Copolymerization of alkyl acrylates with triallyl cyanurate: Kelen-Tüdös method applied for determining copolymerization reactivity ratios

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The copolymerization of methyl acrylate (MA), ethyl acrylate (EA), straight-chain butyl acrylate (n-BA) and styrene (S) with triallyl cyanurate (TAC) has been studied in bulk at 343 ± 1 K using benzoyl peroxide as initiator. The reactivity ratios of the monomers are determined by the Fineman–Ross (F–R) method and compared to those determined by the Kelen–Tüdös (K–T) method.
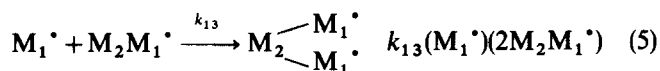
INTRODUCTION

The process of free-radical copolymerization of triallyl cyanurate with chosen alkyl acrylate is investigated. Reactions in the propagation steps for copolymerization of alkyl acrylates (M_1) with triallyl cyanurate (M_2) are[1]:

Form of reaction	Rate of process	
$M_1^{\bullet} + M_1 \xrightarrow{k_{11}} M_1^{\bullet}$	$k_{11}(M_1^{\bullet})(M_1)$	(1)
$M_1^{\bullet} + M_2 \xrightarrow{k_{12}} M_2^{\bullet}$	$k_{12}(M_1^{\bullet})(3M_2)$	(2)
$M_2^{\bullet} + M_2 \xrightarrow{k_{22}} M_2^{\bullet}$	$k_{22}(M_2^{\bullet})(3M_2)$	(3)
$M_2^{\bullet} + M_1 \xrightarrow{k_{21}} M_2M_1^{\bullet\,a}$	$k_{21}(M_2^{\bullet})(M_1)$	(4)
$M_1^{\bullet} + M_2M_1^{\bullet} \xrightarrow{k_{13}} M_2^{\diagup M_1^{\bullet}}_{\diagdown M_1^{\bullet}}$	$k_{13}(M_1^{\bullet})(2M_2M_1^{\bullet})$	(5)

$M_2M_1^{\bullet\,a}$ designates TAC with two remaining allyl groups, one of which polymerizes in equation (5)

Equations (1)–(4) give a linear polymer while equation (5) gives a crosslinked polymer. There are ten other reactions that will also lead to crosslinking, but these are much less likely than equation (5). The importance of equation (5) depends on the concentration of species $M_2M_1^{\bullet}$ which arises from equation (4). Here, as the reaction was stopped before gelation, equation (5) is neglected and calculations are based on equations (1)–(4). Equating the rate of consumption of M_1 and M_2, and assuming a steady state concentration of radical species, the following equations are derived:

$$\frac{dM_1}{dM_2} = \frac{k_{11}(M_1^{\bullet})(M_1) + k_{21}(M_2^{\bullet})(M_1)}{3k_{12}(M_1^{\bullet})(M_2) + 3k_{22}(M_2^{\bullet})(M_2)} \qquad (6)$$

$$M_1^{\bullet} = \frac{k_{21}(M_2^{\bullet})(M_1)}{3k_{12}(M_2)} \qquad (7)$$

$$\frac{dM_1}{dM_2} = \frac{\frac{k_{11}}{3k_{12}}(M_1) + (M_1)(M_2)}{(M_1)(M_2) + \frac{3k_{22}}{k_{21}}(M_2)^2} \qquad (8)$$

The last form of the differential equation (6) is:

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \cdot \frac{\frac{r_1}{3} + M_2}{3r_2M_2 + M_1} \qquad (9)$$

where:

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

The reactivity ratios of the monomers, r_1 and r_2, have been determined using the Fineman–Ross (F–R) method[2], a graphical and a least-squares technique, and the results have been recalculated in a more exact manner using the Kelen–Tüdös (K–T) method[3] also using a graphical and a least squares technique. The Kelen–Tüdös equation (equation (10)) is based on the differential form of the well known monomer–copolymer composition equation and is clearly suitable for low-conversion data (<10%).

The K–T equation[3] is:

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\zeta - \frac{r_2}{\alpha} \qquad (10)$$

where:

$$\eta = \frac{G}{\alpha + F}; \qquad \zeta = \frac{F}{\alpha + F}$$

$$G = \frac{x(y-1)}{y}; \qquad F = \frac{x^2}{y}$$

$$x = \frac{M_1}{M_2}; \qquad y = \frac{m_1}{m_2}$$

M_1, M_2, the molar concentration in the monomer feed, m_1, m_2, the molar concentration in the final polymer,

$$\alpha = \sqrt{F_m \cdot F_M}$$

where: α, an appropriately chosen constant to obtain a uniform spread of the data ($\alpha > 0$). F_m and F_M, the lowest and highest values from experimental data. The variable ζ can take only positive values in the interval (0, 1).

Thus, by plotting η versus ζ according to the linear equation (10), a straight line is obtained, when extrapolated to $\zeta = 0$ and $\zeta = 1$, gives $-r_2/\alpha$ and r_1 (both as intercepts).

For TAC equation (10) is:

$$\eta = \left(\frac{r_1}{3} + \frac{3r_2}{\alpha}\right)\zeta - \frac{3r_2}{\alpha} \tag{11}$$

As it is assumed that the reactivities of three vinyl groups in triallyl cyanurate are identical[1] the factor 3 must enter into equation (11).

The reactivity ratios r_1 and r_2 can be obtained by computation using the least-squares technique[4].

EXPERIMENTAL

Monomers

Triallyl cyanurate (TAC), pure, was prepared from allyl alcohol and cyanuric chloride in the presence of 40 wt % NaOH (aqueous solution), according to the procedure described by Homienkova et al.[5] The temperature of reaction was < 278 K. The resultant crude monomer was purified by being washed in hot water, dissolved in acetone, distilled in vacuo and dried over anhydrous magnesium sulphate. The nitrogen content determined using the Kjeldahl method was 16.86%; melting point, 300–301 K; boiling point, 410–413 K; n_D^{25}, 1,5049; n_D^{20}, 1,5060.

Methyl acrylate (MA), pure (Fluka, A. G., Switzerland) was purified by distillation under reduced pressure and dried over anhydrous magnesium sulphate, n_D^{20}, 1,4041. Ethyl acrylate (EA), pure (Koch–Light, Great Britain). The monomer was purified in the same manner as methyl acrylate, n_D^{20}, 1,4040. Straight-chain acrylate (n-BA), pure (Fluka, A. G., Switzerland). The monomer was purified in the same manner as methyl acrylate, n_D^{20}, 1,4190. Styrene (S), pure (International Enzymes Limited, Great Britain). The monomer was freshly distilled under reduced pressure just before use, n_D^{20}, 1,5466. Benzoyl peroxide (BP), pure (Argon–Łódź, Poland). Its reactivity[7] was 89%.

Copolymerization

The copolymerizations of MA, EA, n-BA, S with TAC were carried out in bulk in glass ampules which were flushed with prepurified nitrogen before being sealed. The process was carried out at 343 ± 1 K in the presence of benzoyl peroxide as the initiator for the experimentally established time which was sufficiently long to ensure the percentage conversion was < 10. The copolymers were purified twice by reprecipitating from acetone with methanol and the deposit was dried in vacuo at room temperature to constant weight. The products were analysed for nitrogen using the Kjeldahl method.

RESULTS

The results of the copolymerization experiments for alkyl acrylates (AA), styrene (S) with TAC are shown in *Tables 1-4*. For each pair of comonomers two series of

Table 1 Copolymerization of methyl acrylate (M_1) with triallyl cyanurate (M_2) at 347 ± 1 K in the presence of benzoyl peroxide (0.2% by weight)

No.	Composition of starting mixture (mol %)		Polymerization time (min.)	Polymer yield (wt%)	N content in copolymer (wt%)	Concn. triazine in copolymer (mol %)
	M_1	M_2				
1	90	10	15	5.26	1.45	3.1361
2	80	20	24	4.86	2.90	6.6947
3	70	30	36	5.93	4.35	10.7223
4	60	40	48	4.86	5.80	15.3353
5	50	50	55	4.12	7.27	20.7508
6	40	60	62	5.31	8.73	27.0548
7	30	70	71	5.50	10.17	34.4305
8	20	80	85	7.78	11.64	43.5123
9	10	90	98	6.79	13.10	54.6179

Table 2 Copolymerization of ethyl acrylate (M_1) with triallyl cyanurate (M_2) at 347 ± 1 K in the presence of benzoyl peroxide (0.2% by weight)

No.	Composition of starting mixture (mol %)		Polymerization time (min.)	Polymer yield (wt%)	N content in copolymer (wt%)	Concn. triazine in copolymer (mol %)
	M_1	M_2				
1	90	10	20	3.55	1.45	3.6418
2	80	20	28	3.30	2.95	7.8497
3	70	30	42	3.76	4.40	12.4221
4	60	40	55	3.65	5.85	17.5883
5	50	50	60	4.20	7.30	23.4720
6	40	60	70	4.72	8.78	30.3601
7	30	70	80	7.43	10.25	38.3818
8	20	80	92	7.75	11.70	47.6667
9	10	90	115	9.36	13.22	59.3754

Table 3 Copolymerization of straight-chain butyl acrylate (M_1) with triallyl cyanurate (M_2) at 347 ± 1 K in the presence of benzoyl peroxide (0.2% by weight)

| No. | Composition of starting mixture (mol %) | | Polymerization time (min.) | Polymer yield (wt%) | N content in copolymer (wt%) | Concn. triazine in copolymer (mol %) |
	M_1	M_2				
1	90	10	36	5.50	1.20	3.7909
2	80	20	48	6.65	2.40	7.8634
3	70	30	61	7.15	3.62	12.3262
4	60	40	73	3.70	4.85	17.1048
5	50	50	90	7.62	6.02	22.2138
6	40	60	104	6.40	7.25	27.9509
7	30	70	120	5.53	8.45	34.0669
8	20	80	140	3.96	9.62	40.5927
9	10	90	155	4.62	10.85	48.1440

Table 4 Copolymerization of styrene (M_1) with triallyl cyanurate (M_2) at 347 ± 1 K in the presence of benzoyl peroxide (0.2% by weight)

| No. | Composition of starting mixture (mol %) | | Polymerization time (min.) | Polymer yield (wt%) | N content in copolymer (wt%) | Concn. triazine in copolymer (mol %) |
	M_1	M_2				
1	90	10	20	13.90	0.69	1.7440
2	80	20	23	11.93	1.38	3.6102
3	70	30	24	9.80	2.09	5.5737
4	60	40	28	8.44	2.88	7.9255
5	50	50	33	7.49	3.80	10.8396
6	40	60	40	10.60	4.79	14.2126
7	30	70	48	9.48	5.95	18.5587
8	20	80	55	5.56	7.59	25.4913
9	10	90	61	5.73	10.30	39.6165
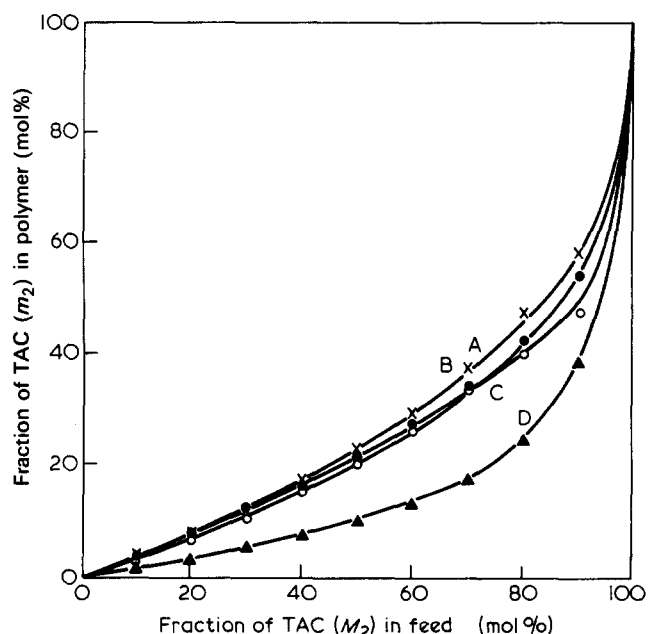
Figure 1 Copolymer composition curves. A, MA and TAC; B, EA and TAC; C, n-BA and TAC; D, S and TAC

measurements for nine compositions were made. Mean values for two experiments are given in the Tables. Each copolymer has been analysed three times for nitrogen by the Kjeldahl method.

Figure 1 shows the copolymer composition curves for the TAC copolymers. Similar curves have been obtained for the systems: MA–TAC, EA–TAC, nBA–TAC and S–TAC.

Table 5 summarizes the reactivity ratios which have been determined graphically for nine monomer

combinations, according to the F–R method, and K–T method using equation (11). The least squares method was used also.

For comparison, *Table 6* shows values of reactivity ratios obtained previously for alkyl methacrylates (AM) and TAC calculated using the F–R method[8] and now recalculated by K–T method.

DISCUSSION

The values of reactivity ratios quoted in the literature often present significant differences dependent upon the method used. Therefore, it appeared useful to calculate reactivity ratios applying the Fineman–Ross (F–R) method and for comparison the Kelen–Tüdös (K–T) method. In investigations on copolymerization of triallyl cyanurate with chosen alkyl acrylates it is evident that the rate of polymerization is a function of concentration of triallyl cyanurate and of the nature of alkyl groups of acrylates (*Tables 1–3*). In the copolymerization of alkyl acrylates and styrene the reactivity order is: S>MA>EA>n-BA. *Figure 1* shows % mol fraction of TAC (m_2) in copolymer as a function % mol fraction of TAC in the monomer feed (M_2). For all the investigated copolymers the composition curves are similar and it is evident that conversion rate of TAC is relatively low, even if the initial mol fraction of TAC is high (90 mol %). This is in sufficient agreement with low values of r_2.

A comparison of the r_1 and r_2 values resulting from the K–T method with those computed by classical F–R method shows slight deviations of r_1 values and higher deviations of r_2 values. *Table 6* gives r_1 and r_2 values of MA and TAC that were calculated previously by the F–R method and then recalculated by the K–T method. Again,

Table 5 Reactivity ratios of alkyl acrylates (M_1) and styrene (M_1) with triallyl cyanurate (M_2)

Monomer (alkyl group)	Fineman — Ross method		Kelen — Tüdös method			
			Graphical		Least squares	
	r_1	r_2	r_1	r_2	r_1	r_2
Methyl	9.900 ± 0.175	0.028 ± 0.005	9.3	0.01	9.4641	0.140
Ethyl	8.670 ± 0.150	0.086 ± 0.002	8.4	0.05	8.3137	0.044
Straight-chain butyl	8.156 ± 0.140	0.043 ± 0.004	8.1	0.01	8.0083	0.0119
Styrene[a]	18.377 ± 0.323	−0.036 ± 0.004	19.5	−0.01	19.6151	−0.0109

[a] $r_2 < 0$ — attributable to experimental error

Table 6 Reactivity ratios of alkyl methacrylates (M_1) and triallyl cyanurate (M_2)

Monomer (alkyl group)	Fineman — Ross method		Kelen — Tüdös method			
			Graphical		Least squares	
	r_1	r_2	r_1	r_2	r_1	r_2
Methyl[a]	46.3	0.03 ± 0.05	—	—	—	—
Ethyl[b]	30.0255 ± 0.8035	−0.0101 ± 0.069	30.9	0.03	30.9332	0.0303
Straight-chain butyl[b]	30.5531 ± 1.9716	−0.0723 ± 0.0252	29.7	0.06	29.6422	0.0558
2-Ethylheksyl[b]	19.5225 ± 0.0035	−0.0234 ± 0.0099	20.1	0.02	20.0774	0.0222

[a] The calculations given by Roth and Church[1]
[b] $r_2 < 0$ — attributable to experimental error

slight deviations are observed. A comparison of the r_1 and r_2 values for the investigated systems: AA–TAC, S–TAC and MA–TAC confirms that monomer reactivity depends on the lengt length and branching of unreactive alkyl groups of acrylates or methacrylates[9]. Chain length of unreactive alkyl group influences the steric configuration of the macromolecule and the stability of radicals. The TAC radicals are stable enough because of the influence of the ring and their planar configuration. Here, it is assumed that the reactivity of all three alkyl groups of TAC are identical. The influence of unreacted alkyl groups is limited because of low conversion.

The values r_1 and r_2 for the investigated monomers should be treated as approximate, because the influence of oxygen on copolymerization of acrylates with cyanurate, has not been taken into consideration. However, both for the F–R method and the K–T method the same experimental conditions have been used and the values for the reactivity ratios of the respective comonomers can be considered credible.

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