d) [S]/[VA] volume ratio 6/4, 0.0013 g copolymer/10 mL chloroform; (e) [S]/[VA] volume ratio 7/3, 0.0019 g copolymer/10 mL chloroform.

Table III Styrene–Vinyl Acetate Copolymer Analysis (B)

Copolymer Taken (g/10 mL Chl. $\times$ 10^3)	Absorbance at 252 nm	S_A $\times$ 10^3	VA_A $\times$ 10^3	$[S]_B$ $\times$ 10^3	$[VA]_B$ $\times$ 10^3	[S] mol % in Copolymer (F_1)
#1						
1.40	0.51	0.98	0.42	0.94	0.49	65.8
#2						
1.20	0.48	0.93	0.27	0.89	0.31	74.0
#3						
1.10	0.45	0.88	0.22	0.84	0.26	76.8
#4						
1.30	0.59	1.13	0.17	1.08	0.20	84.6
#5						
1.50	0.64	1.35	0.15	1.30	0.17	88.2

S: styrene, density = 0.909 g/mL, MW = 104.19. VA: vinyl acetate, density = 0.934 g/mL, MW = 86.09. S_A: styrene, g/10 mL chloroform in copolymer from Figure 9. VA_B: VA g/10 mL chloroform in copolymer. $[S]_B$: styrene, mol/L chloroform in copolymer. $[VA]_B$: VA mol/L chloroform in copolymer.

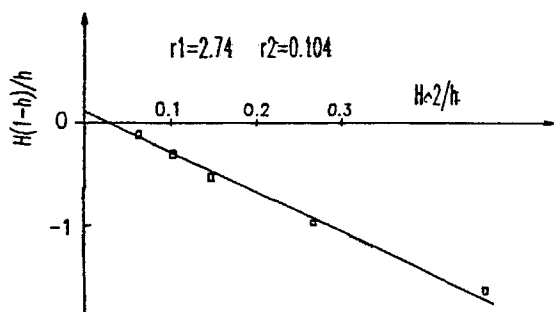[which is expressed as $\ln(M_0/M)$] is drawn vs. irradiation time (Fig. 9).

VA free-radical polymerization is explained by the kinetics equation[21,22]:

$$-d[VA]/dt = k_p(fk_i/k_t)^{1/2}[I]^{1/2}[VA] \qquad (6)$$

where f is the efficiency factor (fraction of the initiator radicals that started polymerization); k_i, k_p, and k_t, rate constants of initiation, propagation, and termination respectively; $[I]$, the initiator concentration; and $[VA]$, the monomer concentration. The integrated form of the above equation is

$$\ln[VA_0]/[VA] = k_p(fk_i/k_t)^{1/2}[I]^{1/2}t \qquad (7)$$

Therefore, a plot of $\ln[VA_0]/[VA]$ vs. irradiation time t should give a straight line. Figure 9 shows such a plot for a UV-irradiated VA sample. Here, $\ln([VA_0]/[VA])$ is approximately equal to $\ln(H_0/H_t)$ and calculated by taking $[VA_0]$ for the nonirradiated
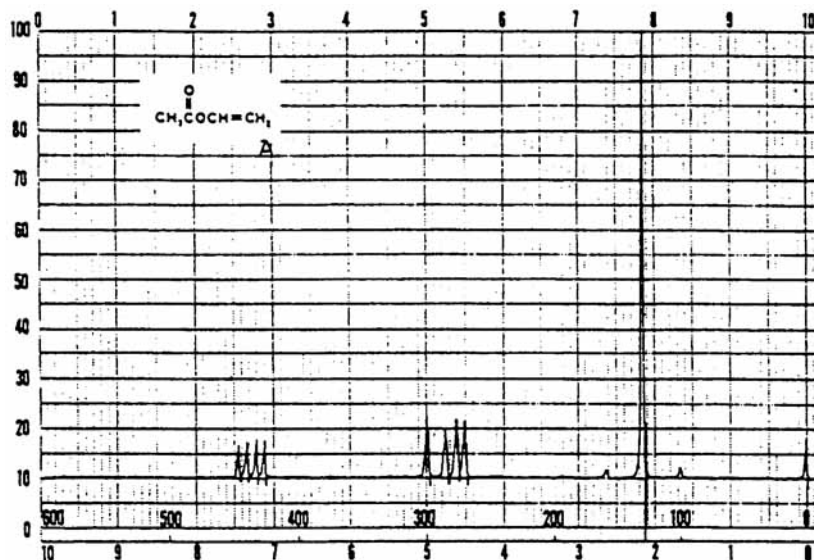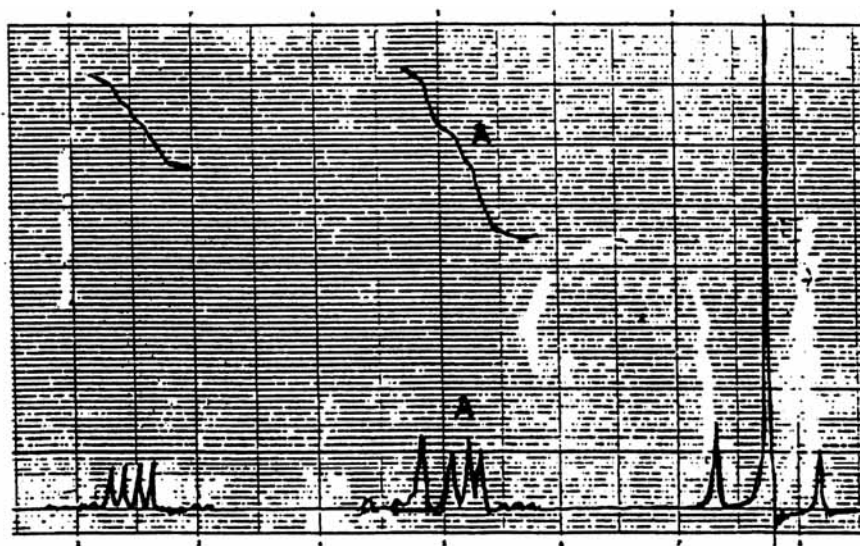
VA concentration and $[VA]$ as the concentration at irradiation time t. Both H_0 and H_t are measured from the height of the integral line obtained for the peak (A) in Figure 7. Two different slopes obtained in Figure 9 correspond to two different rate constants. This is explained by an autoacceleration effect (Norrish–Smith or Trommsdorff effect). As polymerization proceeds, viscosity increases. Due to increased viscosity, the active centers (radicals and chain ends) are unable to meet easily. The rate of termination is, therefore, dramatically reduced. Propagation reactions still take place and the con-

Figure 5 Reactivity ratios determination for styrene–VA copolymers by UV spectroscopic analysis.
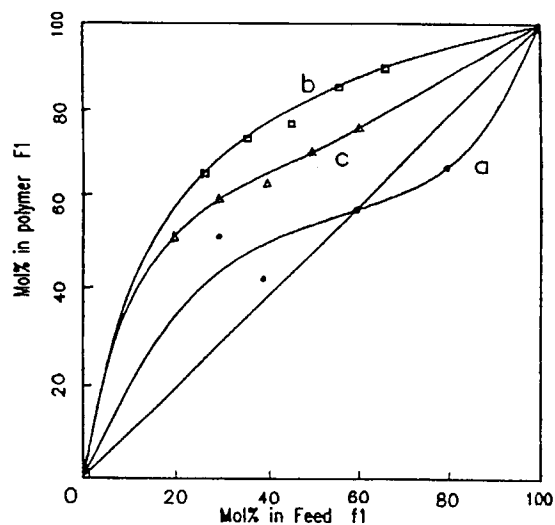
Figure 6 Instantaneous composition of copolymer F_1 (styrene mol %) as a function of monomer composition f_1 (styrene mol %): (a) styrene–methyl methacrylate copolymer ($\bullet$); (b) styrene–VA copolymer ($\square$); (c) styrene–ethyl acrylate copolymer ($\triangle$).

a) Standard NMR spectrum

b) Experimental spectrum

Figure 7   NMR spectrum of VA monomer: (a) standard spectrum; (b) experimental spectrum.

centration of growing chains increases (free-radical concentration increases). The reaction accelerates faster, and the rate constant changes. The addition reactions are exothermic and heat is evolved at an increasing rate since the energy dissipation is poor. The conversion of a double bond to a single bond is accompanied by exothermic heat of polymerization in the order of 10–20 kcal/mol. For VA polymerization, ΔH is -21 kcal/mol. This acceleration continues until the propagation rate is diffusion-controlled rather than by a chemical process; then, the reaction slows down. After 30 min of irradiation, the system becomes very hot and the rate accelerates very fast, as shown in Figure 9.
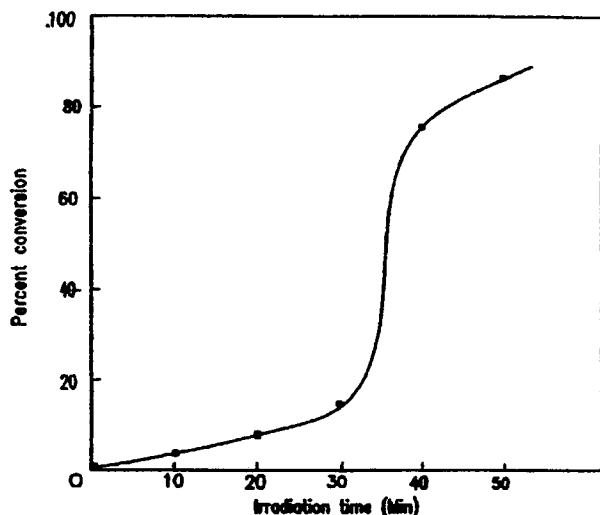
Figure 8 Free-radical polymerization of VA initiated by UV irradiation (at 25°C).

CONCLUSION

The reactivity ratio is the ratio of rate constants for a given radical adding to itself or adding to the other monomer. It has been pointed out that the value of the product $r_1 r_2$ for a copolymeric system is an indication of the selection which the radicals M_1 and M_2 exhibit toward the monomer involved.

In this work, for the styrene–methyl methacrylate system, the obtained reactivity ratios are both less than 0.5. This suggests an alternating copolymerization in which each radical prefers to add the other monomer. The r_1 and r_2 values for styrene–methyl methacrylate system with UV spectroscopic analysis agree with the values given in the literature.[23-25]

Photochemical initiation of polymerization by using UV light was used in previous studies for the homopolymerization of certain monomers.[26-28] Copolymerization of styrene with methyl methacrylate by using UV rays as an initiator was reported previously.[29] However, the copolymerization of styrene with ethyl acrylate and VA initiated with UV radiation and their copolymer analysis by UV spectroscopy has not been reported. The method that we applied avoids the steps of heating to high temperature during thermal initiation of free-radical postpolymerization. High conversions can be reached at shorter times by using UV light and an initiator.

It has been observed that monomer reactivity decreases as the electron-withdrawing character of the side group increases,[29] and it appears that a decreased electron density on the vinyl group leads to a diminishing reactivity of the monomer.[30,31]

Table IV Percent Conversion of Poly(vinyl acetate)

Irradiation Time (Mins)	NMR Integral Peak Height at A	% Conversion	$\ln[VA_0]/[VA]$
0	28	0	0
10	27	3.57	0.036
20	26	7.14	0.074
30	24	14.28	0.154
40	7	75.00	1.386
50	4	85.70	1.946

It has also been observed that an increased hydrogen bonding or dipole–dipole interaction, through the carbonyl of the acetate side group of VA, induces a decreased electron density on the vinyl group of VA, which, in turn, leads to a decreased VA reactivity.[31] Vinyl ester monomer reactivity decreases as the electron-withdrawing character of the ester side group increases. It appears that a decreased electron density on the vinyl group leads to a diminishing reactivity. This is explained by the lower value of the reactivity ratio of VA (0.10) compared to styrene (2.74) obtained in this work. In the case of the styrene–VA copolymer, r_1 for styrene is greater than 1 and r_2 is much less than 1. Such a case leads to the incorporation of monomer 1 almost exclusively in the early stages of polymerization. When r_1 is very high and r_2 is close to zero, one obtains essentially a homopolymer of M_1.

Reactivity ratios are the result of a combination of steric, resonance, and polar effects. Resonance affects reactivity by stabilizing the intermediate radical. The more resonance stabilization, the less reactive the monomer is toward propagation. Styrene, due to conjugate double bonds, forms reso-
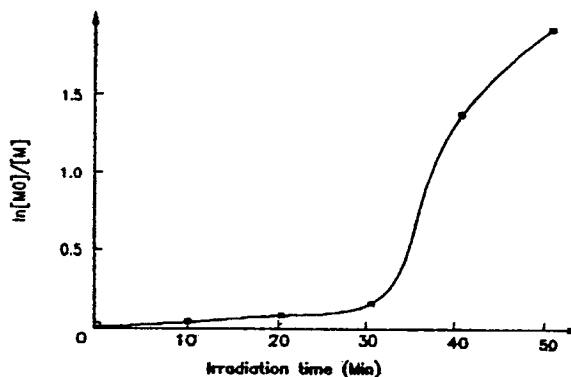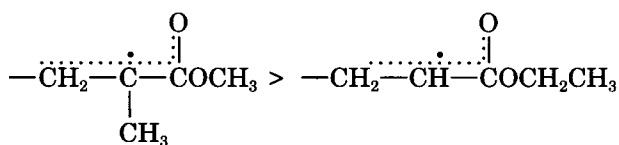

Figure 9 Rate of formation of VA homopolymer as a function of irradiation time.

nance-stabilized free radicals, whereas VA does not have conjugate double bonds and cannot establish resonance stabilization. Thus, resonance-stabilized styrene radicals exhibit little tendency to add to VA because the resultant radical would not be stabilized. This is explained by the different r_1 and r_2 values for the styrene–VA system where r_1 is considerably higher than r_2. (Styrene radicals prefer to add to their own monomer.) The conjugated double bonds establish resonance stabilization to the styrene radical. This decreases the activation energy for reaching the transition state and increases the stability of the radical. Consequently, initial styrene free radicals are formed faster. However, during the initial free-radical formation of VA monomers, due to a partial positive charge on the carbon atom alpha to the acetate group and lack of resonance structure, stability decreases and activation energy increases. This slows the initial free-radical formation process for VA. However, styrene copolymerizes easily with methyl methacrylate since methyl methacrylate, like styrene, forms a delocalized radical.

Both ethyl acrylate and methyl methacrylate form resonance stabilization due to their conjugated double bonds. However, since methyl methacrylate consists of a tertiary carbon and ethyl acrylate consists of a secondary carbon, methyl methacrylate would form a more stable radical compared to ethyl acrylate. This explains the slightly higher value of r_2 for methyl methacrylate, as compared to the one for ethyl acrylate:

$$-\overset{\cdot\cdot}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{C}}-COCH_3 \ > \ -\overset{\cdot\cdot}{CH_2}-\overset{\cdot\cdot}{CH}-\overset{\overset{O}{\|}}{C}OCH_2CH_3$$

The obtained reactivity ratios for all copolymerization reactions in this work are compared with the literature values for the corresponding copolymers which are determined by using methods other than what we have applied in this work:[24]

Literature	Experimental
r_1 = styrene, r_2 = other	
PSMMA[32]: $r_1 = 0.39$, $r_2 = 0.22$	$r_1 = 0.31$, $r_2 = 0.23$
PSVA[32]: $r_1 = 2.87$, $r_2 = 0.12$	$r_1 = 2.74$, $r_2 = 0.10$
PSEA[33]: $r_1 = 1.01$, $r_2 = 0.16$	$r_1 = 1.66$, $r_2 = 0.11$

This indicates that the method developed in this work has a wide range of applicability to copolymeric samples.

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