distribution and the comparison between K_t calculated by using eq 8 and that found experimentally. Usually, in a low conversion free radical polymerization the polydispersity of the molecular weight distribution can be expressed by the ratio of $\overline{X}_w/\overline{X}_n$, which lies between 1.5 and 2. The experimentally found value of the rate constant in a free radical polymerization is the average rate constant for reaction between all possible pairs of radicals existing in the radical population given by

$$\overline{K}_t = \sum_{N_A=1}^{\infty} \sum_{N_B=1}^{\infty} \left[K_t \frac{[P_{NA}{}^0][P_{NB}{}^0]}{\left(\sum_{N=1}^{\infty} [P_N{}^0] \right)^2} \right] \quad (10)$$

where $[P_N{}^0]$ is the concentration of radical of size N and K_t is given by eq 8 as a function of size and total polymer concentration. It is possible to introduce eq 8 into eq 10 and use the kinetic equations to obtain the relation between the average rate constant, $\overline{K}_t$, the average degree of polymerization $\overline{X}_N$, and the total polymer concentration. If this were done the comparison of calculated rate constants with the experimental values would be more reliable. This would also allow one to calculate the effect of concentration dependence of $\overline{K}_t$ on the rate of polymerization and molecular weight of polymer. Work is in progress on this extension and will be reported shortly.[17]

In the present work, however, $\overline{K}_t$ has been calculated by the expedient of assuming that $N_A = 2N_B$. This approximation appears to give reasonable results, but a more exact calculation should be done using eq 10.

In summary, the good results obtained with the present development support its validity. It would appear that the termination reaction in the initial stages of polymerization is controlled by segmental diffusion of chain ends. Further, the concentration dependence of the termination rate constant in the initial stages is mainly due to the effects of intermolecular interactions on the segmental diffusion process.

Acknowledgment. Support of H. K. Mahabadi by Arya-Mehr University of Technology (Iran) is gratefully acknowledged as is support of this work by the National Research Council of Canada.

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Preparation and Polymerization of $\alpha,\alpha,\alpha',\alpha'$-Tetrachloro-2-cyano-*p*-xylylene

Shouji Iwatsuki* and Kimio Inoue

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464, Japan. *Received March 8, 1976*

ABSTRACT: $\alpha,\alpha,\alpha',\alpha'$-Tetrachloro-2-cyano-*p*-xylylene (CTCX) was prepared as follows: 2,5-Dimethylbenzonitrile was obtained by the Sandmeyer reaction of *p*-xylidine with nickel cyanide. 2,5-Ditrichloromethylbenzonitrile was obtained by chlorination of 2,5-dimethylbenzonitrile, and CTCX was obtained by gas phase dechlorination of 2,5-ditrichloromethylbenzonitrile on copper mesh. Spontaneous polymerization of CTCX in toluene was studied. The kinetics of polymerization was approximately of the first order with respect to monomer when its concentration was higher than $2\text{–}3 \times 10^{-3}$ mol/l., whereas it was second order below this monomer concentration. An apparent first-order rate constant is 1.3×10^{-4} s^{-1} at 30 °C at 1.01×10^{-2} mol/l. of initial monomer concentration. An apparent activation energy of polymerization was calculated as 8.8 kcal/mol. Copolymerizations of CTCX–styrene, CTCX–$\alpha,\alpha,\alpha',\alpha'$,2,5-hexachloro-*p*-xylylene(HCX), and CTCX–$\alpha,\alpha,\alpha',\alpha'$-tetrachloro-*p*-xylylene(TCX) were studied. Relative reactivities of CTCX, HCX, and TCX toward two kinds of polymer radicals were determined and compared with some calculated quantum chemical values.

p-Xylylene (QM)[1,2] and its chlorine-substituted derivatives[3–6] show very interesting differences in chemical nature. QM may have a diradical-like character, which plays an important role in its reactions.[7–9]

Considering these unique chemical properties of QM derivatives, it is interesting to study the chemistry of *p*-xylylene derivatives and in particular their polymerization behavior. However, the study has not yet been extensively carried out, probably because it is quite difficult to isolate these substances as pure compounds due to their high reactivity. One derivative, $\alpha,\alpha,\alpha',\alpha'$-tetrachloro-*p*-xylylene (TCX),[3,4] was isolated as a yellow crystalline compound and it polymerizes readily. It may be expected that the derivatives of TCX carrying strongly electron-withdrawing substituents may be less reactive than TCX and, therefore, more easily isolated as pure crystals. In fact, one of the present authors (S.I.) prepared $\alpha,\alpha,\alpha',\alpha'$,2,5-hexachloro-*p*-xylylene (HCX) as pure yellow crystals and studied its polymerization behavior.[6]

The present paper describes the preparation of another TCX derivative with a strong electron-withdrawing substit-

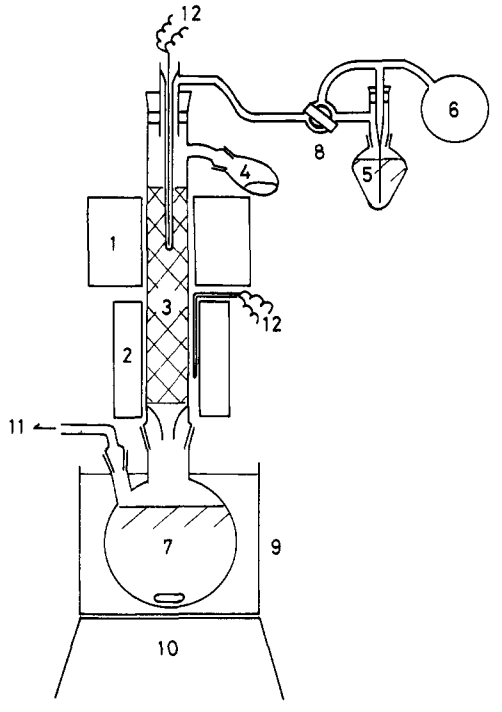


Figure 1. Diagram of the apparatus for preparation of CTCX: No. 1, first electric furnace; No. 2, second electric furnace; No. 3, rolled copper mesh; No. 4, 2,5-ditrichloromethylbenzonitrile; No. 5, solvent for carrier gas; No. 6, a balloon with nitrogen gas; No. 7, trapping solvent; No. 8, stopcock; No. 9, dry ice–methanol bath; No. 10, magnetic stirrer; No. 11, vacuum pump; No. 12, thermocouple.

uent, namely, α,α,α′,α′-tetrachloro-2-cyano-*p*-xylylene (CTCX), and reports its polymerization behavior which is compared with other *p*-xylylenes.

Experimental Section

Preparation of 2,5-Ditrichloromethylbenzonitrile. 2,5-Dimethylbenzonitrile was prepared by the Sandmeyer reaction[10] of *p*-xylidine with nickel cyanide (56% yield, bp_{17} 109–110 °C, (lit.[11] bp_{17} 108–109 °C)).

2,5-Dimethylbenzonitrile (57.5 g) and hexamethylenetetramine (0.5 g) were dissolved in 500 ml of carbon tetrachloride. Two equivalents of chlorine gas were bubbled into the resulting solution at 90–95 °C for 250 h during which time 3-ml portions of 2% benzoyl peroxide–carbon tetrachloride solution were added every 4 h. The carbon tetrachloride was removed under reduced pressure and the solid residue was dissolved in ethyl acetate under refluxing. The solution was cooled to deposit a colorless crystalline compound, which was recrystallized repeatedly using ethyl acetate as solvent to give 48.5 g of 2,5-ditrichloromethylbenzonitrile as colorless plates, mp 116.5–117.5 °C (41.4% yield). Anal. Calcd for $C_9H_3Cl_6N$: C, 32.09; H, 0.80; Cl, 62.96; N, 4.15. Found: C, 32.47; H, 1.26; Cl, 61.81; N, 4.21. UV, 293 nm (ε 1.61×10^3), 283 nm (1.47×10^3), 278 nm shoulder (0.980×10^3) in cyclohexane; ir, $\nu_{C\equiv N}$ 2220 cm^{-1}, ν_{C-Cl} 740 cm^{-1}; NMR, multiplet at 8.2–8.5 ppm (in chloroform-*d*).

Preparation of α,α,α′,α′-Tetrachloro-2-cyano-*p*-xylylene (CTCX). The preparation was carried out by a gas phase dechlorination of 2,5-ditrichloromethylbenzonitrile on copper mesh. A diagram of the apparatus employed is shown in Figure 1. Copper mesh rolled tightly was placed in the Pyrex reaction tube. A 100-ml flask of No. 5 was filled with acetonitrile and about 2 g of 2,5-ditrichloromethylbenzonitrile was set in a 10-ml flask of No. 4 wrapped with a band-electric heater. Anhydrous methanol was placed as a trapping solvent in a 500-ml flask of No. 7 which was cooled in a dry ice–methanol bath. The upper part of the reaction tube was heated at 550 °C in an electric furnace of No. 1 and the lower part at 240 °C in another furnace of No. 2. The pressure in the apparatus was reduced below 0.2 mm. Then, a stopcock of No. 8 was opened appropriately to flow a moderate stream of acetonitrile vapor from top of the reaction tube to the flask of No. 7, as the receiver. The flask of No. 4 was heated at about 150 °C to sublime 2,5-ditrichloromethylbenzonitrile and the resulting vapor was introduced into the reaction tube. During this sublimation, the pressure in the apparatus increased up to 0.5 mm. Once the sublimation terminated, the pressure went down to 0.1 mm again. Then, nitrogen gas was introduced into the apparatus. The reaction product was obtained as a yellow suspension in the flask of No. 7. The suspension was filtered with suction using a well-cooled filtering flask to collect the yellow precipitate. The precipitate was dissolved in 20–30 ml of tetrahydrofuran cooled at −78 °C. The resulting solution was filtered to remove insoluble material and about a half portion of the tetrahydrofuran was removed under reduced pressure. Then, 20–30 ml of methanol cooled at −78 °C was added and the solution was kept at −78 °C to deposit CTCX as yellow needles (40–50% yield). The product was recrystallized repeatedly using a tetrahydrofuran–methanol mixture as solvent.

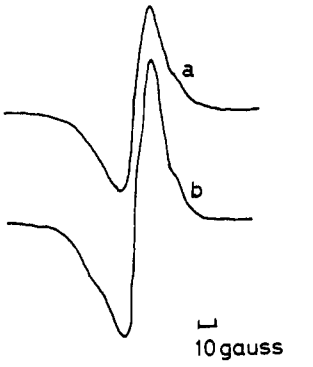


Figure 2. ESR spectra of CTCX: (a) neat crystalline CTCX, g = 2.0069; (b) solid CTCX sample after polymerization for 1 h at room temperature.

All the above-mentioned procedures were carried out under nitrogen.

Elementary analyses of this compound could not be carried out in the monomeric state because it polymerizes very rapidly when it is warmed above room temperature. Analyses of the polymerized product, obtained by allowing yellow CTCX to remain at room temperature, were carried out to infer the empirical formula of the monomer. Anal. Calcd for $C_9H_3Cl_4N$: C, 40.50; H, 1.13; Cl, 53.12; N, 5.25. Found: C, 40.48; H, 1.41; Cl, 50.36; N, 5.17. NMR, two singlets at 7.15 and 7.80 ppm (area ratios 2:1) in chloroform-*d*; UV, λ_{max} 384 nm (ε 1.42×10^4), 366 nm (3.23×10^4), 351 nm (2.89×10^4), and 338 nm shoulder (1.88×10^4) in cyclohexane, 370 nm (2.55×10^4) and 357 nm shoulder (2.23×10^4) in toluene, and 365.5 nm (8.66×10^3), 353 nm (8.60×10^3), and 326.5 nm (4.59×10^3) in 2-methyltetrahydrofuran; ESR results are shown in Figure 2.

Pure crystalline CTCX could be kept unchanged at −78 °C under nitrogen.

Polymerization Procedure. All procedures were carried out under nitrogen.

A given amount of CTCX was added to a given amount of well degassed and cooled toluene, and the mixture was stirred vigorously to dissolve CTCX. This stirring was necessary to obtain the toluene solution of CTCX with a concentration higher than 10^{-3} mol/l. The actual concentration of the resulting solution was determined spectrophotometrically, after dilution, using absorbances at 370 and 357 nm.

In the case of homopolymerization, 5–6 ml of the solution was placed into an ampule which was degassed completely by the freeze–thaw technique and sealed. The ampule was wrapped with aluminum foil to exclude light and placed in a thermostated bath without stirring. After the polymerization, the ampule was cooled in a dry ice–methanol bath and then opened. Cooled toluene was added and the solution was filtered with suction using a well cooled filtration flask to remove precipitated polymer. The concentration of CTCX in the filtrate was determined spectrophotometrically. The amount of CTCX polymerization was calculated from the difference in concentration of CTCX before and after polymerization.

In cases of copolymerization, toluene solutions of TCX and HCX were prepared in the same way as in the preparation of CTCX solution. In CTCX–TCX and CTCX–HCX systems, the respective monomers in toluene solutions were placed in an ampule. In the CTCX–styrene (St) system, the CTCX solution and St were placed in an ampule. The ampule containing the monomer mixture solution was degassed by the freeze–thaw technique, sealed, wrapped with aluminum foil, and set in a bath thermostated at 20 °C without stirring for a fixed time of polymerization. It was again cooled to −78 °C and opened and an excess amount of cooled methanol was added to deposit copolymer, which was filtered, washed repeatedly with cooled

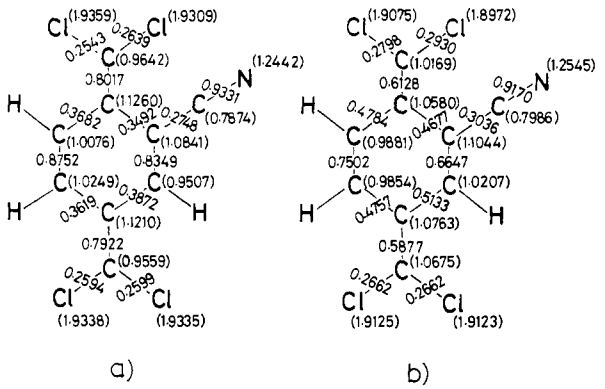


Figure 3. π-electron density and bond order of CTCX: (a) ground state, (b) singlet excited state.

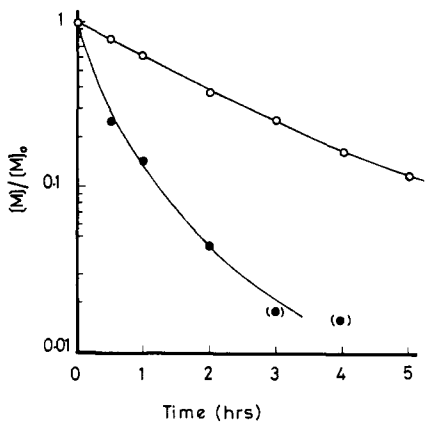


Figure 4. Effect of oxygen gas on polymerization of CTCX in toluene at 30 °C ($[M]_0 = 1.01 \times 10^{-2}$ mol/l.) (○) degassed condition, (●) with oxygen gas.

methanol, and dried under reduced pressure to constant weight. The copolymers were obtained as white powders. Compositions of the copolymers were determined by elemental analyses.

Reagents and Instruments. Reagent grade commercial *p*-xylidine, sodium nitrite, sodium cyanade, nickel nitrate, and benzoyl peroxide were used without further purification. Styrene as comonomer and all solvents were purified by the conventional method. HCX and TCX were prepared by the method described previously[6] and by that of Gilch,[3] respectively.

The instruments employed in this work were as follows: spectrophotometer of Hitachi Model 123, Yanagimoto microdetermining apparatus for element Model MX-3, ESR spectrometer of Nippon Denshi Corp. Model JES-3BX, and NMR spectrometer of Nippon Denshi Corp. Model C-60HL.

Results and Discussion

Free-radical chlorination of 2,5-dimethylbenzonitrile was carried out by the method of Schein and Yagupolskii.[12] The first four chlorine atoms were introduced easily, but introduction of the last two chlorine atoms occurred with difficulty and needed a very long reaction time. 2,5-Ditrichloromethylbenzonitrile was obtained as colorless plates. Its crystallization from ethyl acetate solution took place with difficulty, requiring seeding with crystals obtained previously.

When dechlorination of 2,5-ditrichloromethylbenzonitrile was carried out using the apparatus[6] for HCX, CTCX could not be obtained in monomeric form. Nevertheless the dechlorination took place successfully, since a significant amount of poly(CTCX) was deposited as a white powder or brittle transparent film on the walls of the apparatus between the generator and the monomer collector. Many modifications were tried to improve the procedure. The most successful utilized a diluent stream of a carrier gas (solvent vapor) to minimize residence time in the reaction tube and thereby improved the efficiency of monomer accumulation in the liquid trap. A polar aprotic solvent, such as tetrahydrofuran and acetonitrile, was found to be better as a carrier gas than nonpolar solvent, such as cyclohexane and *n*-hexane. The prime requirements of the trapping solvent are that it be liquid at −78 °C and also inert to CTCX. Moreover, it is preferable to be a good solvent for recrystallization of CTCX. When acetonitrile was employed as carrier gas and methanol as trapping solvent, the product was obtained as a yellow suspension. Copper chloride was deposited on the copper mesh of the lower part of the reaction tube of No. 2. Acetonitrile and methanol were preferred as carrier gas and trapping solvent, respectively. Recrystallization of CTCX was carried out using a mixture of tetrahydrofuran and methanol, since CTCX is insoluble in methanol but very soluble in tetrahydrofuran.

The yellow color of crystalline CTCX was found to fade rapidly when exposed to air even at −78 °C. Accordingly, all procedures handling CTCX were carried out under nitrogen (in a nitrogen tent), and all the solvents were degassed well by the freeze–thaw technique prior to use in these experiments to avoid any consumption of monomer via reaction with oxygen gas.

Results of ESR measurement of CTCX at liquid nitrogen temperature are shown in Figure 2. Crystalline CTCX, which was placed carefully in a sample tube under nitrogen atmosphere at low temperature, manifested an absorption peak at $g = 2.0067$, as shown in Figure 2a. The peak is conceivably indicative of the α,α-dichlorobenzyl type radical, considering that 1,1-dichloroethyl and 1,1-dichloro-2,2,2-trifluoroethyl radicals show peaks at $g = 2.007\,27$ and $2.007\,97$, respectively.[13] However, when the sample was dissolved in cold tetrahydrofuran after the measurement, a slight cloudy solution was given instead of a clear solution, inferring the contamination with a minute amount of poly(CTCX). It could not be concluded in this work whether the peak is due to the diradical of CTCX or due to the polymer radical which is easily produced in the sample during the ESR measurement. The same ESR spectrum was observed after polymerization of CTCX as shown in Figure 2b.

In Figure 3 are shown the π-electron density and bond order of CTCX in its ground and excited states. The values were calculated by the ASMO–SCF method on the basis of the following geometric structure of the CTCX molecule; all atoms are positioned on a plane, bond angles being of typical sp^2 and sp^1 carbons, bond distances of C–Cl, C=C of extracyclic position, C–C in the ring, C–H, C–C between the ring carbon and cyano group and C≡N being 1.72, 1.38, 1.40, 1.08, 1.45, and 1.16 Å, respectively. Excitation energies from the ground state to the singlet and triplet excited states were calculated to be 3.41 and 1.06 eV, respectively. The former value (3.41 eV = 362.8 nm) agrees well with the value observed in electronic excitation (λ_{max} 366 nm in cyclohexane). Similar results were also observed with TCX[4] and HCX,[6,14] when uv absorption was measured in cyclohexane.

An effect of oxygen gas on spontaneous homopolymerization of CTCX was examined. In Figure 4 are shown first-order rate plots of the polymerizations in toluene at 30 °C, where plots of a and b correspond to the system degassed completely by the freeze–thaw technique and to the system saturated with oxygen gas by bubbling it into the polymerization solution, respectively. In the former system, the rate of disappearance of CTCX monomer is approximately of the first order with respect to monomer concentration and an apparent rate constant being calculated as 1.3×10^{-4} s^{-1}, whereas in the latter system the rate is higher than the rate of the former system by a factor of about 4 and it is of higher order with respect to monomer concentration. In addition, the difference in the uv absorption spectrum in wavelength range from 290

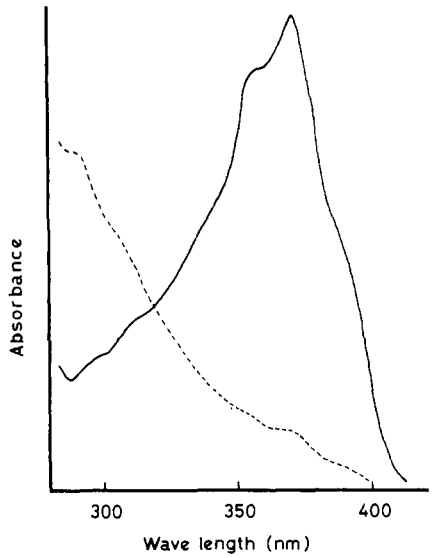


Figure 5. UV spectra of CTCX–toluene solutions after polymerization of CTCX: full line, degassed; dotted line, with oxygen gas.

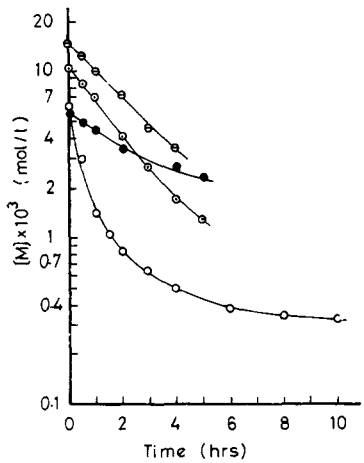


Figure 6. First-order rate plots of CTCX polymerization in toluene at various temperatures: (○) 60 °C, (⊙) 30 °C, (⊖) 20 °C, (●) 10 °C.

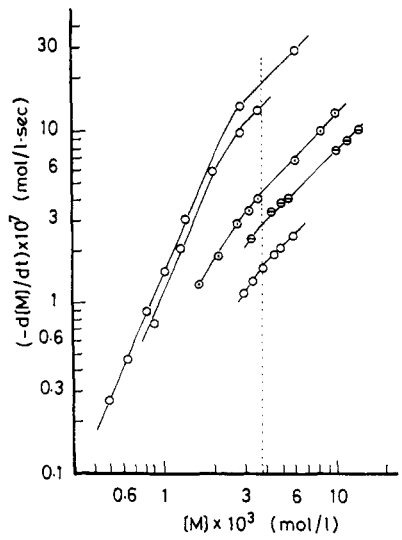


Figure 7. Log–log plots of rate of CTCX polymerization vs. monomer concentration: (○) 60 °C, (⊙) 30 °C, (⊖) 20 °C, (●) 10 °C.

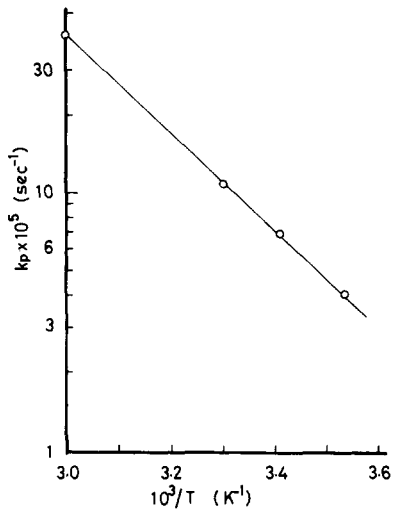


Figure 8. Arrhenius plot of CTCX polymerization.

to 430 nm was observed as shown in Figure 5. In the former system, the ratio OD_{370}/OD_{357} of absorbances at wavelengths of 370 and 357 nm was found to be always almost constant during the whole time of polymerization, indicating that no additional compound is produced to interfere with the absorpiton of CTCX during the polymerization. On the other hand, in the latter system the absorption spectrum of the sample after 4 h of reaction showed additional absorption at wavelengths lower than 290 nm which never appeared in the former system, probably because CTCX reacts rapidly with oxygen gas to give the corresponding CTCX–peroxide as described by Errede and Hopwood, for QM.[15] Consequently, it was concluded that oxygen gas affects markedly the polymerization of CTCX.

Spontaneous homopolymerization of CTCX in toluene was studied. The polymerization took place heterogeneously except in the very early stage of polymerization. Results at various temperatures are shown in Figure 6, where rates of the polymerization are approximately of the first order with respect to monomer concentration in the early stage of the polymerization and they become of higher order in the latter stage of the polymerization.

Log–log plots of rates of the polymerization vs. monomer concentration were examined, as shown in Figure 7, in order to check dependence of the rate on monomer concentration in a different way. The rates were found to be almost of the first order with respect to monomer concentration in the range of monomer concentration above 2–3 × 10^{-3} mol/l. and of the second order below this value. This behavior of the polymerization of CTCX is different from the corresponding ones of QM[1] and HCX[6] because the polymerizations of both latter monomers obey the first-order kinetics over a wide range of monomer concentration.

The polymerization of CTCX at high monomer concentration which obeys approximately the first-order kinetics may presumedly be treated by the equations proposed by Errede et al.[1] for the polymerization of QM. Apparent first-order rate constants of the polymerization at various temperatures were estimated at monomer concentration of 3.8 × 10^{-3} mol/l. from Figure 7 and the Arrehenus plot of the rate constants gave a good straight line as shown in Figure 8. The apparent activation energy of spontaneous polymerization of CTCX is calculated as 8.8 kcal/mol. The value is in good agreement with the corresponding values reported for QM (8.7 kcal/mol)[1] and HCX (8.23 kcal/mol).[6] In addition, the temperature at which the apparent rate constant is to be 5.6 × 10^{-5} s^{-1} was obtained from the plot of Figure 8 to be 15 °C for CTCX. Corresponding ones for QM and HCX were reported at −68[1] and 30 °C,[6] respectively. Homopolymerizability of

Table I
Copolymerization of CTCX and St[a]

Run No.	Monomer feeds: CTCX, mmol/l.	St, mmol/l.	CTCX, mol %	Vol, ml	Copolymer: Yield, mg	Conversion % to: CTCX	ST	Elemental Anal., %: C	H	N	CTCX unit,[b] mol %
ST-1	4.79	36.20	11.7	55.0	5.5	6.6	0.4	48.68	2.51	4.44	68.2
2	10.39	88.72	10.5	59.4	21.1	10.5	0.7	50.12	2.64	4.32	64.5
3	10.40	174.39	5.6	60.3	22.2	9.5	0.6	55.88	2.88	3.75	49.4
4	10.50	307.60	3.3	62.0	15.6	6.0	0.3	58.05	2.48	3.51	44.1

[a] Temperature of polymerization, 20 °C; time of polymerization, 30 min; and solvent, toluene. [b] Calculated from N %.

Table II
Copolymerization of CTCX and HCX[a]

Run No.	Monomer feeds: CTCX, mmol/l.	HCX, mmol/l.	CTCX, mol %	Vol, ml	Copolymer: Yield, mg	Conversion % to: CTCX	HCX	Elemental Anal. %: C	H	N	CTCX unit,[b] mol %
H-1	10.70	7.24	59.7	66.1	41.0	12	13	36.00	2.38	2.81	57.3
2	8.15	11.33	41.9	63.4	72.0	21	24	34.21	2.30	1.81	38.0
3	5.00	16.46	23.1	65.5	98.1	31	26	33.10	1.50	1.25	26.5

[a] Temperature of polymerization, 20 °C; time of polymerization, 30 min; and solvent, toluene. [b] Calculated from N %.

Table III
Copolymerization of CTCX and TCX[a]

Run No.	Monomer feeds: CTCX, mmol/l.	TCX, mmol/l.	CTCX, mol %	Vol, ml	Copolymer: Yield, mg	Conversion % to: CTCX	TCX	Elemental Anal. %: C	H	N	CTCX unit,[b] mol %
T-1	10.33	2.37	81.4	54.3	33.5	16	32			3.67	67.8
2	5.99	1.07	84.9	65.8	16.4	10	37	40.01	3.0	3.22	59.0
3	3.15	2.26	58.3	60.0	19.9	17	35	39.98	2.8	2.27	40.9

[a] Temperature of polymerization, 20 °C; time of polymerization, 30 min; and solvent, toluene. [b] Calculated from N %.

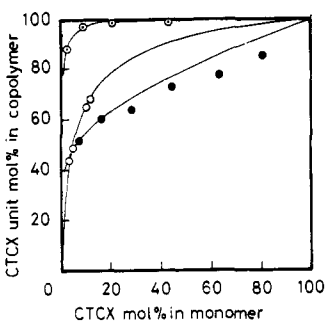


Figure 9. Composition diagram of copolymerization of CTCX and St: (○) experimental values; (●) those for copolymerization of HCX and St; (⊙) those for copolymerization of TCX and St; solid lines, calculated in theoretical equation using monomer reactivity ratios (r_1 (CTCX) = 12 and r_2(St) = 0.03 for this system, r_1(HCX) = 3.0 and r_2(St) = 0.02 at 50 °C for HCX–St system,[6] and r_1(TCX) = 85 and r_2(St) = 0 at 22 °C for TCX–St system[16]).

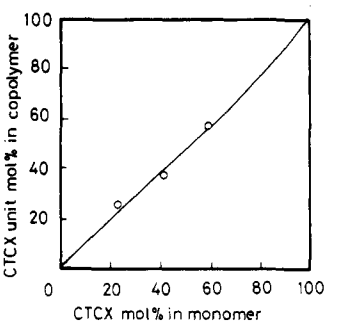


Figure 10. Composition diagram of copolymerization of CTCX and HCX: (○) experimental value; and solid line, calculated line in theoretical equation using r_1(CTCX) = 0.8 and r_2(HCX) = 0.95.

CTCX was concluded to be higher than that of HCX and much lower than that of QM (QM ≫ CTCX > HCX).

Results of copolymerizations of CTCX–St, CTCX–HCX, and CTCX–TCX systems are summarized by Tables I–III and their composition diagrams are shown in Figures 9–11, respectively. All copolymers obtained were insoluble in available organic solvents, so their examination by NMR and their solution properties could not be carried out. The copolymerizations were assumed to obey a conventional scheme of copolymerization and they were treated with equations derived from the above scheme.

Copolymerization of the CTCX–St system was analyzed using the differential from the Mayo–Lewis equation of copolymerization since conversion of polymerization did not exceed 10%. Monomer reactivity ratios were calculated as r_1(CTCX) = 12 ± 6 and r_2(St) = 0.03 ± 0.02 at 20 °C.

Copolymerizations of CTCX–HCX and CTCX–TCX systems were analyzed using the integral form of the Mayo–Lewis equation of copolymerization because conversion of polymerization exceeded 10%. The monomer reactivity ratios obtained are as follows: r_1(CTCX) = 0.8 ± 0.4 and r_2(HCX) = 0.95 ± 0.20 at 20 °C for the CTCX–HCX system, and r_1(CTCX) = 0.25 ± 0.20 and r_2(TCX) = 1.7 ± 1.0 at 20 °C for CTCX–TCX system.

It is evident in the three copolymerization systems that

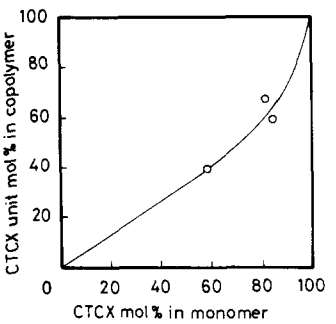


Figure 11. Composition diagram of copolymerization of CTCX and TCX: (O) experimental value; and solid line, calculated line in theoretical equation using r_1(CTCX) = 0.25 and r_2(TCX) = 1.7.

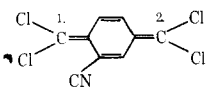
products, $r_1 \cdot r_2$, of monomer reactivity ratios are less than unity as well as observed in common radical vinyl copolymerizations, implying that real copolymerization takes place rather than mixed homopolymerizations.

Relative reactivity of TCX, HCX, and CTCX can be estimated from the monomer reactivity ratios obtained. Comparison of reciprocals of r_2(St) among CTCX–St, HCX–St,[6] and TCX–St[16] systems gives an order of relative reactivity toward the polymer reactive site with the terminal unit of St of TCX(1/0) > HCX(1/0.02) ≥ CTCX(1/0.03), when the monomer reactivity ratios were assumed to be essentially unchanged in the temperature range of polymerization of 20 to 50 °C. The second comparison of reciprocals of r_1(CTCX) between CTCX–HCX and CTCX–TCX systems gives another order of relative reactivity toward the polymer reactive site with the terminal unit of CTCX of TCX(1/0.25) > HCX(1/0.8) ≥ CTCX(1/1). Both orders were found to be in good agreement. In addition, the found value of relative reactivity was compared with some values estimated in quantum chemical calculations, such as π-electron density, frontier electron density, and free valence at extracyclic carbon, which are summarized in Table IV. CTCX has different values at two extracyclic carbons because of its asymmetric structure and the higher value is presumably preferred for this comparison. Values of π-electron density and free valence were found to be in good agreement with the found values of relative reactivity. The consistent results correspond with the findings of Kooyman and Farehorst[17] on the relationship between the relative reactivity of the trichloromethyl radical toward the aromatic hydrocarbon and the highest free valence index of

Table IV
π-Electron Density, Frontier Density, and Free Valence at Extracyclic Carbon of CTCX, HCX, and TCX[a]

	π-electron density			
	Ground state	Singlet excited state	Frontier density	Free valence
CTCX[b] 1	0.9642	1.0169	0.4048	0.412
2	0.9556	1.0675	0.4598	0.421
HCX	0.9691	1.0676	0.4469	0.424
TCX	0.9869	1.0716	0.4620	0.440

[a] Calculated by the ASMO–SCF method. [b] Following structure.



the hydrocarbon and also with the suggestion of Hush[18] on the relationship between polymerizability of quinodimethane monomers and free valence at their corresponding extracyclic atom.

Discrepancy in the orders between relative reactivity toward a given polymer radical and homopolymerizability will be discussed elsewhere in the near future.

References and Notes

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