

The Cyclocopolymerization of Triallyl Citrate with Several Vinyl Monomers

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Triallyl citrate (TAC) was copolymerized with allyl benzoate (ABz), vinyl acetate (VAc), vinyl chloride (VC), acrylonitrile (AN), and styrene (St) at 60 °C with benzoyl peroxide or 2,2'-azobisisobutyronitrile as the initiator; it was considered kinetically in terms of cyclocopolymerization. The following monomer reactivity ratios were obtained: VAc: $r_1=1.29$, $r_2=0.76$, $r_c=0.61$; ABz: $r_1=1.63$, $r_2=1.10$, $r_c=0.47$; VC: $r_1=0.40$, $r_2=1.90$, $r_c=0.31$; AN: $r_1=0.01$, $r_2=8.7$; St: $r_1=0.03$, $r_2=53.0$, where r_1 , r_c and r_2 denote the monomer reactivity ratio of the uncyclized, cyclized, and monovinyl radicals respectively. In the copolymerization of TAC with AN, the penultimate effect was also observed: $r_1=r'_1=0.01$, $r_2=k_{122}/k_{121}=11$, $r'_2=k_{222}/k_{221}=5$.

In a previous paper¹⁾ we have suggested that the polymerization of triallyl citrate (TAC) proceeds by means of a cyclocopolymerization mechanism analogous to that²⁻⁴⁾ proposed for the polymerization of the diallyl ester. It may, therefore, be expected that the behavior of the copolymerization of TAC with monovinyl monomers can also be accounted in terms of the extension of the cyclocopolymerization mechanism for the copolymerization of the diallyl ester with monovinyl monomer.²⁻⁴⁾

Thus, this paper is concerned with the copolymerizations of TAC with several monovinyl monomers, including allyl benzoate (ABz), vinyl acetate (VAc), vinyl chloride (VC), acrylonitrile (AN), and styrene (St); radical copolymerizations were conducted, and the results thus obtained will be kinetically discussed in detail. It will deal also with the penultimate effect observed in the copolymerization of TAC with AN.

Experimental

Materials. TAC was prepared by the reaction of citric acid with allyl alcohol according to the method described in the literature.¹⁾

ABz was obtained as has been described in a previous paper.²⁾

VAc,⁴⁾ AN,⁶⁾ St,⁷⁾ and VC⁸⁾ as comonomers, 2,2'-azobisisobutyronitrile (AIBN)⁸⁾ as an initiator, and *N,N*-dimethylformamide⁶⁾ as a solvent—these reagents were purified as has been described respectively.

Copolymerization Procedure. The copolymerizations of TAC with VAc,⁴⁾ ABz,²⁾ AN,⁶⁾ St,⁷⁾ and VC⁸⁾ were allowed to proceed in a sealed glass ampoule. After a definite reaction time, the copolymer thus produced was precipitated by pouring the reaction mixture into a large amount of a ethyl ether-petroleum ether mixture (1 : 4 by volume); it was then washed repeatedly with the mixed ether and dried *in vacuo* until a constant weight was obtained. The copolymer was then purified by dissolving in acetone and by subsequently reprecipitating with the mixed ether.

Analyses of Copolymers. The compositions of the purified copolymers were determined by elemental analyses. In the case of the copolymerization of TAC with VAc, the composition of the copolymer was indirectly calculated from the amounts of the unreacted monomer because of the difficulty of direct determination from the analyses of the copolymer; after a definite reaction time, the unreacted VAc monomer was determined by removing it at room temperature from the reaction mixture with a vacuum pump, after which the unreacted TAC monomer was determined by pouring the reaction mixture into a large amount of the

ether. The unreacted pendant allyl groups of the TAC-VC copolymer were calculated from the iodine value using the Wijs method,⁹⁾ while in the other copolymers, it was calculated from the bromine value determined by the bromide-bromate technique.¹⁾

The residual unsaturation, R_{us} , was then exhibited as the molar ratio of the unreacted pendant allyl group to the total allyl groups of the TAC incorporated into the copolymer.

Results and Discussion

Figure 1 shows the relations between the relative rate of copolymerization, which is presented as a ratio of the rate of copolymerization to that of the homopolymerization of TAC under the same conditions, and the feed-monomer composition.

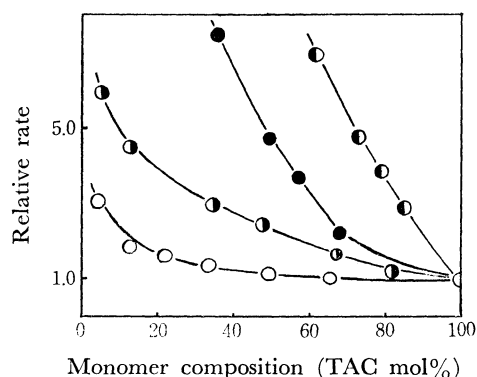


Fig. 1. Relation between the relative rate of copolymerization and the feed-monomer composition.

●: St, ●: AN, ◐: VC, ○: VAc

The relative rate tended to decrease, as a whole, with an increase in the mole fraction of TAC in the feed; this may be ascribable to the degradative chain transfer of the growing chain end to TAC. On the other hand, its decreasing tendencies changed with the kind of comonomer from the linear lowering for the conjugated monomer (St) to the abrupt one in the low feed-mole fraction of TAC for the unconjugated monomer (VAc); this may be interpreted by considering that the ability of the growing radicals to abstract the allylic hydrogen of TAC decreases with an increase in the conjugation of comonomer, while the possibility of the allyl radical's re-initiating the comonomer is the reverse.

Figure 2 shows the copolymer composition curves based on the data shown in Tables 1-5. In the

TABLE 1. COPOLYMERIZATION OF TAC (M_1) WITH VAc (M_2)^{a)}

Monomer			Time (min)	Conversion (%)	Copolymer	
[M_1] (mol/l)	[M_2] (mol/l)	[M_1] (mol %)			d[M_1] ^{b)} (mol %)	R_{us}
3.09	1.63	65.49	210	9.18	84.99	0.494
2.73	2.71	50.12	200	9.19	70.94	0.488
2.18	4.34	33.44	180	9.57	63.25	0.485
1.64	5.97	21.40	160	9.90	48.16	0.481
1.09	7.60	12.55	90	6.15	34.74	0.479
0.73	8.68	7.73	60	4.44	—	0.476

a) In bulk, total volume 20 ml, [BPO]=0.04 mol/l, polymerization temperature 60 °C. b) The composition of the copolymer was determined by tracing the unreacted monomer.

TABLE 2. COPOLYMERIZATION OF TAC (M_1) WITH ABz (M_2)^{a)}

Monomer			Time (min)	Conversion (%)	Copolymer		
[M_1] (mol/l)	[M_2] (mol/l)	[M_1] (mol %)			Carbon contents (%)	d[M_1] (mol %)	R_{us}
2.91	1.29	69.19	140	7.32	58.87	86.99	0.463
2.54	1.94	56.71	160	6.68	60.08	75.23	0.441
2.18	2.59	45.71	190	5.17	61.54	62.81	0.436
1.64	3.56	31.47	230	6.48	62.89	52.73	0.414
1.09	4.53	19.39	235	4.85	65.13	38.40	0.418
0.55	5.50	9.01	330	2.85	68.61	20.58	0.397

a) In bulk, total volume 10 ml, [BPO]=0.1 mol/l, polymerization temperature 60 °C.

TABLE 3. COPOLYMERIZATION OF TAC (M_1) WITH VC (M_2)^{a)}

Monomer			Time (min)	Conversion (%)	Copolymer		
[M_1] (mol/l)	[M_2] (mol/l)	[M_1] (mol %)			Chlorine contents (%)	d[M_1] (mol %)	R_{us}
1.17	0	100	350	7.37	0	100	0.396
1.06	0.50	67.73	250	8.45	4.11	71.93	0.409
0.94	1.01	48.26	200	10.13	8.57	52.93	0.431
0.82	1.51	35.24	160	10.67	12.29	41.98	0.452
0.70	2.01	25.91	130	7.77	16.62	32.57	0.459
0.47	3.02	13.45	100	9.44	25.93	19.20	0.473
0.23	4.02	5.51	80	9.84	36.41	10.04	0.497
0	5.02	0	40	7.20	56.72	0	—

a) Benzene 10 ml, total monomer *ca.* 5 ml, [AIBN]=*ca.* 0.05 mol/l (123 mg), polymerization temperature 60 °C.

TABLE 4. COPOLYMERIZATION OF TAC(M_1) WITH AN(M_2)^{a)}

Monomer			Time (min)	Conversion (%)	Copolymer		
[M_1] (mol/l)	[M_2] (mol/l)	[M_1] (mol %)			Nitrogen contents (%)	d[M_1] (mol %)	R_{us}
1.82	0	100	300	3.51	0	100	0.435
1.73	0.38	81.97	260	3.57	4.93	42.52	0.448
1.64	0.76	68.29	220	5.60	6.71	33.27	0.501
1.54	1.14	57.55	180	7.44	8.11	27.70	0.522
1.45	1.52	48.90	150	8.02	9.47	23.29	0.540
1.27	2.28	35.82	120	10.15	11.85	17.26	—
1.09	3.04	26.41	90	9.61	13.23	14.46	—
0.73	4.56	13.75	70	10.38	17.51	7.94	—
0.36	6.08	5.64	50	7.30	22.03	3.37	—

a) Dimethylformamide 10 ml, total monomer 10 ml, [BPO]=0.01 mol/l, polymerization temperature 60 °C.

TABLE 5. COPOLYMERIZATION OF TAC (M_1) WITH St (M_2)^{a)}

Monomer			Time (min)	Conversion (%)	Copolymer		
[M_1] (mol/l)	[M_2] (mol/l)	[M_1] (mol %)			Carbon contents (%)	d[M_1] (mol %)	R_{us}
3.39	0.58	85.36	250	2.95	73.80	27.65	0.560
3.27	0.87	78.94	250	4.03	77.47	19.96	—
3.15	1.16	73.02	230	4.70	80.46	14.73	—
2.91	1.75	62.48	210	6.38	84.56	8.72	0.565
2.67	2.33	53.38	200	7.02	86.71	6.00	0.575
2.42	2.91	45.44	190	8.35	87.59	4.95	0.595

a) In bulk, total volume 15 ml, [BPO]=0.01 mol/l, polymerization temperature 60 °C.

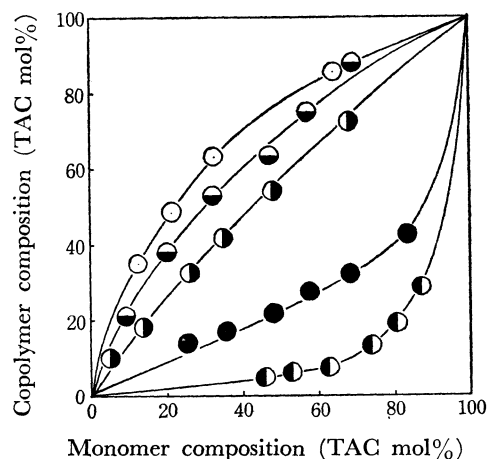


Fig. 2. Copolymer composition curves for the copolymerizations of TAC with several monovinyl monomer at 60 °C; (—) calculated curves based on the monomer reactivity ratios (see Table 6), (○) experimental results.

○: VAc, ◐: ABz, ◑: VC, ●: AN, ◒: St

copolymerization with ABz, VAc, and VC, the mole fraction of TAC in the copolymer is always larger than that in the feed, but in the other copolymerization systems (M_2 : AN and St) it is always smaller. These tendencies were also observed in the copolymerizations of diallyl phthalate.^{2,4,6-8)}

The relations between R_{us} and the mole fraction of TAC in the feed are shown in Fig. 3, where the different values of R_{us} denoted for the homopolymerization of TAC are due to the difference in the possibility of cyclization reaction between the bulk copolymerization for the TAC-St, VAc, and ABz copolymerization systems and the solution copolymerization for the TAC-AN and VC systems. In the copolymer of TAC with St, AN, and VC (M_2), R_{us} increases with an increase in mole fraction of M_2 in the feed, while with ABz and VAc (M_2) it decreases with an increase in the mole fraction of M_2 . Now, it should be noted that R_{us} must be 0.667 if no cyclization and crosslinking reactions occur. On the other hand, in the early stage of polymerization the crosslinking reaction is probably negligible. The deviation of R_{us} from 0.667 may, therefore, be attributed predominantly to the intramolecular cyclization reaction. Thus, the above results suggest that, in the copolymerizations with St, AN, and VC, the cyclization reaction has a tendency to be hindered with an increase in the mole fraction

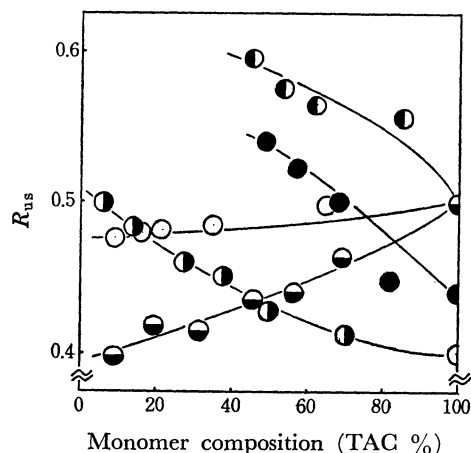


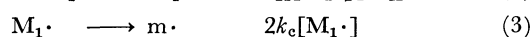
Fig. 3. Relationships between R_{us} and the feed-monomer composition.

○: St, ●: AN, ○: VAc, ◐: ABz, ◑: VC

of the comonomer in the feed, while in the copolymerizations with ABz and VAc the cyclization reaction comes to be promoted with an increase in the mole fraction of the comonomer. Similar results were also obtained in the copolymerizations of the diallyl ester;^{2-4,6,8)} these results can be understood by considering the competition among the unimolecular cyclizations with the allyl group of the same monomer unit, the bimolecular propagation with another diallyl-ester monomer or with the comonomer of the uncyclized radical produced by the radical attack on one allyl group of the diallyl ester.

Determination of the Monomer Reactivity Ratio. In the copolymerizations of TAC with several monovinyl monomers, the cyclization reaction of TAC is not negligible, as may be seen in Fig. 3. On considering the copolymerization mechanism of the triallyl ester (M_1) with the monovinyl monomer (M_2), it is necessary to discuss the possibility of a bicyclo-intramolecular propagation of M_1 . However, in the copolymerization of TAC the occurrence of the bicyclo-intramolecular propagation reaction is negligible, as can be seen from the results of the homopolymerization of TAC in our previous paper.¹⁾

Thus, these copolymerizations may be treated as extensions of the mechanism of the cyclocopolymerization of the divinyl monomer with the monovinyl monomer.⁴⁾ The reactions, (1)–(7), can, then, be given as the propagation reactions for copolymerization.



where M_1 is the TAC monomer; M_2 , the monovinyl monomer, and $m\cdot$, the cyclized radical formed by the intramolecular cyclization of $M\cdot$. On the basis of the seven propagation reactions presented above, Eqs. (8)–(10) were derived:

$$\frac{3(2-3R_{us})}{3R_{us}+\alpha-1}[M_1]=2K_c-\frac{1}{r_1}\cdot\frac{2-3R_{us}}{3R_{us}+\alpha-1}\cdot[M_2] \quad (8)$$

$$r_2 = \frac{F}{f} \cdot \frac{(1+r_cF)(1+r_1F+2K_c'/[M_2])}{1+r_cF+2K_c'/[M_2]} - F \quad (9)$$

$$r_2 = \frac{F^2}{f(2-3R_{us})} \cdot \frac{2K_c'(r_c+1/F)}{2K_c'+3[M_1](r_c+1/F)} - F \quad (10)$$

where $r_1=k_{11}/k_{12}$, $r_2=k_{22}/k_{21}$, $r_c=k_{c1}/k_{c2}$, $K_c=k_c/k_{11}$, $K_c'=k_c/k_{12}$ ($r_1 \times K_c$), $f=d[M_1]/d[M_2]$, and $F=3[M_1]/[M_2]$. Here, α is the ratio of the non-consecutive cyclization to the intramolecular cyclization in the same monomer unit, as in the homopolymerization of TAC.¹⁾

The experimental results may be discussed on the basis of Eqs. (8)–(10). First, in the copolymerizations of TAC with VC, VAc, and ABz, the values of r_1 and K were evaluated by using Eq. (8), and consequently K_c' was determined from $r_1 \times K_c$. By using the results thus obtained, we can further evaluate the values of r_2 and r_c from Eq. (9) or (10). The results thus obtained are summarized in Table 6.

TABLE 6. MONOMER REACTIVITY RATIOS

M_2	r_1	r_2	r_c
VAc ^{a)}	1.29	0.76	0.61
VBz ^{a)}	1.63	1.10	0.47
VC ^{a)}	0.40	1.90	0.31
AN ^{b)}	0.01	8.7	—
St ^{b)}	0.03	53.0	—

a) Estimated on the basis of cyclocopolymerization mechanism. b) Estimated from the general copolymer composition equation.

On the other hand, to the copolymerization of TAC with St the treatment of cyclocopolymerization could not be applied since the copolymerizability was very low; therefore, the accuracy of the analyses was significantly influenced by scatter of the experimental data. As a result, the value shown in Table 6 was obtained by using the usual copolymer composition equation.

Now, it should be noted that the penultimate effect

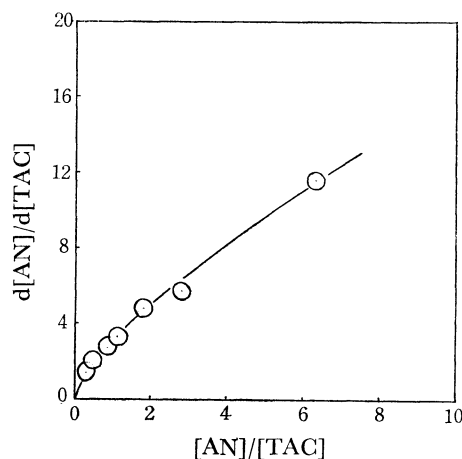


Fig. 4. Evaluation of r_2 and r_2' in the copolymerization of TAC with AN.

was observed in the copolymerization of TAC with AN. Therefore, the relation between $d[AN]/d[TAC]$ and $[AN]/[TAC]$ was plotted in order to estimate the values of r_2 and r_2' using the method of Joshi⁹⁾ (Fig. 4); thus, $r_1=r_1'=0.01$, $r_2=11$, and $r_2'=5$. This suggests that the rate of the addition of the AN monomer to the AN radical with the penultimate TAC unit is twice as large as that with the penultimate AN unit.

The difference between r_1 and r_c is also a matter of interest, since r_1 and r_c correspond to the reactivities of the uncyclized and the cyclized radicals respectively. The experimental results show that r_1 is considerably larger than r_c ; this may be due to the fact that the existence of steric hindrance in the addition reaction of the cyclized radical with TAC can be expected in light of the molecular model. Such a tendency has also been observed in the copolymerizations of diallyl phthalate with several monovinyl monomers, as has been reported previously.^{2,4,8)}

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