

Copolymerizations with Triallyl Cyanurate, Triallyl Isocyanurate, and Diallylmelamine

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Introduction

Triallyl cyanurate and triallyl isocyanurate have been shown to improve the heat stability of unsaturated polyesters when added before the curing process.¹⁻¹⁰ Generally, allylic esters copolymerize poorly with reactive monomers forming mixtures of copolymer and homopolymers if the polymerization is forced to completion. This work was undertaken to determine reactivity ratios for triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), and diallylmelamine (DAM) with methyl methacrylate (MMA), styrene, and vinyl acetate. Optimum conditions for incorporating the maximum amount of the triazine into the copolymers were desired.

TABLE I
Reactions in the Propagation Steps for Copolymerization of TAC

Equation	Form of reaction	Rate of process
(1)	$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1\cdot$	$k_{11}(M_1\cdot)(M_1)$
(2)	$M_1\cdot + M_2 \xrightarrow{k_{12}} M_2\cdot$	$k_{12}(M_1\cdot)(3M_2)$
(3)	$M_2\cdot + M_2 \xrightarrow{k_{22}} M_2\cdot$	$k_{22}(M_2\cdot)(3M_2)$
(4)	$M_2\cdot + M_1 \xrightarrow{k_{21}} M_2M_1\cdot^a$	$k_{21}(M_2\cdot)(M_1)$
(5)	$M_1\cdot + M_2M_1\cdot \xrightarrow{k_{13}} M_2 \begin{array}{l} \nearrow M_1\cdot \\ \searrow M_1\cdot \end{array}$	$k_{13}(M_1\cdot)(2M_2M_1\cdot)$

* $M_2M_1\cdot$ designates TAC with two remaining allyl groups, one of which polymerizes in eq. (5).

Table I presents the more important propagation steps involved in the copolymerization of a trivinyl compound (M_2) having three "independent" vinyl groups, with a monofunctional monomer (M_1). The corresponding rate processes are also shown.

Equations (1)–(4) afford a linear polymer while eq. (5) yields a cross-

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linked polymer. There are ten other reactions that will also lead to crosslinking, but these are much less likely than eq. (5). The importance of eq. (5) depends on the concentration of species $M_2M_1\cdot$ which arises from eq. (4). In this work, since reaction was stopped before gelation—except in a few cases—eq. (5) is neglected and calculations are based on eqs. (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.

$$\frac{dM_1}{dM_2} = \frac{k_{11}(M_1\cdot)(M_1) + k_{21}(M_2\cdot)(M_1)}{3k_{12}(M_1\cdot)(M_2) + 3k_{22}(M_2\cdot)(M_2)}$$

$$M_1\cdot = \frac{k_{21}(M_2\cdot)(M_1)}{3k_{12}(M_2)}$$

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

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \frac{\frac{r_1}{3} + M_2}{3r_2M_2 + M_1}$$

where r_1 is k_{11}/k_{12} and r_2 is k_{22}/k_{21} .

Integration gives an equation similar to that derived by Mayo and Lewis for the copolymerization of monofunctional monomers.¹¹

$$\log \frac{M_2}{(M_2)_0} = \frac{3r_2}{1 - 3r_2} \log \frac{(m_2)_0(M_1)}{(M_1)_0(M_2)} - \frac{1 - r_1r_2}{(1 - 3r_2) \left(1 - \frac{r_1}{3}\right)} \log \frac{\left(\frac{r_1}{3} - 1\right) \frac{M_1}{M_1} - 3r_2 + 1}{\left(\frac{r_1}{3} - 1\right) \frac{(M_1)_0}{(M_2)_0} - 3r_2 + 1}$$

The factor 3 enters into the equation because of the identical reactivities of three unsaturated groups in TAC and TAIC. A corresponding factor of two is involved in DAM calculations. This is true whether or not the two vinyl groups in DAM finally polymerize by a linear¹² (cyclic) or crosslinking mechanism.

Experimental

Purification of Materials

Methyl methacrylate (E. I. du Pont de Nemours & Co.) was washed with 5% aqueous sodium bisulfite, 5% aqueous sodium hydroxide and water and distilled, b.p. 48–50°C./100 mm.

Styrene (Dow Chemical Co.) and vinyl acetate (Union Carbide Chemical Co.) were freshly distilled before use.

Triallyl cyanurate (American Cyanamid Co.) was washed twice with 1*N* sodium hydroxide and water and distilled, b.p. 135–140°C./0.5 mm., m.p. 27.32°C. (99.4 mole-% purity).

Triallyl isocyanurate (American Cyanamid Co.) was recrystallized from methanol, m.p. 24.10°C. (94.8 mole-% purity).

Diallylmelamine (American Cyanamid Co.) was recrystallized twice from 85% aqueous isopropanol, m.p. 141.5°C.

Azobisisobutyronitrile (Westville Laboratories) was recrystallized from benzene, decomposition temperature 104°C.

Reactivity Ratios

Reactivity ratios were determined by the procedure of Mayo and Lewis¹¹ and, for comparison, by the method of Fineman and Ross.¹³ The copolymerizations were run at 60.0°C. using azobisisobutyronitrile as the initiator. Triallyl cyanurate and triallyl isocyanurate copolymerizations were run in bulk, while the DAM reactions were run in dimethylformamide. The copolymers were purified by reprecipitating twice from acetone with methanol and dried *in vacuo* at 60°C. to constant weight. The copolymers were analyzed for nitrogen by the Kjeldahl method.

Results

The results of the copolymerization experiments are shown in Table II.

Table III summarizes the reactivity ratios that were determined graphically for the nine monomer combinations, according to the method of Mayo and Lewis,¹¹ by using eq. (6).

Figure 1 shows the copolymer composition curves for the TAC copolymers. Similar curves were obtained for TAIC and DAM copolymers.

For comparison, Table IV shows the values that were obtained using the simplified method of Fineman and Ross.¹³ Again, since three vinyl groups are present per TAC and TAIC molecule and two groups per DAM molecule, these factors are considered in the final equations (7) and (8), respectively.

$$\frac{F}{f} (f - 1) = \frac{r_1}{3} \frac{F^2}{f} - 3r_2, \text{ for TAC and TAIC} \quad (7)$$

$$\frac{F}{f} (f - 1) = \frac{r_1}{2} \frac{F^2}{f} - 2r_2, \text{ for DAM} \quad (8)$$

Discussion

Table III shows that the reactivity ratios for the three allylic triazines are about those expected for allylic compounds. In a table of relative reactivities with polymer radicals,¹⁴ these compounds would fall close to allyl chloride and vinyl acetate.

TABLE II
Copolymerization of Triallyl Cyanurate, Triallyl Isocyanurate, and Diallylmelamine
with Methyl Methacrylate, Styrene, and Vinyl Acetate at 60°C. in the Presence of
Azobisisobutyronitrile

Composition starting mixture, moles $\times 10^2$		Catalyst concn., mole/liter	Polymer- ization time, min.	Polymer yield, %	N content in copolymer	Concn. triazine in co- polymer, wt.-%
Methyl methacrylate						
TAC						
1.33	7.32	0.0123	65	12.48	0.51	3.02
1.76	5.29	0.0123	72	12.52	0.88	5.22
2.82	3.32	0.0123	80	11.02	2.11	12.52
4.96	1.65	0.0123	98	12.01	4.49	26.63
4.37	0.81	0.0123	100	9.28	7.94	47.10
Styrene						
0.92	6.54	0.050	452	33.08	0.15	0.89
1.33	5.77	0.050	462	28.57	0.38	2.25
1.82	4.59	0.050	474	25.16	0.70	4.15
2.10	2.99	0.050	479	17.54	1.28	7.59
2.66	1.98	0.050	598	13.29	2.42	14.35
Vinyl acetate						
1.15	9.64	0.050	79	8.80	8.61	51.06
1.56	6.95	0.050	140	10.85	11.09	65.77
2.55	4.81	0.050	215	11.79	13.35	79.17
3.15	2.71	0.050	390	16.85	14.59	86.53
3.50	0.99	0.050	440	19.07	15.70	93.11
Methyl methacrylate						
TAIC						
0.95	7.35	0.010	73	12.41	0.35	2.07
1.51	6.29	0.010	69	11.23	0.48	2.84
2.40	3.19	0.010	65	8.62	1.45	4.25
2.94	2.31	0.010	61	12.88	2.13	12.64
Styrene						
0.95	6.69	0.050	451	34.54	0.26	1.54
1.40	5.53	0.50	456	30.67	0.36	1.54
2.28	4.59	0.050	470	15.42	0.78	4.63
2.44	2.87	0.050	480	19.43	1.33	7.89
3.05	2.08	0.050	670	16.41	2.38	14.12
Vinyl acetate						
1.13	9.32	0.050	34	6.05	8.48	50.29
1.73	7.62	0.050	51	8.88	10.68	63.34
2.67	4.88	0.050	79	9.45	13.61	80.72
3.27	2.82	0.050	125	12.14	14.94	88.61
3.68	1.49	0.050	130	11.18	15.71	93.17
Methyl methacrylate						
DAM						
0.72	4.39	0.011	80	16.33	2.77	6.97
1.10	3.33	0.011	166	24.97	2.54	6.23

(continued)

TABLE II (continued)

Composition starting mixture, moles $\times 10^2$		Catalyst concn., mole/liter	Polymer- ization time, min.	Polymer yield, %	N content in copolymers	Concn. triazine in co- polymer, wt.-%
1.24	2.82	0.011	250	30.86	2.63	6.45
1.35	1.44	0.011	276	19.42	2.96	7.26
1.48	1.16	0.011	286	15.22	4.03	9.88
Styrene						
0.76	4.23	0.050	358	22.02	0.43	1.05
1.04	2.69	0.050	373	16.71	0.92	2.26
1.28	1.85	0.050	373	11.22	1.04	2.55
1.36	1.15	0.050	374	7.62	1.40	3.43
1.46	0.81	0.050	374	5.08	2.01	4.93
Vinyl acetate						
0.81	5.39	0.100	211	16.35	12.47	30.60
1.12	2.99	0.100	300	19.44	19.81	48.61
1.32	1.58	0.100	314	12.36	25.95	63.68
1.39	0.96	0.100	321	9.44	28.82	70.72
1.40	0.79	0.100	331	8.89	29.56	72.54

Since no crossover points exist for the TAC copolymerizations (Fig. 1), there is no monomeric ratio of TAC and MMA, for example, which will form a copolymer of constant composition. There will be a continual drift in composition. This is illustrated graphically by determining several integral composition distribution curves according to the method of Skeist¹⁵ (Fig. 2). Because of the trifunctionality of TAC, the monomer composition equation is modified to

$$\frac{\Delta A}{\Delta A + \Delta B} = A_p = \frac{\frac{r_1}{3} A^2 + AB}{\frac{r_1}{3} A^2 + 2AB + 3r_2 B^2}$$

for these calculations. If the copolymerization is carried to completion, homopolymer of TAC will be formed (almost 5%) even if the initial mole fraction of methyl methacrylate (A_0) is 0.90. This is not unexpected, considering the low values of r_2 .

Theoretically, it should be possible to eliminate this heterogeneity of copolymer composition by carefully controlled incremental addition of the more reactive monomer throughout the polymerization. However, with a polyfunctional monomer, gelation would prevent good mixing. Also, the continuous and instantaneous analysis that would be required to maintain a constant composition would be difficult. It would appear that if homopolymer is to be eliminated, a pre-copolymer should be prepared by isolating the product before complete polymerization. For example, from

TABLE III
Reactivity Ratios, Mayo and Lewis Method

M ₂	Methyl methacrylate, M ₁		Styrene, M ₁		Vinyl acetate, M ₁	
	r ₁	r ₂	r ₁	r ₂	r ₁	r ₂
TAC	50.2 ± 7.5	0.00 ± 0.07	90.6 ± 13.2	0.00 ± 0.08	0.71 ± 0.02	0.62 ± 0.05
TAIC	48.9 ± 7.3	-0.10 ± 0.12	90.1 ± 13.1	-0.01 ± 0.05	0.91 ± 0.03	0.75 ± 0.06
DAM	28.9 ± 2.3	-0.18 ± 0.19	102.3 ± 15.1	-0.13 ± 0.15	1.41 ± 0.06	0.19 ± 0.004

TABLE IV
Reactivity Ratios, Fineman and Ross Method

M ₂	Methyl methacrylate, M ₁		Styrene, M ₁		Vinyl acetate, M ₁	
	r ₁	r ₂	r ₁	r ₂	r ₁	r ₂
TAC	46.3 ± 5.3	0.03 ± 0.05	80.7 ± 9.3	0.20 ± 0.05	0.77 ± 0.15	0.52 ± 0.07
TAIC	45.0 ± 5.1	-0.08 ± 0.08	87.6 ± 10.0	0.10 ± 0.03	0.95 ± 0.18	0.70 ± 0.09
DAM	27.8 ± 3.2	-0.15 ± 0.18	103.0 ± 11.8	-0.12 ± 0.15	1.44 ± 0.28	0.20 ± 0.03

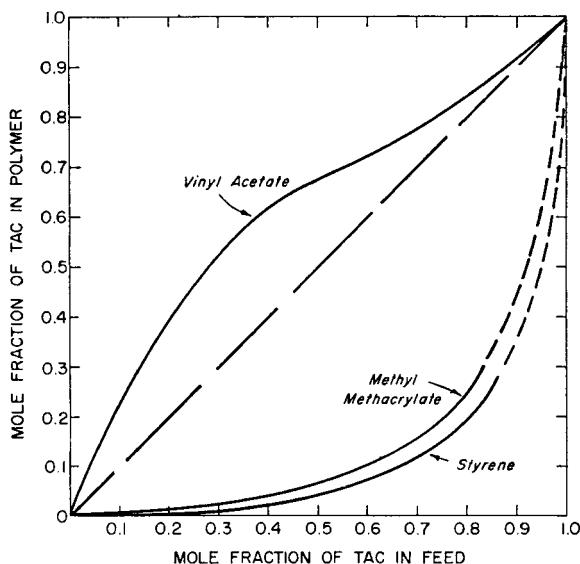


Fig. 1. Copolymer composition curves.

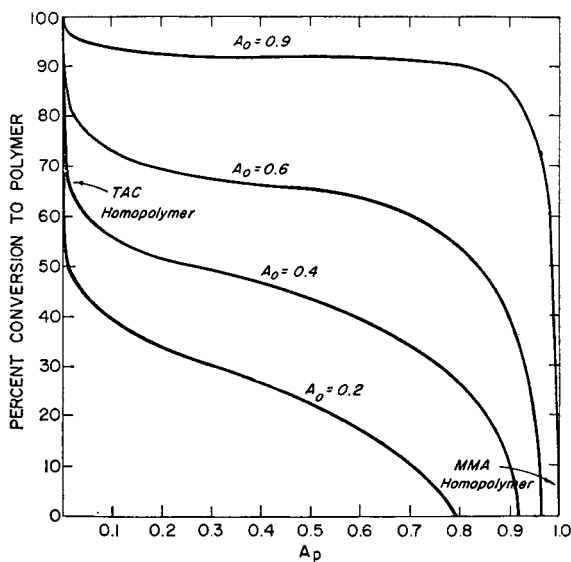
Fig. 2. Integral composition distribution curves for methyl methacrylate-triallyl cyanurate (A_0 = initial mole fraction of methyl methacrylate).

Figure 2 with 80 mole-% TAC initially ($A_0 = 0.20$) stopping the copolymerization at 40% conversion would yield a copolymer varying considerably in composition from 20 to 90 mole-% TAC, but containing no homopolymer. Since homopolymer and the resulting heterogeneity is normally

undesirable, preparation and utilization of pre-copolymer may have application advantages.

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Synopsis

Reactivity ratios for the copolymerization of triallyl cyanurate, triallyl isocyanurate, and diallylmelamine with methyl methacrylate, styrene, and vinyl acetate have been determined. Integral composition distribution curves have been determined for the triallyl cyanurate-methyl methacrylate system.

Résumé

Les rapports de réactivité dy cyanurate de triallyle, de l'isocyanurate de triallyle et de la diallylamine avec le méthacrylate de méthyle, le styrène et l'acétate de vinyle ont été déterminés. Les courbes de distribution de composition intégrées furent déterminées pour le système cyanurate de triallyle-méthacrylate de méthyle.

Zusammenfassung

Die Reaktivitätsverhältnisse für die Copolymerisation von Triallylcyanurat, Triallyl-isocyanurat und Diallylmelamin mit Methylmethacrylat, Styrol und Vinylacetat wurden bestimmt. Kurven für die integrale Zusammensetzungsverteilung wurden im System Triallylcyanurat-Methylmethacrylat aufgestellt.