

Vinyl Polymerization. XCII. Polymerization of Propenyl Chloride Isomers

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Synopsis

The effect of the substituent on polymerization of isopropenyl chloride (IPC), *cis*-propenyl chloride (CPC), and *trans*-propenyl chloride (TPC) has been investigated. These monomers homopolymerized only very slightly in the presence of radical or ionic catalyst, and only a low molecular weight polymer of IPC was isolated. However, these monomers copolymerized with radical initiator with vinyl acetate, vinyl chloride, and acrylonitrile, and their reactivities towards the poly(vinyl acetate) radical decreased in order of $IPC \gg TPC \geq CPC$. The Q, e values for the monomers were estimated as follows: for IPC, $Q = 0.06, e = -0.85$; for CPC, $Q = 0.005, e = -1.66$; for TPC, $Q = 0.009, e = -1.33$. Further results on copolymerization with maleic anhydride indicated that the steric effect of the substituent for these monomers increased in order $IPC \ll TPC \leq CPC$. On radical polymerization of IPC, its degradative chain transfer reactivity was suggested to be also significant.

INTRODUCTION

Previous papers have reported on the effect of an *endo*- or *exo*-substituent on radical polymerizations of bicyclo-[2.2.1]-heptane-2-carboxylates¹ and of bornyl methacrylates.² In radical polymerizations of bornyl methacrylates,² the results indicated that an *endo*-bornyl substituent showed the same electric and steric effects on the rate and the reactivity as a methyl substituent, but the *exo*-bornyl substituent showed somewhat increased steric effect.

In order to elucidate further the steric effect of the substituent on the vinyl polymerization, a study of the effect of the substituent in isopropenyl chloride (IPC), *trans*-propenyl chloride (TPC), and *cis*-propenyl chloride (CPC) on their polymerizations was taken up in the present work. Several studies on polymerization of IPC or an isomeric mixture of propenyl chlorides have been reported,³⁻⁶ but no detailed study as to the polymerizations of the respective pure propenyl chloride isomers under similar conditions has been found. The present paper deals with the effect of the substituent on polymerization and copolymerization of the various propenyl chloride isomers.

EXPERIMENTAL

Preparation of IPC, CPC, and TPC

The isomeric mixture of propenyl chlorides was prepared by dehydrochlorination of 1,2-dichloropropane. The dehydrochlorination was carried out by dropping 1,2-dichloropropane (1 mole) into 20% alcoholic solution of potassium hydroxide (1.5 mole) maintained at 74°C. (81% yield). The percentages of the various propenyl chloride isomers in the resulting isomeric mixture were found by gas chromatography to be 18.1 (IPC), 59.6 (TPC), and 22.3% (CPC). The crude mixture was then fractionated by using a precision fractionation column having a theoretical plate number of more than 50 into IPC, CPC, and TPC.

TABLE I
Purities and Properties of the Propenyl Chloride Isomers

Monomer	Purity, %	b.p., °C.	d_4^{20}	n_D^{20}	Relative retention volume ^a
IPC	99.84	22.5–23.0	0.931	—	156
TPC	99.42	37.0–38.0	0.932	1.4112	374
CPC	99.38	32.4–33.0	0.947	1.4069	294

^a Relative retention volume of the propenyl chloride isomers was calculated by assuming that the retention time for air was unity.

The physical properties of the resulting pure monomers are shown in Table I, in which their purities determined by gas chromatography are also indicated. Gas chromatography of the respective propenyl chloride isomers was determined by using a tricresyl phosphate (TCP) column in a stream of hydrogen (30 ml./min.) at 40°C. The infrared spectra (Fig. 1) showed characteristic absorption bands at 798 cm^{-1} for IPC, 1179 cm^{-1} for TPC, and 685 cm^{-1} for CPC, in good agreement with the reported values.⁷

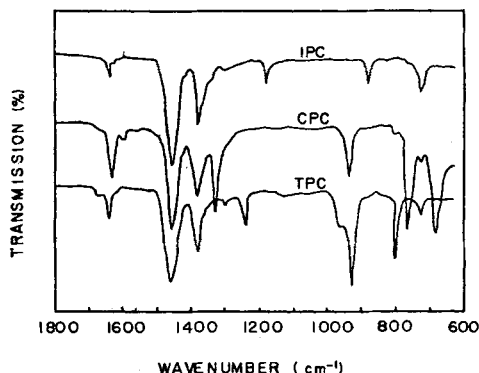


Fig. 1. Infrared spectra of propenyl chloride isomers (Nujol mull).

Other Materials

Vinyl acetate (VAC), vinyl chloride (VC), acrylonitrile (AN), and maleic anhydride (MAH) used as comonomers were purified by the conventional methods.⁸ Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Boron trifluoride-diethyl etherate was used after distillation. Butyllithium (Hans Heinrich Hutte), diethylaluminum chloride (Texas Alkyl Co.), and titanium trichloride (Stauffer Chem. Co.) were used without further purification.

Polymerization Procedure

Polymerization and copolymerization were carried out in a sealed tube of 20 ml. capacity. The required amounts of initiator, solvent, and comonomers were placed in the tube, and this tube was connected to a vacuum system. After degassing of its content by repeating freezing and thawing, the required amount of monomer which had been weighed beforehand in a vacuum system was charged into the tube by distillation, and the tube was then sealed off. In the case of ionic polymerization, a hard glass tube provided with rubber stopper from which catalyst was charged through a syringe next to the connection to the vacuum system was used.

Polymerization and copolymerization were carried out with shaking in a thermostat maintained at a constant temperature for a given time. After polymerization, the contents of the tube were poured into a large amount of methanol (ether was used in copolymerization with MAH) to precipitate the polymer. The resulting polymer was washed thoroughly, filtered, dried under vacuum at room temperature, and then weighed.

Analysis of the Polymer

The composition of the resulting polymer and copolymer was determined by elementary analyses for C, H, N, and Cl. Monomer reactivity ratios (r_1 and r_2) were calculated by the Fineman-Ross method.⁹

The content of 1,2-dichloride unit in the copolymers with VC was determined as follows.¹⁰ A given amount of the copolymer (0.2–0.3 g.) was placed in a glass tube containing about 1 g. of potassium iodide and 15 ml. of peroxide-free dioxane. The content of the tube was degassed by alternate freezing and thawing and then sealed off. The reaction was carried out for 96 hr. in boiling water and then the contents of the tube were poured into a mixture of 20 ml. of chloroform and 100 ml. of water. The free iodine was titrated with 0.05*N* sodium thiosulfate, 5% aqueous starch solution being used as an indicator. The percentage of 1,2-dichloride units present (Δ) was calculated from the equation:

$$\Delta = \frac{1}{2}(\text{free I}_2 \text{ eq./g. of polymer})(76.5 dM_1 + 62.5 dM_2) \times 100$$

where dM_1 and dM_2 are mole fractions of propenyl chloride and VC in the copolymer, respectively.

RESULTS

Polymerization of IPC, TPC, and CPC

The results of the homopolymerization of these propenyl chloride monomers with radical or ionic initiators are summarized in Table II. These monomers were found to be not polymerized by the presence of butyllithium (1.0×10^{-2} mole/l. in toluene at -78°C . for 65 hr.), boron trifluoride-diethyl etherate (5.0×10^{-2} mole/l. in toluene at $26-27^\circ\text{C}$. for 120 hr.), and diethylaluminum chloride-titanium trichloride ($\text{Al/Ti} = 2$) (0.167 mole/l. in *n*-heptane at 60°C . for 30 hr.).

TABLE II
Results of Polymerization of Propenyl Chloride Monomers

Initiation	Mono- mer ^a	Temp., $^\circ\text{C}$.	Time, hr.	Yield, %	η_{sp}/c of polymer ^b	Analyses of polymers ^c		
						C, %	H, %	Cl, %
[AIBN] = 1.84×10^{-2} mole/l. in bulk	IPC	60	100	2.1	0.017	74.42	8.92	16.47
	TPC	60	100	0.02	—	—	—	—
	CPC	60	100	Nil	—	—	—	—
γ -ray (5.089×10^5 r/hr.) in bulk	IPC	26-27	96	4.8	0.026	52.12	8.25	24.95
	TPC	26-27	96	0.04	—	—	—	—
	CPC	26-27	96	Nil	—	—	—	—
[(C_2H_5) ₂ AlCl] = 5.0×10^{-2} mole/l. in <i>n</i> - heptane	IPC	-78	79	Nil	—	—	—	—
	IPC	0	15	9.8	0.037	63.87	8.58	26.38
	IPC	26-27	192	1.9	—	—	—	—
	TPC	-78	122	Nil	—	—	—	—
	TPC	26-27	136	Nil	—	—	—	—
	CPC	-78	122	Nil	—	—	—	—
	CPC	26-27	42	Nil	—	—	—	—

^a Monomer concentrations were as follows: [IPC] = [TPC] = 12.2 mole/l., [CPC] = 12.4 mole/l. in bulk; [IPC] = [TPC] = 6.1 mole/l., [CPC] = 6.2 mole/l. in *n*-heptane.

^b Determined by viscosity measurement of 0.2% benzene solution at 30°C . in an Ubbelohde viscometer.

^c Calculated value for polypropenyl chloride: C, 47.06%; H, 6.54%; Cl, 46.40%.

From these results it was clear that these monomers polymerized slightly in the order $\text{IPC} \gg \text{TPC} \geq \text{CPC}$. During the polymerization of these monomers by AIBN or by ionic initiator, the polymerization mixtures changed in color from yellow to brown, and the colored polymer of IPC which showed a quite low specific viscosity were isolated. This polymer was also gradually converted to a deep-colored crosslinked polymer on being allowed to stand in air at room temperature.

Infrared spectra of the polymers which were allowed to stand in air for a week at room temperature are shown in Figure 2. Strong absorption bands attributed to carbon-carbon double bonds ($1610, 1630 \text{ cm}^{-1}$) and carbonyl group ($1720, 1740 \text{ cm}^{-1}$) were observed. These observations were also supported by the fact that the observed chlorine contents in the

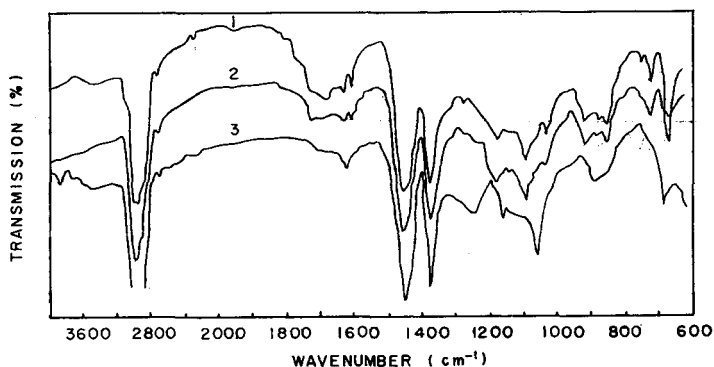


Fig. 2. Infrared spectra of poly(isopropenyl chlorides) obtained under various conditions (KBr disk): (1) polymer obtained with AIBN, (2) polymer obtained by γ -irradiation; (3) polymer obtained with Et_3AlCl .

polymers were less than those calculated for propenyl chloride as indicated in Table II. These results might indicate that the dehydrochlorination and oxidation of the resulting IPC polymer occurred during the polymerization or on standing in air.

Copolymerization with VAC

The results of the radical copolymerization of these monomers with VAC at 60°C. are shown in Table III. There is some question regarding the analytical values of the copolymers of IPC, because dehydrochlorination of the homopolymer took place readily, as stated above. In order to confirm this point, the observed carbon and hydrogen contents in the copolymers were compared with those calculated from their observed chlorine contents. The results shown in Table IV indicate that both values for

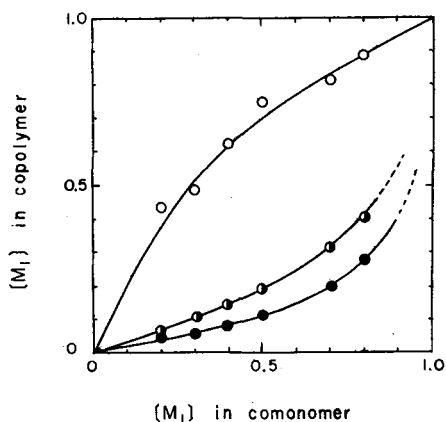


Fig. 3. Monomer-copolymer composition curves for copolymerization of propenyl chlorides (M_1) and VAC (M_2) initiated by AIBN at 60°C.: (O) IPC-VAC system; (\odot) TPC-VAC system; (\bullet) CPC-VAC system.

TABLE III. Results of Copolymerization of the Propenyl Chloride Monomers with VAC, VC, and AN at 60°C. in Benzene

Polymerization system	[M ₁] in comonomer, mole-%	Time, hr.	Yield, %	Rate of copolymerization, %/hr.	Copolymer	
					Cl, %	[M ₁], mole-%
IPC(M ₁)-VAC(M ₂)	20.0	12.0	11.4	1.0	18.7	43.1
	30.1	14.8	9.2	0.6	21.1	48.3
	39.9	15.5	5.7	0.4	27.4	61.9
	50.0	20.5	11.0	0.5	33.5	74.4
	70.2	40.9	2.7	0.07	36.6	80.8
	80.0	54.5	1.9	0.03	40.4	88.4
TPC(M ₁)-VAC(M ₂)	19.9	5.5	13.4	2.4	3.2	7.7
	30.2	6.0	10.3	1.7	4.7	11.1
	40.0	7.3	8.1	1.1	6.0	14.7
	50.0	17.8	10.2	0.6	8.1	19.6
	70.4	69.7	7.1	0.1	13.2	31.3
	80.0	83.2	2.9	0.03	17.1	40.4
CPC(M ₁)-VAC(M ₂)	20.2	4.0	11.0	2.8	1.8	4.3
	30.4	6.0	9.8	1.6	2.5	6.0
	40.1	10.0	9.4	0.9	3.4	8.2
	50.0	22.0	11.9	0.5	4.8	11.2
	70.8	37.5	4.3	0.1	8.2	19.7
	80.4	37.5	1.9	0.05	11.8	28.2
IPC(M ₁)-VC(M ₂)	10.0	3.0	15.6	5.2	52.3	38.7
	20.0	4.0	14.4	3.6	50.4	56.5
	30.1	5.0	10.8	2.2	49.1	70.2
	49.5	11.5	7.8	0.7	46.8	95.5
	69.8	39.2	7.4	0.2	38.1	—
	79.6	40.9	4.7	0.1	37.1	—
TPC(M ₁)-VC(M ₂)	10.1	2.0	13.5	6.8	56.8	0.1
	20.0	2.5	12.3	4.9	56.2	5.2
	30.2	5.0	10.6	2.1	55.4	11.5
	49.9	11.8	10.7	0.9	54.6	18.4
	70.0	24.0	4.0	0.2	52.6	35.7
	80.2	45.0	1.0	0.02	50.2	58.7
CPC(M ₁)-VC(M ₂)	10.1	1.2	5.7	5.0	57.3	1.0
	20.2	2.4	7.9	3.3	56.6	1.7
	30.4	4.5	10.7	2.4	56.1	5.7
	50.1	5.0	4.5	0.9	56.0	6.3
	70.4	16.8	3.1	0.2	54.8	16.7
	80.5	37.8	0.9	0.02	51.9	42.4
IPC(M ₁)-AN(M ₂)	9.9	0.3	2.8	9.3	10.4	7.5
	19.8	0.6	2.2	3.7	21.1	15.6
	41.6	0.6	1.2	2.0	35.0	27.2
	49.5	1.4	2.0	1.4	40.4	31.9
	69.3	2.0	1.6	0.8	46.5	37.7
	79.2	5.3	3.0	0.6	49.7	40.7
TPC(M ₁)-AN(M ₂)	10.0	0.3	2.0	6.7	1.5	1.1
	19.8	0.6	2.6	4.3	1.9	1.3
	29.7	0.6	1.5	2.5	3.0	2.1
	49.6	1.4	1.8	1.3	5.5	3.9
	69.4	2.0	0.9	0.5	14.2	10.3
	79.3	5.3	0.9	0.2	22.8	17.0

TABLE III (continued)

Polymerization system	[M ₁] in comonomer, mole-%	Time, hr.	Yield, %	Rate of copolymerization, %/hr.	Copolymer	
					Cl, %	[M ₁], mole-%
CPC(M ₁)-AN(M ₂)	10.0	0.3	7.2	24.0	1.3	0.9
	20.1	0.6	7.5	12.5	1.7	1.2
	30.2	0.6	3.9	6.5	2.4	1.6
	50.4	1.4	3.7	2.6	4.4	3.1
	70.5	2.0	1.2	0.6	8.4	6.0
	80.6	5.3	0.9	0.2	14.7	10.7

carbon and hydrogen are the same within experimental error, and hence no dehydrochlorination of the copolymer occurred.

As is clearly shown in Table III, the rates of copolymerization of the monomers with VAC markedly decreased as the concentration of the propenyl chloride monomer increased. The resulting monomer-copolymer composition curves based on the results of Table III are shown in Figure 3. The resulting copolymers were almost colorless powders and were soluble in acetone, benzene, and tetrahydrofuran. Their infrared spectra showed no absorption band due to the carbon-carbon double bond.

TABLE IV

Comparison of the Carbon and Hydrogen Contents in the Copolymers of IPC with VAC

Carbon, %		Hydrogen, %		Chlorine, % (obs.)
Obs.	Calcd. ^a	Obs.	Calcd. ^a	
52.73	52.29	6.97	6.80	18.68
52.20	51.84	6.75	6.78	21.06
51.26	50.64	6.59	6.72	27.41
50.36	49.50	6.86	6.66	33.45
49.73	48.91	6.87	6.63	36.60
49.16	48.19	6.79	6.60	40.44

^a Calculated from the observed chlorine contents.

Copolymerization with VC

The results are shown in Table III. The resulting monomer-copolymer composition curves are shown in Figure 4. Figure 4 indicates that the copolymerization of the propenyl chloride monomers with VC followed almost the same trend as with VAC. The resulting copolymers were colorless or light yellow powders and were soluble in cyclohexanone, tetrahydrofuran, and nitrobenzene.

In order to determine the regularity of the head-to-tail configuration on radical polymerization of the monomers, the content of 1,2-dichloride unit in the copolymers with VC was determined by the potassium iodide method. The results are shown in Figure 5; the content of 1,2-dichlorides

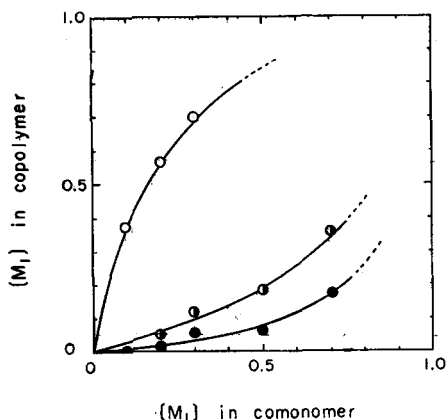


Fig. 4. Monomer-copolymer composition curves for copolymerization of propenyl chlorides (M_1) with VC (M_2) initiated by AIBN at 60°C.: (O) IPC-VC system; (○) TPC-VC system; (●) CPC-VC system.

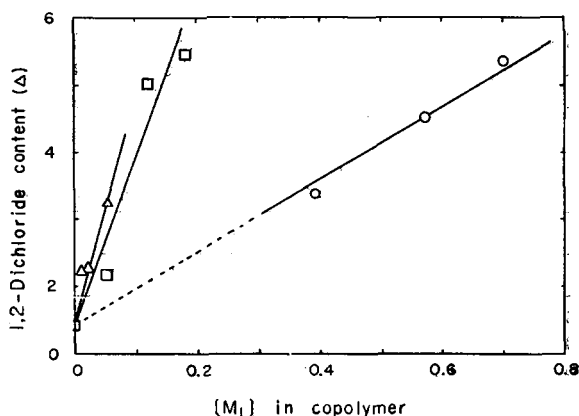


Fig. 5. Relationship between the percentage of 1,2-dichloride unit and the concentration of propenyl chloride (M_1) in copolymer with VC: (O) IPC-VC copolymer; (□) TPC-VC copolymer; (Δ) CPC-VC copolymer.

increased linearly with an increase of the propenyl chloride content in the copolymers. The slopes of these straight lines, which might indicate the rate of formation of the 1,2-dichloride unit, were observed to become greater in the order of $IPC \ll TPC \leq CPC$. By extrapolating these lines to $[PC] = 0$, the same intercepts were obtained as 1.49 which showed the content of the 1,2-dichloride unit for poly(vinyl chloride).

Copolymerization with AN

The results are shown in Table III; the monomer-copolymer composition curves are shown in Figure 6. The resulting colorless or light yellow copolymers were soluble in dimethylformamide.

Copolymerization with MAH

The results of copolymerizations of the propenyl chloride monomers with MAH initiated by AIBN at 60°C. are shown in Table V, and the monomer-copolymer composition curves are shown in Figure 7.

As can be seen from Table V, IPC copolymerized quite readily with MAH to give a colorless polymer which showed a relatively high specific viscosity. However, TPC and CPC copolymerized at rather slow rates and light red-colored copolymers having a lower specific viscosity were obtained.

TABLE V
Results of Copolymerization of Propenyl Chlorides (M_1) with MAH (M_2) at 60°C.;
[AIBN] = 1.68×10^{-2} mole/l. in Benzene

M_1	[M_1] in comono- mer, mole-%	Time, hr.	Yield, %	Rate of copoly- merization, %/hr.	Copolymer		
					Cl, %	[M_1], mole-%	η_{sp}/c^a
IPC	19.9	3.5	48.4	13.8	18.7	45.6	—
	39.9	3.5	84.1	24.0	20.0	49.2	0.51
	61.4	3.5	73.1	20.9	20.5	50.0	—
	80.0	3.5	39.3	11.2	22.5	54.3	—
TPC	19.9	20	2.9	0.15	12.5	32.0	—
	40.0	20	6.0	0.30	16.9	42.3	0.065
	61.4	20	7.8	0.39	19.3	47.8	—
	79.9	20	5.3	0.27	21.8	53.2	—
CPC	20.2	20	4.1	0.21	11.8	30.5	—
	40.3	20	7.4	0.37	15.2	38.5	0.046
	61.8	20	10.2	0.51	17.4	43.5	—
	80.3	20	7.5	0.38	19.1	47.3	—

* Determined by viscosity measurement of 0.4% tetrahydrofuran solution in an Ubbelohde viscometer.

From Table V, the composition of the resulting copolymers was found to be independent of monomer feed ratio and to consist of 1:1 molar composition of MAH and propenyl chloride monomer.

Monomer Reactivity Ratios and Q - e Values for Propenyl Chloride Isomers

According to the Fineman-Ross method,⁹ the monomer reactivity ratios (r_1 and r_2) were calculated for these copolymerization systems. The results are summarized in Table VI. From the r_1 and r_2 values obtained, Q and e values for the monomers were calculated by assuming the values: VAC($Q_2 = 0.026$, $e_2 = -0.22$);¹¹ VC($Q_2 = 0.044$, $e_2 = 0.20$);¹¹ AN($Q_2 = 0.6$, $e_2 = 1.2$).¹¹ In Table VI, the reported values for allyl chloride (AC) which may be considered a propenyl chloride isomer are also indicated.

As understood from this table, the values of Q_1 for the propenyl chloride isomers and the values of $1/r_2$ which might indicate the reactivity of the propenyl chloride isomers to polymer radicals were found to be of the same

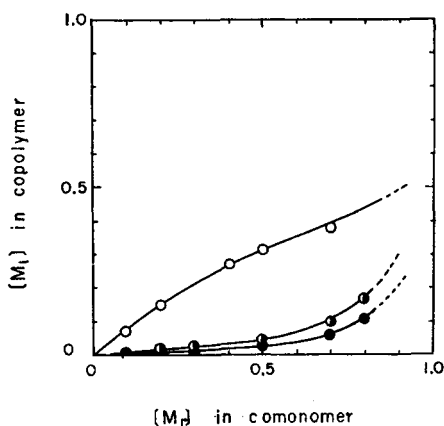


Fig. 6. Monomer-copolymer composition curves for copolymerization of propenyl chloride (M_1) with AN (M_2) initiated by AIBN at 60°C.; (○) IPC-AN copolymer; (◐) TPC-AN copolymer; (●) CPC-AN copolymer.

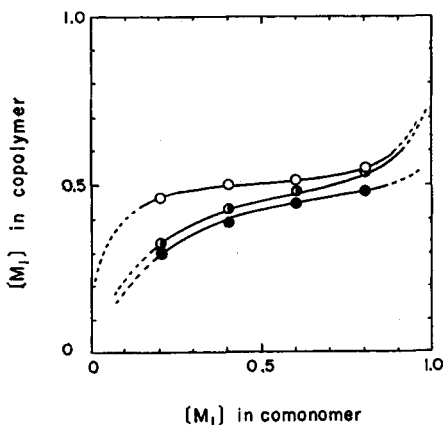


Fig. 7. Monomer-copolymer composition curves for copolymerization of propenyl chloride (M_1) with MAH (M_2) initiated by AIBN at 60°C.; (○) IPC-MAH copolymer; (◐) TPC-MAH copolymer; (●) CPC-MAH copolymer.

order as their reactivities for homopolymerization. The products r_1r_2 which are used as a measure of alternative tendency for copolymerization were calculated as 0.0004 for IPC-MAH, 0.013 for TPC-MAH, and 0.0002 for CPC-MAH copolymerization systems.

TABLE VI
Monomer Reactivity Ratios(r_1 , r_2) and Q_1 , e_1 Values for Propenyl Chloride Isomers

M_1	M_2	r_1	r_2	$1/r_2$	Relative reactivity	Q_1	e_1
IPC	VAC	1.84	0.22	4.55	33	0.06	-0.85
IPC	VC	5.21	0.18	5.56	67	0.24	-0.14
IPC	AN	0.01	1.4	0.72	21	0.04	-0.86
IPC	MAH	0.06	0.06	16.7	6.8	—	—
TPC	VAC	0.08	3.56	0.28	2	0.009	-1.33
TPC	VC	0.18	4.0	0.25	3	0.01	-0.37
TPC	AN	0.01	18.0	0.057	2	0.008	-0.11
TPC	MAH	0.05	0.26	3.84	1.6	—	—
CPC	VAC	0.01	7.0	0.14	1	0.005	-1.66
CPC	VC	0.08	12.1	0.083	1	0.004	0.02
CPC	AN	0.005	29.5	0.034	1	0.005	-0.18
CPC	MAH	0.004	0.41	2.44	1	—	—
AC	VAC	0.67 ^a	0.7 ^a	1.43	10	0.056 ^b	0.11 ^b
AC	AN	0.05 ^a	3.0 ^a	0.33	9.7	0.056 ^b	0.11 ^b

^a Data of Agron et al.¹² (68°C.).

^b Data of Chapin et al.¹³ (60°C.).

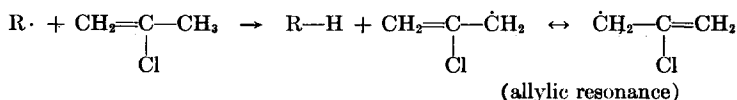
^c Data of Young.¹¹

DISCUSSION

As can be seen from Table II, the reactivities of these propenyl chloride isomers for their homopolymerization were quite low and decreased in the order of IPC \gg TPC \geq CPC. The same reactivity order was also found for their copolymerizations (Table VI). The low reactivities of TPC and CPC which were 1,2-disubstituted ethylene monomer might be understood by an increased steric effect of the substituent in their monomers.

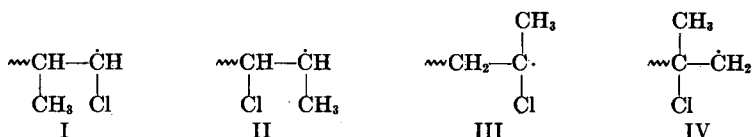
From Table VI, TPC was about two or three times as reactive towards the polymer radicals as CPC. This difference coincided with the results on *cis*- or *trans*-1,2-dichloroethylene observed by Lewis and Mayo,¹⁴ who reported that the *trans* isomer was six times as reactive as the *cis* isomer towards attack of the poly(vinyl acetate) radical. Accordingly, the rather low reactivity of CPC compared to TPC might be understood by a decreased resonance stabilization energy in its transition state as the result of the steric effect of the *cis* substituent. It might be also supported by the lower Q value for CPC than TPC as indicated in Table VI.

However, in radical polymerization of IPC which is known to have a smaller steric effect than TPC or CPC, the degradative monomer chain transfer (allylic termination) might be indicated as an important factor in the lower reactivity as well as that for AC:



where $R\cdot$ is an initiator or polymer radical. This fact could be supported by the results that IPC copolymerized without retardation more easily with MAH than TPC or CPC to yield a high molecular weight alternating copolymer. However, it was found that the rates of copolymerizations with VAC, VC, and AN decreased with increasing concentration of the propenyl chloride monomer, indicating that the degradative PC monomer chain transfer reactivity and the steric effect of the substituent might be also important for the copolymerizations.

Let us consider the growing polymer ends for each of the isomers to be as shown in I-IV:



where structures I and II are those for TPC and CPC, and structure III and IV are alternative ones for IPC.

As can be expected from the observed Q values (Table VI), the difference in resonance stabilization energy was not so large between the structures of I and II in the *cis* and *trans* isomers. In the case of IPC, however the structure of III was more stable than that of IV and also than the structures of I and II. These differences might be expected to give the irregularity of the head-to-tail configuration in the repeated monomer unit of the resulting polymer chain.

This possibility was checked by the determination of the 1,2-dichloride content in the copolymers with VC. As clearly indicated in Figure 5,

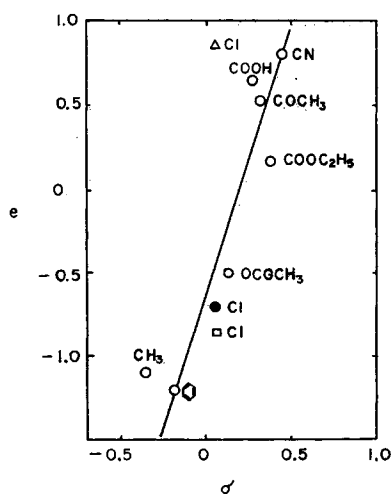


Fig. 8. Relationship between e values and σ constants for substituted isopropenyl monomers: (Δ) Young's value; (\bullet) calculated from Tkachenko's data;⁶ (\square) observed value.

the rate of formation of the 1,2-dichloride unit in the propenyl chloride copolymers with VC increased in the order $IPC \ll TPC \leq CPC$, which was found to be an order which is the reverse of their reactivities for polymerization.

Although the observed e values for TPC and CPC were in agreement with the reported value for the isomeric propenyl chloride mixture, the e value (-0.85) for IPC was quite different from this value (0.86).¹¹ In order to check this point, the reported e values for substituted isopropenyl monomers were plotted against the σ values of the substituent. As shown in Figure 8, the result indicated that there was clearly a linear relationship between the e values of the monomers, including that for IPC, obtained in this study and the σ values of the substituent. Accordingly, it was concluded that the e value obtained in this study was the appropriate value.

The homopolymer of IPC was very unstable and dehydrochlorination and oxidation leading to formation of a colored polymer took place easily during the polymerization, or on standing afterwards. However, it was suggested that the IPC unit in the polymer chain was stabilized by copolymerization with the other monomers.

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Résumé

On a étudié l'influence du substituant sur la polymérisation du chlorure d'isopropényle (IPC), du chlorure de *cis*-propényle (CPC) et du chlorure de *trans*-propényle (TPC). Ces monomères homopolymérisent fortement en présence de catalyseurs radicalaires ou ioniques: on a pu isoler seulement un polymère de faible poids moléculaire de l'ICP. Cependant ces monomères copolymérisent par initiation radicalaire avec l'acétate de vinyle, le chlorure de vinyle et l'acrylonitrile, et leurs réactivités vis-à-vis du radical de l'acétate de polyvinyle diminuent dans l'ordre $IPC \gg TPC > CPC$. Les valeurs de Q

et de e pour ces monomères sont les suivantes: IPC: $Q = 0.06$, $e = -0.85$; CPC: $Q = 0.005$, $e = -1.66$; TPC: $Q = 0.009$, $e = -1.33$. A partir des résultats obtenus lors de la copolymérisation avec l'anhydride maléique, l'effet stérique du substituant pour ces monomères augmente dans l'ordre $IPC \ll TPC \leq CPC$. Lors de la polymérisation radicalaire de l'IPC, la réactivité du transfert de chaîne dégradant est également important.

Zusammenfassung

Der Einfluss des Substituenten auf die Polymerisation von Isopropenylchlorid (IPC), *cis*-Propenylchlorid (CPC) und *trans*-Propenylchlorid (TPC) wurde untersucht. Diese Monomeren zeigten in Gegenwart von radikalischen oder ionischen Katalysatoren kaum eine Homopolymerisation: lediglich ein niedrigmolekulares Polymeres von IPC wurde isoliert. Mit radikalischen Startern trat jedoch eine Copolymerisation dieser Monomeren mit Vinylacetat, Vinylchlorid und Acrylnitril ein, wobei ihre Reaktivität gegen das Polyvinylacetatradikal in der Reihenfolge $IPC \gg TPC \geq CPC$ abnahm. Für diese Monomeren wurden folgende Q - und e -Werte bestimmt: IPC: $Q = 0.06$, $e = -0.85$; CPC: $Q = 0.005$, $e = -1.66$; TPC: $Q = 0.009$, $e = -1.33$. Ergebnisse bei der Copolymerisation mit Maleinsäureanhydrid zeigen weiters, dass der sterische Effekt des Substituenten bei diesen Monomeren in der Reihenfolge $IPC \ll TPC \leq CPC$ zunimmt. Für die radikalische Polymerisation von IPC wurde auch eine charakteristische degradative Kettenübertragung angenommen.

Received April 8, 1964

Revised July 9, 1964