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Structure-Reactivity Relations of Conjugated and Unconjugated Monomers: Acrylates and Methyl Vinyl Ketone in Copolymerization with Styrene Compared with Vinyl Esters in Copolymerization with Ethylene

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Synopsis

This article describes the copolymerization of methyl vinyl ketone (MVK), methyl acrylate (MA), and methyl methacrylate (MMA) with styrene (St) as reference monomer at 3.4 MPa and 335 K with toluene as solvent. In addition, the effect of pressure on the binary copolymerizations of St-MA-MMA is discussed. It appears that in case of conjugated monomers reactivity decreases as the electron-donating character of the substituents increases, whereas the reverse is found in unconjugated monomers. This is explained by the finding that in conjugated monomers resonance effects induced by polar factors play a dominant role, whereas in unconjugated monomers mainly polar factors are governing the relative reactivities. The r values at 3.4 MPa are compared with those predicted by means of the $Q-e$ scheme and *Patterns*. No definite conclusions could be drawn about the applicability and validity of either scheme, although *Patterns* shows excellent result in case of the H function of Mayo. In vinyl ester copolymerizations and Le Noble and Asano's example of the Menshutkin reaction one single factor (polarity and steric hindrance, successively) dominates ΔG^\ddagger , ΔG , and ΔV^\ddagger . This allows a straightforward interpretation of the results with the Hammond postulate and is in full agreement with Evan's potential-energy calculations. In conjugated monomers, however, an interplay of resonance and polar factors is found. The general validity of these findings needs further experimental and theoretical support.

INTRODUCTION

In previous articles¹⁻⁵ the effects of monomer structure, pressure, and solvent on the reactivity of a series of vinyl esters have been discussed. However, the results of these investigations raise new questions concerning the effects of the relevant variables on the reactivity of various other types of vinyl monomers and corresponding radicals.⁶ Vinyl monomers can be roughly divided into two classes: reactive (conjugated) monomers and unreactive (unconjugated) monomers. In this context, conjugated monomers are those monomers in which the double bond of the vinyl group is conjugated with another multiple bond, whereas in unconjugated monomers this type of conjugation is not present. Conjugated monomers exhibit a strong tendency to add to any radical chain end, because the resulting radical is strongly stabilized by resonance. Unconjugated monomers, on the other hand, exhibit a weaker tendency to add to any given radical, because in this case the resulting radical is much less stabilized by res-

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onance. These arguments have been graphically shown by Walling⁷ in a representation of Evan's calculations^{8,9} for systems dominated by resonance factors.

The differences in copolymerization behavior between conjugated monomers (i.e., unreactive radical and reactive monomer) and unconjugated monomers (i.e., reactive radical and unreactive monomer) find expression in various ways:

In case of vinyl esters (unconjugated monomers) reactivity appears to increase as the electron-donating character of the substituents increases,^{2,4,6} whereas the reverse is found in conjugated monomers.¹⁰⁻¹⁵

Asai and Imoto¹⁶ observed different pressure effects between systems with two conjugated monomers and binary systems in which one of the monomers is unconjugated.

The variation in r values with solvent is dependent on the nature of both monomer and corresponding radical. However, the effect of a substituent on reactivity is much greater at a radical than at a monomer. For example, the styrene macroradical is about 1000 times less reactive than the vinyl acetate radical toward a given monomer (if polar effects are of minor importance), but styrene monomer is only about 50 times more reactive than vinyl acetate monomer toward a given radical. Therefore, the extent to which a monomer and the corresponding radical, and through this the r values, are affected by the solvent will be different in conjugated and unconjugated monomers.

These observations are sufficient motives to call for the investigation of a series of conjugated monomers. In addition the comparison of the results with those obtained from the investigation of unconjugated monomers^{2,4,6} is of the utmost importance. The actual choice of the monomers was chiefly determined by the following requirements. Variation in substituents should result in a significant change in monomer reactivity, but the monomers should not be too different in reactivity in order to allow a reliable determination of r values.

As a consequence, in the present investigation monomers possessing a $C=C-C=O$ group, viz. (meth)acrylates and vinyl ketones, were chosen.

STRUCTURE-REACTIVITY RELATIONS

The free-radical copolymerization of styrene (St) with methyl methacrylate (MMA) at normal pressure has been the subject of more scientific research and publication than any other monomer pair. In 1944 Mayo and Lewis¹⁷ used this copolymerization to illustrate their derivation of the Alfrey-Mayo model. Later on, many investigators used this monomer pair to support new experimental techniques or (improved) calculation procedures for r values. This led to r values for St-MMA failing to show mutual agreement.¹⁸ The discrepancies among r values far beyond the experimental errors should serve as a warning against the casual acceptance of any single set of data. Furthermore, this points to the need for a scrutiny of the calculation procedures.

A number of (meth)acrylates and vinyl ketones have been investigated by means of copolymerization with a reference monomer.^{10-15,19} The relative reactivities toward the reference macroradical are described by the Taft relation [eq. (1)] and a modified Hammett equation derived by Yamamoto [eq. (2)].²⁰

$$\log(\text{rel. react.}) = \rho^* \sigma^* + \delta E_S \quad (1)$$

$$\log(\text{rel. react.}) = \rho \sigma + \gamma E_R \quad (2)$$

TABLE I
Copolymerization of Series of (Meth)acrylates and Vinyl Ketones with Various Reference Monomers

Type of series of monomers	Reference monomer	ρ^*	δ	ρ	γ	Reference
1 Methacrylates	Styrene	0.33	0			12
2 Methacrylates	β -Chloroethyl methacrylate	0.13	0			12
3 Methacrylates	Methyl methacrylate	ca. 0.2	0			13
4 Acrylates	Styrene	0.56	0			11
5 Vinyl ketones	Styrene	0.40	0			15
6 α -Alkyl acrylates	Styrene	0	ca. 0.6			19
7 <i>p</i> -Substituted phenyl vinyl ketones	Styrene			0.34	2.0	15
8 Nuclear-substituted phenyl methacrylates	Styrene			0.21	1.0	11

In eq. (2) σ is Hammett's polar substituent constant, E_R is the resonance substituent constant, and ρ and γ are reaction constants. The results are summarized in Table I. In most cases (1-5) the relative reactivities of these monomers toward the reference macroradical appears to be influenced exclusively by polar factors ($\delta = 0$). In the case of *p*-substituted phenyl vinyl ketones (7) and nuclear-substituted phenyl methacrylates (8), both polar and resonance effects are important in the explanation of the relative reactivities. In α -alkyl acrylates (6) it is obvious that steric hindrance plays an important role, since the alkyl group is attached directly to the reacting vinyl site.

The results obtained in the investigations of the solvent effect on copolymerizations involving acrylates and vinyl ketones are diverse and inconsistent.^{15,21-24} On increasing the polarity of the solvents, the r values may go in either direction. The apparent discrepancies between the results of these investigations may be partly due to an unreliable determination of r values. In addition, a detailed interpretation of the solvent effect is hampered by the fact that the solvent affects the reactivity of the two monomers and the two radicals at the same time. As a consequence, the overall result may vary with the solvent.

A number of copolymerizations involving (meth)acrylates and vinyl ketones have been investigated under pressure.^{16,25-32} Three models have been described for the explanation of the effect of pressure on reactivity in free-radical copolymerization.^{1,6,31,32} A model based on the $Q-e$ scheme has been developed by Jenner and Aieche.^{31,32} Furthermore, van der Meer et al.¹ proposed a simple concept based on the assumed additivity of activation volumes. Third, a new method based on the Hammond postulate has been described.⁶ However, neither method seems to be able to provide an all-inclusive interpretation of the effect of pressure on r values.⁶ This may be due to an unreliable determination of r values, the great number of monomer-solvent interactions possible, and the differences in pressure sensitivity of these interactions.

From the foregoing it may be concluded that the insufficient and even contradictory information found in the literature justifies a thorough investigation of reactivity and relations between structure and reactivity in conjugated

monomers. This article describes the investigation of copolymerizations of methyl vinyl ketone (MVK, $\text{CH}_2=\text{CH}-\text{COCH}_3$), methyl acrylate (MA, $\text{CH}_2=\text{CH}-\text{COOCH}_3$), and methyl methacrylate (MMA, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOCH}_3$) with styrene (St) as reference monomer at 3.4 MPa and 335 K with toluene as solvent. In addition, the effect of pressure on the binary copolymerizations of St-MA-MMA is discussed. Furthermore, the relations between reactivity and monomer structure are discussed and compared with those found in the homologous series of unconjugated monomers, viz. vinyl esters.^{2,4,6}

EXPERIMENTAL

Materials

The monomers styrene (Fluka), methyl vinyl ketone (Merck), methyl acrylate (BDH), and methyl methacrylate (Fluka) were distilled at reduced pressure in a nitrogen atmosphere. The middle fraction of the distillate was collected and used. In all cases the distillate was found to be >99.5% pure by GLC analysis. The free-radical initiator α, α' -azobisisobutyronitrile (Fluka, p.a.) and the solvent toluene (Merck, p.a.) were used without further purification.

Copolymerization

At all relevant pressure levels the free-radical copolymerizations were carried out at 335 K by means of the "sequential sampling" method^{6,33,34} using toluene as solvent, with total initial monomer concentration 1 mol/dm³ and initiator concentrations between 0.8 and 12.2 mmol/dm³. Monomer conversions were mostly between 10 and 20%. The monomer feed composition was determined by means of quantitative GLC. The GLC conditions were stationary phase, 10–15 wt % of squalane on chromosorb W AW DMCS 80–100 mesh (Johns Manville); column length and temperature between 360 and 380 K, depending on the binary combination involved; detector temperature 423 K. Further experimental details are given elsewhere.⁶

The r values have been evaluated by means of the VLG procedure³⁵ and the WLS method.³⁶

RESULTS

The r values of the binary copolymerizations of St-MA-MMA at various pressures and 335 K in toluene are given in Table II. As can be seen from this table, the results obtained by means of the VLG method³⁵ and the WLS method³⁶ are the same within experimental error, proving the applicability of the latter, relatively simple, pencil and paper method. The 95% confidence regions are given in Figure 1.

The r values of St-MVK at 3.4 MPa and 335 K in toluene are:

$$r_1 = 0.54 \pm 0.02, \quad r_2 = 0.22 \pm 0.01 \quad (\text{VLG method})$$

$$r_1 = 0.53 \pm 0.03, \quad r_2 = 0.22 \pm 0.01 \quad (\text{WLS method})$$

Upon applying the F test,³⁷ it was concluded that all copolymerizations could

TABLE II
 Monomer Reactivity Ratios of the Binary Copolymerizations of Styrene (St)-Methyl Acrylate (MA)-Methyl Methacrylate (MMA) in Toluene at Various Pressures
 and 335 K Resulting from the VLG³⁵ and the WLS³⁶ Methods

Pressure (MPa)	VLG method			WLS method		
	r_1	r_2	$r_1 r_2$	r_1	r_2	$r_1 r_2$
3.4	1.19 ± 0.03	0.09 ± 0.01	0.11 ± 0.04	1.20 ± 0.04	0.09 ± 0.01	0.11 ± 0.04
59	1.16 ± 0.02	0.11 ± 0.01	0.13 ± 0.03	1.12 ± 0.03	0.11 ± 0.003	0.12 ± 0.03
118	1.11 ± 0.02	0.13 ± 0.01	0.14 ± 0.03	1.10 ± 0.02	0.13 ± 0.003	0.14 ± 0.03
3.4	0.84 ± 0.02	0.36 ± 0.02	0.30 ± 0.04	0.86 ± 0.03	0.38 ± 0.02	0.33 ± 0.05
59	0.82 ± 0.02	0.39 ± 0.01	0.32 ± 0.03	0.82 ± 0.02	0.39 ± 0.01	0.32 ± 0.03
118	0.76 ± 0.01	0.41 ± 0.01	0.31 ± 0.02	0.77 ± 0.02	0.41 ± 0.01	0.32 ± 0.03
3.4	2.48 ± 0.03	0.32 ± 0.004	0.79 ± 0.03	2.42 ± 0.03	0.31 ± 0.01	0.75 ± 0.04
59	2.41 ± 0.03	0.31 ± 0.005	0.75 ± 0.04	2.36 ± 0.03	0.31 ± 0.005	0.73 ± 0.04
118	2.39 ± 0.03	0.30 ± 0.006	0.72 ± 0.04	2.40 ± 0.02	0.30 ± 0.006	0.72 ± 0.03

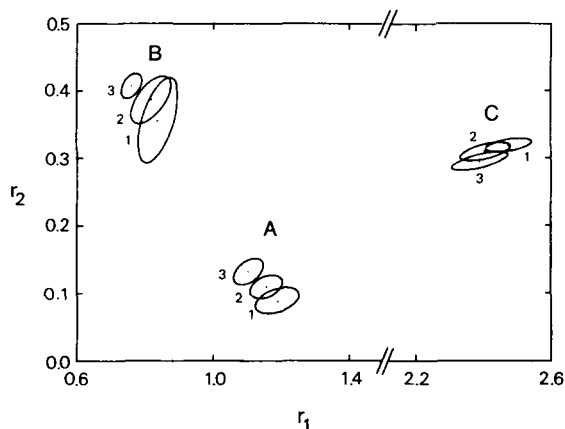


Fig. 1. 95% confidence regions for the copolymerizations of styrene-methyl acrylate (A), styrene-methyl methacrylate (B), and methyl methacrylate-methyl acrylate (C) at various pressures: 3.4 (1), 59 (2), and 118 MPa (3).

be described by the Alfrey-Mayo model. In particular, the present r values for St-MMA differ considerably from the literature values observed under comparable conditions ($0.45 < r_1 < 0.64$, $0.44 < r_2 < 0.57$).³⁸ However, the azeotropic composition, which can be calculated from the present r values [$r_1 = 0.84$, $r_2 = 0.36$; $q_{az} = (1 - r_2)/(1 - r_1) = 4$], perfectly corresponds with q_{az} directly observed from the primary experimental data.⁶ This supports our confidence in both procedures used for the calculation of r values. As a consequence, the discrepancy with literature values may be attributable to the application of unreliable experimental techniques and/or calculation procedures, or unreported differences in experimental conditions.

Table III shows the activation-volume differences of the St-MA-MMA binary copolymerizations using the r values calculated by the VLG method.

DISCUSSION

Relations between Structure and Reactivity in (Meth)acrylates and Methyl Vinyl Ketone; Comparison with Vinyl Esters

In the copolymerization of a series of monomers M_2 with a reference monomer M_1 the ratio $1/r_1$ is a direct measure of monomer reactivity. The $1/r_1$ values of

TABLE III
Activation Volume Differences of Binary Copolymerizations of Styrene (St)-Methyl Acrylate (MA)-Methyl Methacrylate (MMA) in Toluene (Pressure Range 3.4-118 MPa)

Monomer combination (1)-(2)	$\Delta V_{11}^\# - \Delta V_{12}^\# = A$	$\Delta V_{22}^\# - \Delta V_{21}^\# = B$
St-MA	2.0 ± 0.3^a	-8 ± 2^a
St-MMA	2.0 ± 0.5	-2.8 ± 0.5
MMA-MA	0.9 ± 0.2	1.8 ± 0.3

^a Estimated standard deviation.

TABLE IV
 Reactivity of Methyl Vinyl Ketone, Methyl Acrylate, and Methyl Methacrylate toward the Styrene Macroradical and the Reactivity of a Homologous Series of Vinyl Esters toward the Ethylene Macroradical^a

	$\begin{array}{c} \text{R}_1 \quad \text{O} \\ \quad \\ \text{CH}_2=\text{C}-\text{C}-\text{R}_2 \end{array}$			$\begin{array}{c} \text{O} \\ \\ \text{CH}_2=\text{CH}-\text{O}-\text{C}-\text{R} \end{array}$		
	R ₁	R ₂	1/r ₁ ^b	R	1/r ₁ ^c	
MVK	H	CH ₃	1.89	VAc	CH ₃	1.35
MA	H	OCH ₃	0.85	VP	CH ₂ (CH ₃)	1.48
MMA	CH ₃	OCH ₃	1.19	ViB	CH(CH ₃) ₂	1.64
				VPV	C(CH ₃) ₃	1.55

^a All copolymerizations at 3.4 MPa and 335 K.

^b Solvent toluene.

^c Solvent *tert*-butyl alcohol.

the copolymerizations of MVK, MA, and MMA with St, together with the results of the copolymerization of the homologous series of vinyl esters with ethylene as reference monomer,² are given in Table IV. When the CH₃ group in MVK is replaced by the more electron-donating OCH₃ group, a decrease in monomer reactivity is observed. The greater reactivity of MMA than MA may be explained by hyperconjugation of the methyl group with the double bond. The results fit in well with the generally observed behavior of monomers possessing a C=C—C=O group.^{10-15,19} In most cases the relative reactivities are correlated with the Taft polar substituent constants of the monomers, as can be seen from Table I. The results may be explained by greater polarization of the carbonyl group with increasing electron-donating ability of the substituent attached to the alkyl C atom next to the group. As a result, the conjugation of the vinyl group with the carbonyl group is decreased, so reducing the reactivity. Thus, in contrast to the vinyl esters a decreasing reactivity occurs despite the increasing electron density on the vinyl group. As a consequence, it may be concluded that resonance factors are of major importance in the relative reactivities of (meth)acrylates and vinyl ketones. However, according to Otsu and Tanaka,¹⁵ the values of the resonance substituent constants E_R of alkyl vinyl ketones are very close to each other, making it difficult to differentiate between the resonance effects pertaining to the various substituents. The reason for this apparent contradiction is not clear.

On the other hand, if only resonance effects were the determining factor in the copolymerization of St (1) and MMA (2),

$$r_1 = [\text{St} \cdot + \text{St}](k_{11})/[\text{St} \cdot + \text{MMA}](k_{12}),$$

$$r_2 = [\text{MMA} \cdot + \text{MMA}](k_{22})/[\text{MMA} \cdot + \text{St}](k_{21})$$

r_1 (k_{11}/k_{12}) would be greater than 1 and r_2 (k_{22}/k_{21}) would be less than 1. The propagation reactions involving St monomer (with rates k_{11} and k_{21}) would be faster than the corresponding reactions involving MMA monomer (with rates k_{12} and k_{22}), because the resulting macroradical is more stabilized by resonance. However, the observed r_1 value for St-MMA is less than 1 (Table II), pointing to the role of polar factors as well in the propagation rates. The St-MVK copolymerization shows similar behavior, whereas for St-MA r_1 is slightly above

1. However, it still may be inferred that also in the latter system polarity affects reactivity. Therefore, it must be concluded that in *conjugated* monomers the activation energy and pertaining reaction rate constants are affected both by resonance and polar factors.

In the other type of system, viz. the *unconjugated* monomers, reactivity is mainly governed by polar factors. The reactivity of the homologous series of vinyl esters toward both the ethylene macroradical² and the vinyl acetate⁴ macroradical appears to be a function of the electron density on the double bond. By means of the *Q-e* scheme³⁹ (mindful of the limits of its validity, i.e., $r_1 r_2 < 1$), it was found that the amount of resonance stabilization remains the same and that the electron density on the double bond increases with increasing electron-donating character of the substituents. Furthermore, the vinyl ester reactivity order is susceptible to the polar character of the reference macroradical, which may be concluded from the fact that the reaction constant ρ^* may be both positive and negative.² In the case of conjugated monomers the reactivity order remains the same toward any macroradical; ρ^* is positive (Table I) regardless of the nature of the macroradical. This supports the suggestion that in the case of conjugated monomers mainly resonance factors and to a lesser degree polar factors are important in the interpretation of the relative reactivities.

From Table IV it might be inferred that conjugated and unconjugated monomers have comparable reactivities, whereas it is stated above that conjugated monomers are much more reactive than unconjugated monomers toward any macroradical. This apparent contradiction originates from the fact that the information obtained by means of copolymerization is restricted to the *relative* reactivity of two monomers with respect to the same macroradical. In Table IV the binary systems contain reacting species which are either all conjugated or all unconjugated, and this explains the apparent similarity in the reactivities when the systems are compared.

Various attempts have been made to describe the reactivity of *individual* monomers and corresponding radicals by characteristic constants enabling a reliable description of structure-reactivity relations, which furthermore would permit a prediction of copolymerization behavior. The *Q-e* scheme³⁹ may be useful in this respect because it is the most widely used scheme, whereas the *Patterns* method^{40,41} inherently provides a better approach to reactivity. The latter is achieved by using only experimentally accessible parameters and the assignment of different polarity parameters to radicals and monomers. The difference between the *Q-e* scheme and *Patterns* was decisively shown by Jenkins⁴¹ in a comparison of the value of the *H* function of Mayo⁴² experimentally observed and calculated by means of both schemes. The observed values correlated well with those calculated by means of *Patterns*, whereas the *Q-e* scheme completely failed to cope with the situation.

In Table V the presently observed *r* values are compared with those calculated according to both schemes. The *Q* and *e* values given by Greenley⁴³ have been used. This author claims the calculation of more precise values of *Q* and *e* by the application of a roundabout least-squares technique applied to practically all the *r* values relevant to a selection of vinyl monomers. However, from Table V no definite conclusions can be drawn about the validity of either scheme for the prediction of individual *r* values. On the other hand, the correspondence between the experimental value of the *H* function of Mayo and the value calcu-

TABLE V

Monomer Reactivity Ratios of the Binary Copolymerizations of Styrene (St)–Methyl Acrylate (MA)–Methyl Methacrylate (MMA) Calculated by the *Q-e* Scheme³³ and the *Patterns* Method⁴⁰ Together with the *r* Values Observed at 3.4 MPa and 335 K with Toluene as Solvent

Binary combination		<i>Q-e</i>	<i>Patterns</i>	Experimental
St-MA	r_1	0.70	0.42	1.19
	r_2	0.18	0.10	0.09
St-MMA	r_1	0.49	0.86	0.84
	r_2	0.48	0.43	0.36
MMA-MA	r_1	1.91	1.32	2.48
	r_2	0.49	0.42	0.32

lated by means of *Patterns* appears to be excellent, as can be seen in Table VI. The better fit of *H* as compared to the individual *r* values found by using *Patterns* may be due to the effect of solvent on the various propagation reactions in the St-MA-MMA system. In this manner the overall result might be that *H* becomes independent of solvent.

The investigation of the solvent effect on reactivity ratios in free-radical copolymerization requires the use of comonomers such as, for instance, Eth, the reactivity of which is unaffected by the nature of the solvent.⁵ However, the reactivities of Eth with (meth)acrylates and vinyl ketones are too disparate to allow a reliable determination of *r* values. Therefore, as also appears from a review by Madruga et al.,²⁴ the results of investigations of the solvent effect on the reactivity of (meth)acrylates and vinyl ketones should be interpreted with great care.

Effects of Pressure on the St-MA-MMA System

As has been shown by the experiments discussed above, the *relative* reactivities of conjugated monomers appear to be influenced by resonance effects induced by polar factors. Moreover, the height of the activation energy barriers in the various addition reactions, and with that the *absolute* magnitude of the *r* values, are a function of polar *and* resonance factors. On the other hand, the sign of the activation volume differences *A* and *B* for St-MA and St-MMA given in Table III show the more exothermic reactions, forming the more stable St macroradical, to be accompanied by a less negative activation volume (earlier transition state) as required by the Hammond postulate. This is in full agreement with the potential-energy calculations of Evans.^{8,9} Thus, on going from the transition state to the final state the gain in resonance stabilization gradually becomes the more important factor.

To summarize, in the copolymerization of St with (meth)acrylates and vinyl ketones the *height* of the activation energy barrier, and with that the *r* values,

TABLE VI
H Factor According to Mayo⁴² for St-MA-MMA Binary Copolymerizations

	<i>Q-e</i>	<i>Patterns</i>	Experimental
<i>H</i>	1 (by definition)	0.7	0.7 ± 0.1

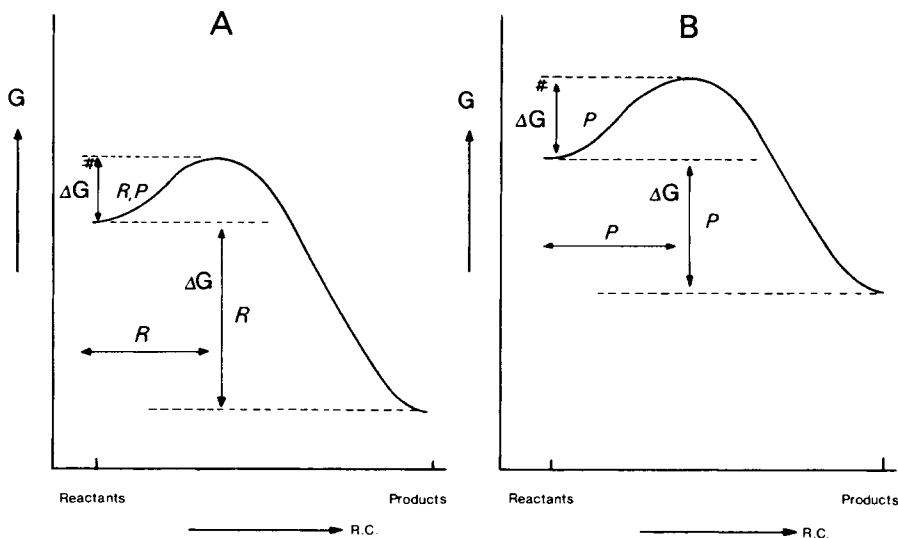


Fig. 2. Factors affecting the various processes on going from the initial state to the final state for copolymerizations involving conjugated (A) and unconjugated monomers (B); R : (mainly) resonance factors, P : (mainly) polar factors.

are governed by *resonance and polar* factors. Furthermore, the *location* of the transition state on the reaction coordinate, and with that the activation volume, is mainly governed by *resonance* factors [Fig. 2(A)]. In other words, in conjugated monomers a more exothermic reaction has a less negative activation volume, but there is not a clear correlation with the activation energy.

A different situation occurs when considering unconjugated monomers, viz. vinyl esters, where the absolute magnitude of the r values as well as the magnitude of the activation volume are a function of polar factors.^{2,6} Thus it can be inferred that the behavior of these unconjugated monomers is a straightforward demonstration of the Hammond postulate since in this case the process of going from the initial state to the transition state (in terms of ΔG^\ddagger and ΔV^\ddagger) as well as the process of going from the initial to the final state (in terms of ΔG) are affected by polar factors in the same manner [Fig. 2(B)]. In this way activation energy, activation volume, and exothermicity are directly related. This is comparable with the results of Le Noble and Asano's example⁴⁴ of the Menschutkin reaction, where the correlation of ΔG^\ddagger , ΔG , and ΔV^\ddagger , in terms of the Hammond postulate, develops because the steric effect is dominant.

An equally straightforward interpretation is not possible for the St-MA and St-MMA systems, in which the activation volume correlates as expected with the exothermicity, but not with the activation energy. This is a partial deviation from the Hammond postulate, in the form in which it was expressed by Le Noble and Asano,⁴⁴ but the evidence discussed above concerning the role of resonance and polar factors is considered to support the possibility that the postulate can be refined and extended to include the more complex behavior of systems in which reactivity is not dominated by a single factor (e.g., polarity, resonance stabilization, or steric hindrance). This requires adoption of the principle that the Hammond postulate remains valid in comparisons of those features of the reaction processes which are governed by similar reactivity factors. In these

conjugated systems it appears that the activation volume and the reaction ΔG are dominated by resonance factors, while the height of the activation energy barrier is determined by both polar and resonance factors. A modified Hammond postulate might thus account for the experimental result that ΔV^\ddagger and the exothermicity show a correlation, while ΔV^\ddagger and the reaction rates (r values) do not. Confirmation of the extended postulate will require further experimental evidence.

It may indeed be expected that in case of the copolymerization of monomers exhibiting relatively small differences in resonance factors, as e.g., MMA-MA, the polar effects will show up more strongly, and a possible dominance of either effect may not be distinguishable as clearly as in the St-MA and St-MMA systems. This is confirmed by the results of the MMA-MA copolymerization (Table III), where a more stable radical only gives rise to an earlier transition state with the MMA macroradical ($\Delta V_{\ddagger 1}^\ddagger - \Delta V_{\ddagger 2}^\ddagger = +0.9 \pm 0.2 \text{ cm}^3/\text{mol}$), but where the contrary is observed with respect to the MA macroradical ($\Delta V_{\ddagger 2}^\ddagger - \Delta V_{\ddagger 1}^\ddagger = +1.8 \pm 0.3 \text{ cm}^3/\text{mol}$).

In conclusion, we may summarize the present results as follows. In the vinyl ester copolymerization we have shown that polar factors predominate in ΔG^\ddagger , ΔG , and ΔV^\ddagger , whereas in an example of the Menshutkin reaction⁴⁴ the steric effect is dominant. Both investigations have in common that one single factor governs all features of the reaction process. This allows a straightforward interpretation of the results in terms of the Hammond postulate and is in full agreement with Evan's potential-energy calculations.^{8,9} In our study on conjugated monomers, however, an interplay of resonance and polar factors in ΔG^\ddagger , ΔG , and ΔV^\ddagger is found. This indicates an interesting line of development which needs a considerably broader experimental basis as well as an extended theoretical treatment, e.g., the modification of Evans's calculations to incorporate polar, steric, and resonance effects.

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