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THE COPOLYMERIZATION EQUATION FOR BINARY SYSTEMS INCLUDING ACETYLENIC COMONOMER

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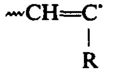
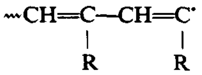
Abstract—An investigation has been made of the mechanism of binary copolymerizations involving an acetylenic monomer. A special copolymerization equation is proposed. It takes into account the difference between the reactivities of the macroradicals



$$\sim CH{=}\underset{R}{\underset{|}{C^{\bullet}}}$$

and



$$\sim CH{=}\underset{R}{\underset{|}{C}}{-}CH{=}\underset{R}{\underset{|}{C^{\bullet}}}$$

Analysis of this equation showed that the values of the monomer reactivity ratios (r_M) calculated from the new equation and from the conventional one should be close while the r_X ratios should be different. The new equation makes it possible to find with greater precision the monomer reactivity ratios for systems under consideration; this is particularly important for comparing the reactivities of monomers and polymer radicals in copolymerization.

IN RECENT years great attention has been paid to the synthesis of polymers with conjugated bonds, by radical or ionic polymerization of acetylenic compounds. Nevertheless, acetylenic hydrocarbons have not been studied intensively as monomers in radical copolymerization. In copolymerizations with vinyl monomers, the acetylenic comonomer retards the polymerization. When its concentration in the reaction mixture exceeds 50 per cent, the copolymerization is almost completely inhibited. In contrast, when the percentage of acetylenic comonomer in the initial mixture is low (5–20 mole per cent), copolymers may be obtained with a considerable conversion and fairly high molecular weight;(1,2) they exhibit greater thermostability than homopolymers of the corresponding vinyl monomers.(3) This is probably due to the inhibition of thermal depolymerization, resulting from the stability of radicals formed from the units of the acetylenic comonomer.

Evidently, this behaviour of acetylenic compounds in radical copolymerization is not associated with the different reactivities in the chain propagation reactions of vinyl and ethynyl groups conjugated with the same structural elements. In fact, the characteristics of conjugation of these two monomer types, which to a large extent determine their reactivity, should be fairly close to each other. Table 1 shows that conjugated acetylenic monomers differ little from their vinyl analogues in the refractometric characteristic of conjugation $\Delta R^0{}_D$.*

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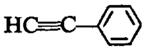
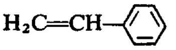
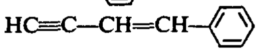
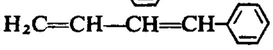
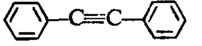
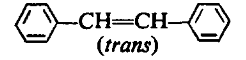
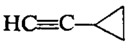
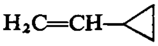
* The refractometric characteristic of conjugation is regarded as exaltation of molecular refraction determined from the new additive scheme.(4,5)

TABLE 1. EXALTATIONS OF CONJUGATED ACETYLENIC AND VINYL MONOMERS(5)

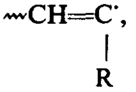
Acetylenic monomer	Mol. refr. $R^{20}_{D_{obs}}$ (cm³)	$R^{\circ}_{D_{add}}$ (cm³)	$\Delta R_D/\Delta R^{\circ}_D$ (cm³)	Vinyl monomer	Mol. refr. $R^{20}_{D_{obs}}$ (cm³)	$R^{\circ}_{D_{add}}$ (cm³)	ΔR^0_D (cm³)
	34·97	32·51	2·46		36·44	34·34	2·10
	46·24	41·09	5·15		48·4	42·92	5·5
	—	—	4·5*		47·37	42·92	4·45
	64·3	56·19	8·1	 (*trans*)	65·9	58·02	7·9
HC≡C—C≡CH	17·88	15·58	2·30	H₂C=CH—CH=CH₂	21·11	19·24	1·87
	21·74(6)	20·68	1·06		23·597(7)	22·507	1·09

* Exaltation ΔR^0_D is calculated from the equation: (3) $\Delta R^0_D = 0{\cdot}752n - 3{\cdot}05$, where n is quantity of conjugated bonds in the molecule; thus for benzene, styrene and *p*-diethynylbenzene the values of n are 6, 8 and 10, respectively.

Hence, the behaviour of conjugated acetylenic compounds in radical copolymerization which greatly distinguishes them from the behaviour of vinyl monomers (styrene, methylmethacrylate, etc.) may be associated only with the reactivity of radicals formed in the chain propagation reaction.

DIFFERENCES IN BEHAVIOUR OF VINYL AND ACETYLENIC MONOMERS IN COPOLYMERIZATION

The main difference between vinyl and acetylenic monomers is that the acetylenic comonomer adding to the growing polymer chain is converted into a stable radical



$$\sim\!\!\sim CH{=}\underset{\displaystyle R}{\underset{|}{C}}^{\cdot},$$

which retards the polymerization. When a second acetylenic monomer is added, a still more conjugation-stabilized radical

$$\sim\!\!\sim CH{=}\underset{\displaystyle R}{\underset{|}{C}}{-}CH{=}\underset{\displaystyle R}{\underset{|}{C}}^{\cdot}$$

is formed (the penultimate unit effect). Analysis of the electronic absorption spectra(1,2) of copolymers of arylacetylenes with vinyl monomers shows that sequences containing more than two units of acetylenic comonomer are very rare. Evidently, the addition of a third acetylenic comonomer leads to chain termination. Chain regeneration is possible only when the vinyl monomer is attacked by the macroradical.

SPECIAL COPOLYMERIZATION EQUATION FOR BINARY SYSTEMS INCLUDING ACETYLENIC COMONOMER

Because of the peculiarities in the copolymerization behaviour of acetylenic compounds, use of the conventional copolymerization equation

$$\frac{(m)}{(x)} \approx \frac{\mathrm{d}M}{\mathrm{d}X} = \frac{(M)}{(X)}\,\frac{r_M\,(M)+(X)}{r_x\,(X)+(M)} \tag{1}$$

based on four elementary chain propagation reactions[8,9] leads to considerable errors in reactivity ratios.

In deriving the copolymerization equation for binary systems including an acetylenic comonomer, it is necessary and sufficient to consider the following 5 elementary propagation reactions

$$M^{\cdot} + M \xrightarrow{k_{MM}} M^{\cdot} \quad v_{MM} = k_{MM}(M^{\cdot})(M) \tag{2}$$

$$M^{\cdot} + X \xrightarrow{k_{MX}} X^{\cdot} \quad v_{MX} = k_{MX}(M^{\cdot})(X) \tag{3}$$

$$X^{\cdot} + M \xrightarrow{k_{XM}} M^{\cdot} \quad v_{XM} = k_{XM}(X^{\cdot})(M) \tag{4}$$

$$X^{\cdot} + X \xrightarrow{k_{XX}} XX^{\cdot} \quad v_{XX} = k_{XX}(X^{\cdot})(X) \tag{5}$$

$$XX^{\cdot} + M \xrightarrow{k_{XXM}} M^{\cdot} \quad v_{XXM} = k_{XXM}(XX^{\cdot})(M) \tag{6}$$

where M and X represent the vinyl and acetylenic monomers respectively and $M^{\cdot}$, $X^{\cdot}$ and $XX^{\cdot}$ the radicals formed from them; v and k are the rates and rate constants of the growth reactions.

Reaction (6) is included to take into account the difference between the reactivities of radicals $\sim\!\!\sim X^{\cdot}$ and $\sim\!\!\sim XX^{\cdot}$.

At low conversions, monomer consumption in the copolymerization can be found from the equations:

$$(m) \sim -\frac{\mathrm{d}M}{\mathrm{d}t} = k_{MM}\,(M^{\cdot})\,(M) + k_{XM}(X^{\cdot})\,(M) + k_{XXM}\,(XX^{\cdot})\,(M) \tag{7}$$

$$(x) \sim -\frac{\mathrm{d}X}{\mathrm{d}t} = k_{XX}(X^{\cdot})\,(X) + k_{MX}\,(M^{\cdot})\,(X). \tag{8}$$

Division of Eqn. (7) by Eqn. (8) gives:

$$\frac{(m)}{(x)} \approx \frac{\mathrm{d}M}{\mathrm{d}X} = \frac{k_{MM}\,(M^{\cdot})\,(M) + k_{XM}\,(X^{\cdot})\,(M) + k_{XXM}\,(XX^{\cdot})\,(M)}{k_{XX}\,(X^{\cdot})\,(X) + k_{MX}\,(M^{\cdot})\,(X)} \tag{9}$$

The steady-state equations for radicals $M^{\cdot}$, $X^{\cdot}$ and $XX^{\cdot}$ can be represented thus:

For $M^{\cdot}$: $k_{XM}(X^{\cdot})(M) + k_{XXM}(XX^{\cdot})(M) = k_{MX}(M^{\cdot})(X)$ (10)

For $X^{\cdot}$: $k_{MX}(M^{\cdot})(X) = k_{XM}(X^{\cdot})(M) + k_{XX}(X^{\cdot})(X)$ (11)

For $XX^{\cdot}$:* $k_{XX}(X^{\cdot})(X) = k_{XXM}(XX^{\cdot})(M)$. (12)

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* Eqn. (12) may be obtained by summing Eqns. (10) and (11).

We obtain from Eqn. (11) the expression for $(M^{\cdot})$:

$$(M^{\cdot}) = \frac{k_{XM}\,(X^{\cdot})\,(M) + k_{XX}\,(X^{\cdot})\,(X)}{k_{MX}\,(X)}. \tag{13}$$

From Eqns. (9), (12) and (13) we obtain

$$\frac{(m)}{(x)} = \frac{r_x\dfrac{(X)}{(M)} + r_X r_M + r_M\dfrac{(M)}{(X)} + 1}{2r_X\dfrac{(X)}{(M)} + 1} \tag{14}$$

where $$r_M = \frac{k_{MM}}{k_{MX}};\ r_X = \frac{k_{XX}}{k_{XM}}.$$

If $(M)/(X) = F$ and $(m)/(x) = f$, we have

$$f = \frac{(r_X + F)\,(r_M F + 1)}{2r_X + F} \tag{14a}$$

or

$$r_M = \frac{r_X(2f - 1) + F(f - 1)}{F(F + r_X)}. \tag{14b}$$

In deriving Eqn. (1), it is assumed that the reactivity of a macroradical does not depend on the penultimate unit, i.e. Eqn. (1) is valid only if the reactivities of macroradicals $\sim MM^{\cdot}$ and $\sim XM^{\cdot}$, and those of $\sim MX^{\cdot}$ and $\sim XX^{\cdot}$ are equal. Nevertheless, as noted above, in the case under consideration the reactivities of the macroradicals $\sim MX^{\cdot}$ and $\sim XX^{\cdot}$ differ greatly. This fact was taken into account in deriving a new Eqn. (14): for the elementary reactions (4) and (6), k_{XM} is not equal to k_{XXM}.

COMPARISON OF RESULTS OBTAINED FROM A SPECIAL EQUATION AND THE USUAL COPOLYMERIZATION EQUATION

Comparing Eqn. (1) and (14) applied to the system under consideration, it should be borne in mind that $(X^{\cdot})$ [in the derivation of Eqn. (1)] is virtually the sum $(X^{\cdot}) + (XX^{\cdot})$ [in the derivation of Eqn. (14)]. Hence, k_{XM} [Eqn. (4)] and k_{XX} [Eqn. (5)] differ from the corresponding constants used in deriving Eqn. (1). Elementary reactions (2) and (3) in both kinetic schemes are identical. Consequently, the monomer reactivity ratios r_M determined from Eqns. (1) and (14) should coincide and the ratios r_X should be different.

Table 2 gives a comparison of the monomer reactivity ratios calculated from the new and the conventional copolymerization equations, using the same experimental data.

The table shows that the r_M values calculated from the two equations are similar and the r_X values differ greatly, in agreement with the above considerations.

TABLE 2. MONOMER REACTIVITY RATIOS CALCULATED FROM A SPECIAL EQUATION AND THE USUAL COPOLYMERIZATION EQUATION

Binary system		From special equation (14)		From usual equation (1)		
Vinyl comonomer,* M	Acetylenic comonomer,* X	r_M	r_X	r_M	r_X	Ref.
MA	PhA	0·65 ± 0·02	0·47 ± 0·1	0·62 ± 0·02	0·27 ± 0·04	8
MMA	PhA	0·85 ± 0·1	0·05	0·81 ± 0·1	—	1
AN	PhA	0·30 ± 0·02	0·69 ± 0·04	0·26 ± 0·03	0·33 ± 0·05	8
St	PhA	0·36 ± 0·04	0·84 ± 0·1	0·34 ± 0·03	0·36† ± 0·02	1
St	*p*-DEB	1·15 ± 0·1	0·87 ± 0·1	1·18 ± 0·1	0·74 ± 0·02	2
MMA	*p*-DEB	0·60 ± 0·1	—	0·606 ± 0·15	—	2
2-VP	PhA	4·0 ± 0·2	0·32 ± 0·15	4·0 ± 0·7	0·2 ± 0·05	9

* MA—methyl acrylate, PhA—phenylacetylene, AN—acrylonitrile, St—styrene, MMA—methyl methacrylate, *p*-DEB—*p*-diethynylbenzene, 2-VP—2-vinylpyridine.

† Calculated from the data of Uzbekova *et al.*(1,2)

Figure 1 presents an example of graphical determination (the intersection method of Mayo and Lewis(10)) of the monomer reactivity ratios r_M and r_X from the new Eqn. (14) for the binary system 2-vinylpyridine (M)-phenylacetylene (X).(9) The curvature of the lines corresponding to experimental results increases with the proportion of the acetylenic component in the initial mixture.

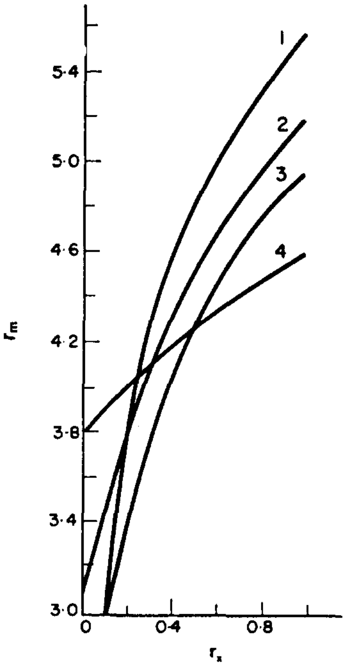

FIG. 1. Graphical determination of the monomer reactivity ratios r_M and r_X by the intersection method for the binary system(9) 2-vinylpyridine (M)-phenylacetylene (X) on the basis of Eqn. (14). The values of F and f for experiments are respectively: (1) 0·393; 1·857; (2) 0·538; 2·226; (3) 1·012; 4·181; (4) 4·000; 16·241.

CONCLUSION

The proposed Eqn. (14) allows determination with greater precision of the monomer reactivity ratios in systems including an acetylenic comonomer. This is of great importance for comparing the reactivities of monomers and radicals in copolymerizations.

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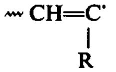
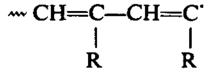
Résumé—On a étudié le mécanisme des copolymérisations binaires impliquant un monomère acétylénoque On propose une équation spéciale de copolymérisation qui tient compte de la différence de réactivités des deux macroradicaux



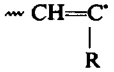
$$\sim CH{=}\underset{\substack{|\\R}}{C}{}^{\cdot}$$



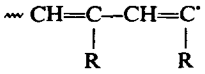
$$\sim CH{=}\underset{\substack{|\\R}}{C}{-}CH{=}\underset{\substack{|\\R}}{C}{}^{\cdot}$$

Une analyse de cette équation montre que les valeurs des rapports de réactivités de monomères (r_M) calculées à partir de la nouvelle équation et à partir de l'équation conventionnelle pourront être voisines, tandis que les rapports r_X seront différents. La nouvelle équation permet de trouver avec une plus grande précision, les rapports de réactivité des monomères pour les systèmes considérés; ceci est particulièrement important pour comparer les réactivités des rédicaux des monomères et du polymère dans la copolymérisation.

Sommario—Si è condotta un'indagine sul meccanismo delle copolimerizzazioni binarie riguardo un monomero acetilenico. Si propone una speciale equazione di copolimerizzazione, che tiene conto della differenza di reattivatà dei macroradicali:



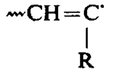
$$\sim CH{=}\underset{\substack{|\\R}}{C}{}^{\cdot}$$



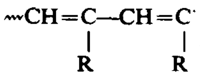
$$\sim CH{=}\underset{\substack{|\\R}}{C}{-}CH{=}\underset{\substack{|\\R}}{C}{}^{\cdot}$$

L'analisi di tale equazione ha mostrato che i valori dei rapporti di reattività del monomero (r_M) calcolati partendo dalla nuova equazione e da quella convenzionale, dovevano essere vicini, mentre i rapporti r_X differenti. La nuova equazione rende possibile trovare con grande precisione i rapporti di reattività del monomero per i sistemi presi in considerazione, ciò che è particolarmente importante per mettere a raffronto la reattività dei monomeri e dei radicali di polimeri durante la copolimerizzazione.

Zusammenfassung—Es wurde eine Untersuchung durchgefürht über den Mechanismus von binären Copolymerisationen unter Beteiligung eines acetylenischen Monomeren. Eine spezielle Gleichung für die Copolymerisation wird vorgeschlagen. Sie berücksichtigt den Unterschied zwischen den Reaktivitäten der Makroradikale



$$\sim CH{=}\underset{\overset{|}{R}}{C^{\cdot}}$$



$$\sim CH{=}\underset{\overset{|}{R}}{C}{-}CH{=}\underset{\overset{|}{R}}{C^{\cdot}}$$

Eine Analyse dieser Gleichung zeigte, daß die Werte der Monomer-Reaktivitätsverhältnisse (r_M), berechnet nach der neuen Gleichung und nach der konventionellen, nahe beieinander liegen sollten, während die r_x Verhältnisse verschieden sein sollten. Nach der neuen Gleichung ist es mögliche, die Monomer-Reaktivitätsverhältnisse für die betrachteten Systeme mit größerer Genauigkeit festzustellen; dies ist besonders wichtig für einen Vergleich der Reaktivitäten der Monomeren und der Polymerradikale bei Copolymerisationen.