Reactivities of cis- and trans-3-Substituted Acrylic Acids on Copolymerization with Acrylamide

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Synopsis

Several pairs of cis- and trans-3-substituted acrylic acids (3SAA) were copolymerized with acrylamide in order to determine the major factors affecting the relative reactivities of geometrical isomers of 1,2-disubstituted ethylenes (1,2-DE). The results were that the relative reactivity of cis isomer is larger than that of trans isomer when one substituent is electron-withdrawing and the other is electron-donating. The trans isomer is more reactive than the cis isomer when both substituents are electron-withdrawing. A new method of reactivity comparison of cis- and trans-1,2-DE is proposed in regard to the inductive substituent constant.

INTRODUCTION

It is well known that the reactivities of 1,2-disubstituted ethylenes (1,2-DE) reduced greatly in copolymerization as compared to monosubstituted or 1,1-disubstituted ethylenes. It is also known that cis and trans isomers of 1,2-DE show different reactivities.[1,2] A few pairs of cis- and trans-3-substituted acrylic acids (3SAA) were copolymerized in previous studies;[3,4] it was found that the reactivities of cis and trans isomers were not simply determined by their thermodynamical stabilities. No quantitative methods of reactivity comparison of cis and trans isomers have been proposed other than that of Mayo and Lewis.[5] Therefore it is desirable to consider more quantitative ways of comparing reactivities cis- and trans-1,2-DE. In this paper, cis- and trans-3SAA having different substituent groups were copolymerized with acrylamide, and a new quantitative method of comparing reactivities of cis- and trans-1,2-DE is proposed.

EXPERIMENTAL

Monomers

cis-Crotonic acid (c-CA), cis-3-bromoacrylic acid (c-BA) and cis-3-ethylacrylic acid (c-EA) were synthesized by Rappe's method.[6–8] c-EA

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was prepared from 1,3-dibromopentanone-2 with 64% yield. c-CA and
c-EA were both purified through distillation under high vacuum. *cis*-
Cinnamic acid (c-CIA) was prepared from partial hydrogenation of phenyl-
propiolic acid obtained by Abbott's method.[9,10] Crude c-CIA was then
purified by distillation under high vacuum.[11] *trans*-3-Bromoacrylic acid
(t-BA) was obtained by thermal isomerization of c-BA. t-BA was purified
by recrystallization from diethyl ether. *trans*-3-Ethylacrylic acid (t-EA)
was synthesized by the Knoevenagel condensation of propionaldehyde with
malonic acid.[12,13] Commercially available *trans*-crotonic acid (t-CA) and
trans-cinnamic acid (t-CIA) were used for copolymerization after recrystal-
lization by the usual methods.

All monomers were regarded pure with respect to infrared, NMR, and
vapor-phase chromatographic methods. The physical constants of these
monomers are shown in Table I. Acrylamide used as a comonomer was
recrystallized twice from acetone. Hydrogen peroxide solution (30%) and
ferrous chloride used as the redox catalyst were commercially available re-
agents.

TABLE I
Physical Constants of 3-Substituted Acrylic Acids

3-Substituted acrylic acid	Mp, °C	Bp, °C/mm Hg	n_D	Dissociation constant $K \times 10^5$ [a]
c-CA	13–14.5	25–26.5/0.025	1.4499(14°C)	3.6
t-CA	72			2.03
c-EA	−13.2	37–38/0.075	1.4481(20°C)	
t-EA	9–9.5	99/10	1.4572(20°C)	2.02
c-BA	63–65			
t-BA	115–116			
c-CIA		95/0.025		13.2
t-CIA	133			3.65

[a] Data of Carton and Meilich.[16]

Copolymerization

The copolymerization of 3-substituted acrylic acid with acrylamide was
carried out in a volumetric flask in the presence of 5×10^{-3} mole/l. of
$FeCl_2 \cdot 4H_2O$ and H_2O_2 at 20.0°C. A mixed solvent of dimethylformamide
and water was used for copolymerization; for copolymerizations of CA, EA,
and BA the solvent ratio was 1/1 (v/v), and for copolymerization with CIA
the ratio was 3/1 (v/v). The monomer concentration was 1.00 mole/l.
The resulting copolymer was precipitated from a large amount of acetone
(some were reprecipitated) and washed with acetone and dried at around
50°C under vacuum until the weight became constant. The compositions
of all copolymers were determined from nitrogen analysis.[14] The results
are shown in Table II. The monomer reactivity ratios shown in Table III
were determined by the Mayo-Lewis method.[15]

TABLE II
Copolymerization of 3-Substituted Acrylic Acid (M_1) with Acrylamide (M_2)

| Monomer | M_1, mole-% | Time, min | Conversion, % | Copolymer | |
				N, %	m_1, mole-%
c-CA	30.0	3.0	10	17.34	10.1
	50.0	19	4.6	16.57	13.5
	60.0	74	9.3	16.14	15.5
	70.0	32	3.2	16.18	15.3
	80.0	96	2.7	14.38	23.4
t-CA	30.0	1.5	10.5	17.40	9.87
	50.0	20	9.7	17.23	10.7
	60.0	48	8.0	16.55	13.6
	70.0	45	5.0	15.72	17.4
	80.0	48	4.1	15.38	18.9
c-EA	30.0	3.0	8.8	17.85	6.88
	40.0	7.0	6.8	17.69	7.52
	50.0	10	5.0	17.20	9.37
	60.0	190	4.6	16.37	12.6
	70.0	1440	4.5	16.18	13.4
	80.0	2880	2.0	14.92	18.5
t-EA	30.0	3.0	10.7	18.20	5.55
	40.0	8.0	9.6	18.00	6.34
	50.00	13	9.2	17.87	6.82
	60.0	85	3.2	17.42	8.55
	70.0	370	2.0	17.08	9.86
	80.0	1440	1.8	16.79	11.0
c-BA	31.2	15.0	9.8	17.35	6.03
	41.4	27	10.3	17.11	6.68
	61.4	110	9.0	16.49	8.43
	71.2	240	6.5	15.91	10.1
	80.9	440	2.0	15.99	9.86
t-BA	30.0	39	9.0	16.38	8.71
	40.0	30	8.6	16.06	9.69
	50.0	38	8.5	16.02	9.81
	60.0	50	4.0	15.76	10.6
	70.0	250	1.5	15.12	12.5
c-CIA	20.0	3.0	5.0	17.45	5.86
	30.0	21	5.8	17.05	6.96
	40.0	44	3.1	16.88	7.44
	50.0	220	4.4	16.32	9.06
	60.0	340	2.6	15.61	11.2
t-CIA	20.0	14	7.5	17.22	6.49
	30.0	65	4.1	16.51	8.49
	40.0	140	2.9	15.05	12.9
	50.0	420	.9	14.44	14.9
	60.0	740	.8	13.92	16.7

TABLE III

Monomer Reactivity Ratios of 3-Substituted Acrylic Acid
(M_1)–Acrylamide (M_2) Systems

3-substituted acrylic acid	r_1	r_2	$1/r_2$
c-CA	$-0.21 \pm 0.02\ (0)$	4.0 ± 0.3	0.25
t-CA	$-0.09 \pm 0.02\ (0)$	6.5 ± 0.4	0.15
c-EA	$-0.11 \pm 0.03\ (0)$	7.1 ± 0.5	0.14
t-EA	$-0.14 \pm 0.03\ (0)$	$11 \quad \pm 0.6$	0.09
c-BA	$-0.14 \pm 0.03\ (0)$	$12 \quad \pm 0.5$	0.08
t-BA	$-0.21 \pm 0.08\ (0)$	6.5 ± 0.6	0.15
c-CIA	$-0.22 \pm 0.07\ (0)$	6.7 ± 0.6	0.15
t-CIA	$-0.26 \pm 0.03\ (0)$	3.0 ± 0.2	0.33

DISCUSSION

Because of the low volatility of the 3SAA monomers experimental errors may be large in connection with monomer reactivity ratios, even though precipitated polymers and reprecipitated polymers showed the same results of the nitrogen analysis. In Table III all r_1 are negative values. These may be because of experimental error and depropagation processes,
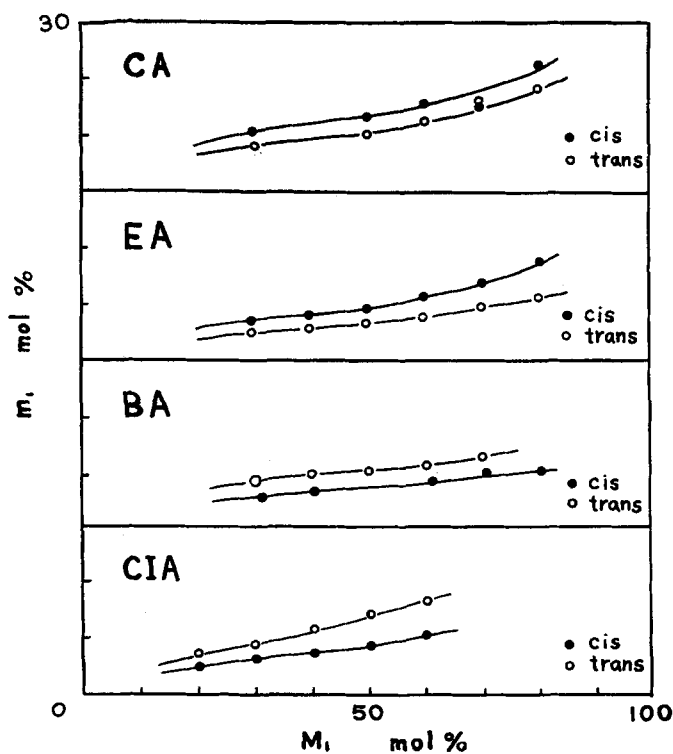

Fig. 1. Plot of copolymer composition vs. monomer feed: (●) *cis*; (O) *trans*.

as the ceiling temperature of 1,2-DE is considered to be low. Papers[1] which give negative monomer reactivity ratios do not make clear the reasons for this. As the problem of the negative reactivity ratios is not central in this study, Ham's[1] suggestion is accepted: that the rate constant k_{11} of 1,2-DE tends to be extremely small, and it is common in such systems for r_1 to be equal to zero within experimental error.

Table III and Figure 1 show that the *cis*- and *trans*-1,2-DE have low reactivities toward comonomer radical, because of steric hindrance. Table III and Figure 1 also show that the relative reactivity decreases as follows:

$$CH_3 > C_6H_5 \approx C_2H_5 > Br \ (\textit{cis isomers})$$

$$C_6H_5 > CH_3 \approx Br > C_2H_5 \ (\textit{trans isomers})$$
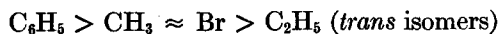
The high (relatively) reactivity of t-CIA is probably attributable to the resonance contribution of the phenyl group in the transition state of the copolymerization, whereas c-CIA is less reactive than t-CIA because of steric inhibition of resonance. This fact may be verified from the following examples; *trans* isomers of 1-phenyl-2-alkyl ethylenes,[17] 1,2-diethyl fumarate,[5] 1,2-dimethyl fumarate,[5] stilbene,[5] 1-ethoxy-1,3-butadiene,[18] and fumaric acid[3] are more reactive than *cis* isomers.

In *trans* isomers of 3SAA, t-CIA is the most reactive because of resonance contribution of phenyl group. This fact may coincide with the fact that α-phenyl acrylate has the highest reactivity toward styrene among α-substituted acrylates.[19] Similar results can be found in Lewis and Mayo's paper,[5] which states that the possibility of resonance in the activated complex is a major factor governing the reactivity of double bonds toward free radicals.

c-CIA and c-EA are more reactive than *trans* isomers. Many other examples (*cis* isomers are more reactive) are shown at Group 1 in Table IV. Mayo and Lewis[5] pointed out that the addition of either *cis* or *trans* isomer presumably results in the formation of the same free radical with the three attached substituents in the same plane or with a pyramidal configuration which is less stable thermodynamically might be expected to require less activation energy, so that less stable isomer (*cis*) should be more reactive. Their idea is applicable in Group 1 (*cis* isomer is more reactive) but not in Group 2 (*trans* isomer is more reactive). Price[22] suggested that polarity must have a more important role. The reactivities of *cis*- and *trans*-1,2-DE in copolymerization are compared in Table IV by considering their inductive substituent constants. The group with the larger substituent constant is placed on 1-position and then the difference between the substituent constant of 1-position and that of 2-position is noted.

In Group 1, the *cis* isomer is more reactive, when one substituent is electron-donating and the other is electron-withdrawing and the difference in substituent constants is bigger than 0.30.

In Group 2, the *trans* isomer is more reactive. In these cases the difference of the two substituent constants is always smaller than 0.20, whether

TABLE IV

Comparison of Reactivities of *cis*- and *trans*-1,2-DE in Copolymerization

| Group | Substituent | | Inductive substituent constant[a] | | Difference of two substituent constants | More reactive isomer | Reference monomer |
	1-position	2-position	1-position	2-position			
Group 1	COOH	CH_3	0.30	−0.05	0.35	*cis*	Acrylamide
	COOH	CH_3	0.30	−0.05	0.35	*cis*	1-Vinyl-2-methylimidazole[b]
	COOH	C_2H_5	0.30	−0.05	0.35	*cis*	Acrylamide
	OCH_3	CH_3	0.25	−0.05	0.30	*cis*	Acrylonitrile[c]
	OC_2H_5	CH_3	0.25[d]	−0.05	0.30	*cis*	Vinyl isobutylether[c]
	OC_2H_5	C_2H_5	0.25[d]	−0.05	0.30	*cis*	Vinyl isobutylether[c]
	OC_2H_5	$i\text{-}C_3H_7$	0.25[d]	−0.05[d]	0.30	*cis*	Vinyl isobutylether[c]
	OC_2H_5	$i\text{-}C_4H_9$	0.25[d]	−0.05[d]	0.30	*cis*	Vinyl isobutylether[c]
	OC_2H_5	$n\text{-}C_5H_{11}$	0.25[d]	−0.05[d]	0.30	*cis*	Vinyl isobutylether[c]
	$i\text{-}OC_3H_7(\text{iso})$	C_2H_5	0.25[d]	−0.05	0.30	*cis*	Vinyl isobutylether[c]
	$i\text{-}OC_4H_9(\text{iso})$	CH_3	0.25[d]	−0.05	0.30	*cis*	Vinyl isobutylether[c]

Group 2

COOH	C₆H₅	0.30	0.10	0.20	trans	Acrylamide
C₆H₅	n-C₃H₇	0.10	-0.05[d]	0.15	trans	Styrene[f]
C₆H₅	i-C₃H₇	0.10	-0.05[d]	0.15	trans	Styrene[f]
C₆H₅	n-C₄H₉	0.10	-0.05[d]	0.15	trans	Styrene[f]
C₆H₅	CH₃	0.10	-0.05	0.15	trans	Styrene[f]
C₆H₅	C₂H₅	0.10	-0.05	0.15	trans	Styrene[f]
Br	COOH	0.45	0.30	0	trans	Acrylamide
COOH	COOH	0.30	0.30	0	trans	Acrylamide[g]
COOH	COOC₂H₅	0.30	0.30	0	trans	Styrene[h]
COOC₂H₅	COOC₂H₅	0.30	0.30	0	trans	Vinyl chloride[h]
COOC₂H₅	COOC₂H₅	0.30	0.30	0	trans	Vinyl acetate[h]
COOC₂H₅	COOC₂H₅	0.30	0.30		trans	Diethyl maleate[h]
COOC₂H₅	COOC₂H₅	0.30	0.30		trans	Diethylfumareate
COOCH₃	COOCH₃	0.30	0.30		trans	Styrene[h]
Cl	Cl	0.47	0.47		trans	Styrene[h]
Cl	Cl	0.47	0.47		trans	Vinyl acetate[h]
Cl	Cl	0.47	0.47		trans	Dichloroethylene[h]
Cl	C₆H₅	0.10	0.10		trans	Maleic anhydride[h]
C₆H₅	COOC₂H₅	0.30	0.30	0	trans	Styrene[h]
CN	COOH	0.58	0.30	0.28	No difference	Styrene[h]

a Data of Furukawa et al.[20]
b Data of Machida and Matsuo.[4]
c Data of Inaki et al.[21]
d Estimated.
e Data of Furukawa et al.[22]
f Data of Yasufuku et al.[17]
g Data of Machida and Narita.[3]
h Data of Lewis and Mayo.[5]

one substituent is electron-donating and the other is electron-withdrawing or not.   As long as the steric inhibition of resonance is concerned in the *cis* isomer, the *trans* isomer is more reactive than the *cis* isomer.   Reaction mechanisms may be different from radical and ionic copolymerization, but a comparison of reactivities of *cis-* and *trans*-1,2-DE on copolymerization can be considered at the same level in regard to inductive, resonance, and steric effects by determining the difference of the two inductive substituent constants and the existance of steric hindrance of resonance.

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