Polymer Bulletin 2, 63–69 (1980)

Polymer Bulletin

A Critical Reevaluation of Reactivity Ratio Data in Radical Copolymerization of Acetylene Monomers

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SUMMARY

Using the copolymerization equation proposed by Kelen and Tüdös, 25 radical copolymerization systems implying acetylenic and vinylic monomers were reexamined. Of these, only 12 can be characterized by the usual terminal copolymerization model. 5 systems present high scattering of experimental data given by the original authors; 2 systems belong to another copolymerization mechanism, and 6 give meaningless reactivity ratio values. The copolymerization equation proposed by Zaitsev et al. for radical copolymerization of acetylenic monomers could not be accepted.

INTRODUCTION

Recently, Kelen and Tüdös proposed a linear method for precise determination of reactivity ratio values (r_1 and r_2) in binary copolymerization. The method also verifies the validity of the terminal copolymerization mechanism [1]. The equation of Kelen and Tüdös (KT) was used for a critical reexamination of carbocationic copolymerization data [2,3].
The aim of this note is to reexamine most of reactivity ratio data for radical copolymerization of acetylenic monomers using the KT equation. As in the paper of Kennedy, Kelen and Tüdös [2], the analysed systems are grouped into three classes : (I) the conventional copolymerization equation adequately describes the mechanism; (II) the simple terminal mechanism does not properly characterize the system and the r_1 and r_2 values given by the authors are false; (III) the recalculated reactivity ratio values are negative and have, therefore, no physical significance. The data obtained in our paper are compared with those obtained by Zaitsev et al. [4,5], according to their equation for radical copolymerization of acetylenic monomers.

0170-0839/80/0002/0063/$01.40

CALCULATION METHOD

The reactivity ratio values were recalculated using the original data given by different authors, through the equation :

$$\eta = (r_1 + r_2/\alpha)\,\xi - r_2/\alpha \qquad \text{where :}$$

$$\eta = \frac{x(y-1)}{\alpha y + x^2};\quad \xi = \frac{x^2}{\alpha y + x^2};\quad \alpha = (x_{min}x_{max})/(y_{min}y_{max})^{1/2}$$

$x = [M_1]/[M_2]$ (the initial feed molar ratio) and

$y = d[M_1]/d[M_2]$ (the structural units molar ratio in copolymer). For the monomers having two identical reactive groups (Nos. 20 and 21, Table 1) $x = 2[M_1]/[M_2]$ [6]. For the other bifunctional monomers, the authors showed that only one of the functional groups participated in copolymerization. The KT straight line was obtained by a least square error algorithm (Gauss) on a JEC-6 computer.

RESULTS AND DISCUSSION

The recalculated reactivity ratio values are given in Table 1. Of the 25 recalculated systems, only 12 can be considered to belong to class I; 5 systems present high scattering of the experimental points (class I!); 2 systems can not be characterized by the simple terminal mechanism (class II), and 6 systems give meaningless reactivity ratio values (class III). Examples of the three classes are given in Figure 1. Figure 1b also represents, together with the η versus ξ plot for the r_1 and r_2 given by authors and recalculated by KT equation, the straight line corresponding to the r_1 and r_2 values recalculated by Zaitsev et al. with the equation they proposed [4]. As shown in the figure, this system can be characterized by the simple terminal mechanism. Therefore, the equation proposed by Zaitsev et al., which is based on the greater reactivity of the -CH=RC• macroradicals than the -CH=RC-CH=RC• ones (penultimate effect given by conjugation stabilization), cannot be accepted, especially because the Zaitsev straight line significantly differs from the KT one. Similar discrepancies are observed for all systems recalculated by Zaitsev et al. (Nos. 8-12 and 20-21, Table 1). It is known [4,11,15] that sequences having more than two arylacetylenic structural units are very rare in the copolymers with vinylic monomers. This fact was thought to be due to the chain interruption through a conjugation stabilized macroradical (inactive) having three arylacetylenic structural units. Recent results show, however, that intramolecular interruption in arylacetylene polymerization (radical and coordinative, also) appears from the intramolecular cyclization reaction of the

cis-polyarylacetylenic chain giving an inactive cyclohexadiene-type radical [18,19]. This reaction is possible in sequences having at least three arylacetylenic structural units. In these conditions, the increase of the macroradical reactivity :
$-(CH{=}RC)_2{-}CH{=}RC^\bullet < -CH{=}RC{-}CH{=}RC^\bullet < -CH{=}RC^\bullet$
does not change the terminal copolymerization mechanism, because the data given in literature verify the KT equation. Furthermore, Zaitsev et al. do not have experimental proofs (composition or sequence distribution)for the higher precision of their reactivity ratio values.

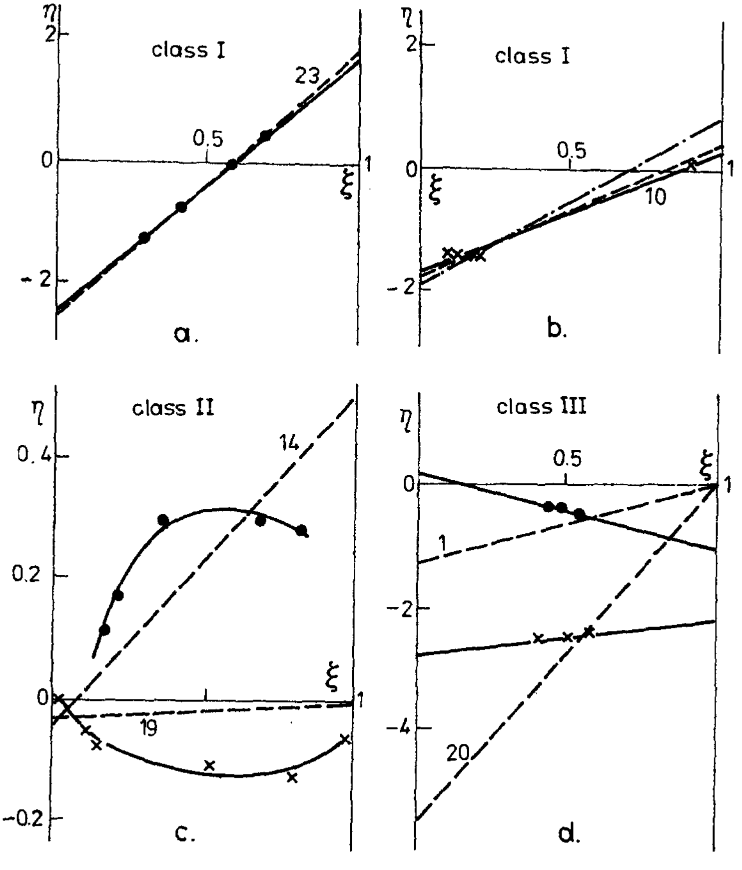

Figure 1. η vs. ξ for typical systems of Table 1.
a. 23(a = 1.29) b. 10(a = 0.19) c. 14(a = 0.96)and 19(a = 45.42) d. 1(a = 9.04) and 20(a = 0.11).
----- r_1 and r_2 values given by the authors
——— KT equation
—·—·— r_1 and r_2 recalculated by Zaitsev et al.

TABLE 1.
Reactivity ratio values

No.	Monomer pair	Initiator/solvent/temp °C	Data by original authors r_1	Data by original authors r_2	Reference	Recalculated data r_1	Recalculated data r_2	Class
1.	nBuA - MA	BP/bulk/60	0	11.2 ± 2	6	-	-	III
2.	nBuA - AN	BP/bulk/60	0	5.4 ± 0.3	6	-	-	III
3.	VA - AN	AIBN/bulk/60	0.60 ± 0.02	0.13 ± 0.01	7	0.70	0.16	I!
4.	IPA - AN	"	0.47 ± 0.01	0.33 ± 0.01	7	0.53	0.32	I!
5.	IPA - 2VPy	"	0.55 ± 0.01	1.65 ± 0.05	7	0.55	1.85	I!
6.	PA - VC	AIBN/THF/70	1.0	2.3	8	-	-	III
7.	PAl - S	AIBN/bulk/60	0.21	0.32	9	0.28	0.34	I
8.	PhA - MA	BP/bulk/60	0.27 ± 0.04	0.62 ± 0.02	6	0.29	0.64	I
8a.	"	"	0.47 ± 0.1	0.65 ± 0.02	4			
9.	PhA - MM	AIBN/bulk/60	-	0.81 ± 0.1	10	-	-	III
9a.	"	"	0.05	0.85 ± 0.1	4			
10.	PhA - S	"	0.36 ± 0.02	0.34 ± 0.03	10	0.33	0.33	I
10a.	"	"	0.84 ± 0.1	0.36 ± 0.04	4			
11.	PhA - AN	BP/bulk/60	0.33 ± 0.05	0.26 ± 0.03	6	0.34	0.28	I
11a.	"	"	0.69 ± 0.04	0.30 ± 0.02	4			
12.	PhA - 2VPy	"	0.2 ± 0.05	4.0 ± 0.7	11	0.09	3.52	I!
12a.	"	"	0.32 ± 0.15	4.0 ± 0.2	4			
13.	PhA - VC	AIBN/THF/70	3.0	0.2	8	5.33	0.25	I
14.	PhA - MAn	γ-ray/A/30	0.50 ± 0.05	0.05 ± 0.05	12	-	-	II
15.	VEA - AN	AIBN/bulk/60	0.63 ± 0.4	0.17 ± 0.01	7	0.53	0.15	I
16.	VEA - 2VPy	"	0.6 ± 0.02	1.5 ± 0.5	7	-	-	III
17.	DPA - MA	BP/bulk/60	0	55 ± 5	6	0.05	50.5	I
18.	DPA - AN	"	0	13.6 ± 1.0	6	0.06	13.9	I
19.	DCA - S	AIBN/THF/55	0	1.4	13	-	-	II
20.	DEB - MM	AIBN/bulk/60	-	0.606 ± 0.15	14	-	-	III
20a.	"	"	-	0.60 ± 0.1	4			

TABLE 1. continued

21.	DEB - S	AIBN/bulk/60	0.74 ± 0.02	1.18 ± 0.1	14	0.49	1.13	I
21a.	"	"	0.87 ± 0.1	1.15 ± 0.1	4			
22.	PhA - NEM	γ-ray/bulk/50	0.030	0.224	15	0.03	0.21	I!
23.	VA - 2VPy	AIBN/bulk/60	1.8	3.33	7	1.68	3.22	I
24.	PhA - MAc	BP/DMF/60	0.07 ± 0.01	2.30 ± 0.05	16	0.03	2.26	I
25.	PhA - BM	AIBN/DMF/60	0.24 ± 0.01	2.5 ± 0.2	16	0.24	2.37	I

! - high scattering of experimental data, the recalculated r_1 and r_2 values are less reliable

a - data recalculated by Zaitsev et al.

nBuA = n-butyl acetylene; MA = methyl acrylate; AN = acrylonitrile; VA = vinyl acetylene; IPA = isopropenyl acetylene; 2VPy = 2-vinyl pyridine; PA = propargyl alcohol; VC = vinyl chloride; PAl = propiolaldehyde; PhA = phenyl acetylene; MM = methyl methacrylate; S = styrene; MAn = maleic anhydryde; VEA = 1-vinyl-2-ethyl acetylene; DPA = diphenyl acetylene; DCA = dicianoacetylene; DEB = p-diethynyl benzene; NEM = N-ethylmaleimide; MAc = methacrylic acid; BM = benzyl methacrylate; AIBN = α,α'azo-bis-isobutyronitrile; BP = benzoyl peroxide; A = acetone; THF = tetrahydrofuran; DMF = dimethylformamide.

Two systems (phenylacetylene - maleic anhydryde and dicyanoacetylene - styrene) belong to class II. Bearing in mind the different donor-acceptor character of these monomers, and the shape of the KT plot (Fig. 1c), one may treat their copolymerization as a charge-transfer copolymerization mechanism [20]. Finally, Figure 1d presents two significant examples of class III systems.

CONCLUSIONS

Reactivity ratio values for 25 systems of radical copolymerization of acetylenic and vinylic monomers have been reexamined. Of these, 12 belong to class I, 5 to class I!, 2 to class II and 6 to class III. In most cases, the authors give relatively few experimental data. The copolymerization equation proposed by Zaitsev et al. has proven to be inadequate.

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Received September 21, 1979
Accepted September 24, 1979