# Preparation and Polymerization of α,α,α′,α′,2,5-Hexachloro-*p*-xylylene

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ABSTRACT: α,α,α′,α′,2,5-Hexachloro-*p*-xylylene (HCX) was prepared in a two-step process: the first step was a chlorination of α,α,α,α′,α′,α′-hexachloro-*p*-xylene to α,α,α,α′,α′,α′,2,5-octachloro-*p*-xylene and the second step was dechlorination of α,α,α,α′,α′,α′,2,5-octachloro-*p*-xylene to HCX. HCX was obtained as crystalline yellow needles. Spontaneous polymerization of HCX in the solid state was found to proceed as a zero-order reaction with respect to monomer concentration. Spontaneous polymerization of HCX in benzene solution was found to be a first-order reaction with respect to monomer concentration. The apparent first-order rate constant is $5.56 \times 10^{-5}$ sec$^{-1}$ at 30°. The apparent activation energy of the polymerization was obtained as 8.23 kcal/mol. Spontaneous copolymerization of HCX with styrene (St) in benzene solution was studied. Analyses of the copolymer composition showed that the copolymerization can be treated well with the theoretical equations of common vinyl compolymerization. The copolymer obtained in high St monomer feed such as 92 mol % was found to be exceptionally soluble in benzene and chloroform. The homopolymer of HCX and other copolymers are not soluble in organic solvent. Nmr study and elemental analyses of this soluble copolymer show that this copolymer is an alternating copolymer of HCX and St. The copolymerization under the condition giving the soluble copolymers was studied. The molecular weight of copolymers obtained was found to increase with conversion of polymerization. The propagation of the copolymerization, thus, was proposed to be close to a stepwise addition type reaction with a somewhat living character.

Since the success in synthesis of *p*-xylylene by Szwarc,[1] many papers on *p*-xylylene and its derivatives have been published.[2] It may be pointed out from those works that *p*-xylylene (QM),[3,4] α,α,α′,α′-tetrachloro-*p*-xylylene (TCX),[5,6] and perchloro-*p*-xylylene (PCX)[7] show very interesting differences in chemical nature with the number of chlorine substituents; QM is so reactive that it polymerizes spontaneously even at −78°. The monomer of QM is stable only in the gas phase or in very dilute solution at very low temperatures.[3] TCX also is highly reactive and its spontaneous polymerization takes place rapidly in both solution and solid states if the sample is held at room temperature. However, its yellow needle crystals can be recrystallized and kept without polymerization if the temperature is below −10°.[5,6,8] Finally, PCX shows no polymerizability at all and is very stable even at elevated temperatures.[7]

In addition, a similar variation of their reactivity with the amount of the substituents is observed in their copolymerizations with vinyl compounds such as styrene (St). In the mixture of QM and St, only QM polymerizes spontaneously and gives its homopolymer. That is, QM may be too reactive to afford cross propagation with St.[4] Copolymerization of TCX with St can give copolymers containing both monomer units, but the St unit content of the copolymers obtained is much smaller than the conjugate TCX unit content[8] even if the St monomer feed is very high. The reactivity of TCX, therefore, is considered to be lower than that of QM though it is still much higher than that of St.

These experimental facts indicate a decrease in reactivity of QM derivatives with the number of electron-withdrawing chlorine substituents.

It is expected, therefore, that QM derivatives carrying more chlorine substituents than TCX but less than PCX, if it is obtained, must be a more stable and more manageable monomer than TCX and have an intermediate polymerizability between TCX and PCX.

In this work are studied preparation and some polymerizations of α,α,α′,α′,2,5-hexachloro-*p*-xylylene (HCX) based on this concept.

## Experimental Section

**Preparation of α,α,α,α′,α′,α′,2,5-Octachloro-*p*-xylene.** The preparation was carried out by using the powerful perchlorinating agent of Ballester, *et al.*[9] From a dropping funnel, a solution of 25 g of α,α,α,α′,α′,α′-hexachloro-*p*-xylene and 7 g of sulfur monochloride in 200 g of sulfuryl chloride was added slowly (*ca.* 20 min) to a boiling solution of 5 g of anhydrous aluminum chloride in 300 g of sulfuryl chloride placed in a flask fitted with refluxed condenser and heated in an oil bath, and then the solution was refluxed for 5 hr. The sulfuryl chloride was then evaporated out under reduced pressure at room temperature to give a black and brown solid, which was treated with 1 l. of water to yield a yellow solid. Solid sodium bicarbonate was added gradually until no more gas evolution took place. The mass was then heated on a steam bath for 1 hr and strongly acidified with concentrated hydrochloric acid. The yellow solid was then collected by filtration, dried, and washed with petroleum ether until the yellow color faded away. The colorless solid obtained was recrystallized from tetrahydrofuran to give colorless cubic crystalline α,α,α,α′,α′,α′,2,5-octachloro-*p*-xylene: 21.5 g (*ca.* 70% yield); mp 201–203° (lit.[9] 202–204°); nmr δ 6.23 ppm singlet (in chloroform-*d*).

**Preparation of α,α,α′,α′,2,5-Hexachloro-*p*-xylylene (HCX).** The preparation was carried out mostly according to the method of Gilch[5] who prepared TCX from α,α,α,α′,α′,α′-hexachloro-*p*-xylene. A sketch of our apparatus is shown in Figure 1. α,α,α,α′,α′,α′,2,5-Octachloro-*p*-xylene (3 g) wrapped in a small sheet of aluminum foil was placed in the upper part of a quartz tube by using small pieces of magnet. The quartz tube containing a copper net rolled tightly was heated at 500–550° in an electric furnace. The pressure in the apparatus was reduced below 1.0 mm and a very small amount of nitrogen gas was introduced through a capillary fitted at the top of the quartz tube. Then, the octachloro-*p*-xylene was dropped down into the heated part of the tube for sublimation and the vapor was reacted with the heated copper net to give HCX, which was trapped in the first trap as a yellow powder and also in the second trap as tetrahydrofuran solution. Both traps were cooled with Dry Ice–methanol solution. After the vapor was not found to come out from the quartz tube, the first trap was washed down with tetrahydrofuran cooled under 0°, and then the tetrahydrofuran solution was added to the tetrahydrofuran solution in the second trap. The combined solution was filtered to remove a small amount of white powder which was regarded as poly(HCX). The filtrate was concentrated under reduced pressure at a temperature below 0°. The concentrated tetrahydrofuran solution was cooled with Dry Ice–methanol to yield a yellow needle crystalline compound which was recrystallized by using tetrahydrofuran below 0°. Pure yellow crystalline HCX (500 mg) was obtained (20% yield). In its ultraviolet spectrum in cyclohexane solution absorptions appear at 360 ($\epsilon$ $5.19 \times 10^4$), 341 ($\epsilon$ $3.31 \times 10^4$), and 326 nm ($\epsilon$ $1.42 \times 10^4$). Its nmr spectrum in chloroform-*d* solution shows only a singlet peak at δ 7.23 ppm. Its X-ray diffraction powder pattern is shown in Figure 2. It is paramagnetic (in esr measurement). Elemental analyses of this compound could not be carried out in the monomeric state because it polymerizes very rapidly when it is heated above room temperature. White powder of poly(HCX) obtained by standing yellow HCX at room temperature was employed as a probe for the analyses, which gave the fol-

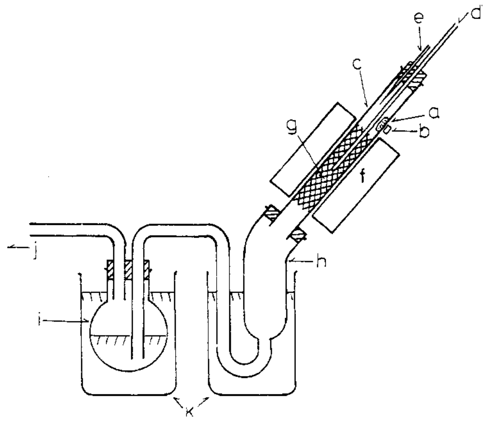

Figure 1. Sketch of an apparatus for preparation of HCX: a, sample wrapped in a small sheet of Al foil; b, magnet; c, quartz tube; d, thermocouple; e, nitrogen gas inlet capillary; f, electric furnace; g, copper net rolled; h, first trap; i, second trap; j, vacuum pump; k, Dry Ice–methanol bath.

lowing results. *Anal.* Calcd for $C_8H_2Cl_2$: Cl, 68.44; C, 30.91; H, 0.65. Found: Cl, 69.60; C, 30.85; H, 0.51.

**Polymerization Procedure. Solid State Polymerization of HCX.** Sample powder was placed on the glass holder of the X-ray diffractometer and stood without any movement for the whole time of the measurement at room temperature. Heights of X-ray diffraction profiles at various diffraction angles were measured at regular time intervals.

**Solution Polymerization of HCX.** A given amount of HCX was added to a given amount of purified and cooled benzene without delay to give a yellow clear solution with a fixed HCX concentration. A given volume of the benzene solution was placed using a pipet in an ampoule which then was cooled to the Dry Ice–methanol temperature, flushed with nitrogen gas, and sealed. The ampoule was set in an oil bath of a fixed temperature without stirring for a given time of polymerization. Then, it was cooled again to the Dry Ice–methanol temperature and opened. After melting of the benzene solution in gentle heating, the solution was filtered immediately to remove poly(HCX) as white precipitate. Then, the concentration of HCX in the filtrate was measured spectrophotometrically by using absorbance at 360 nm.

**Solution Copolymerization of HCX with St.** A given amount of HCX and St, and 10 ml of purified benzene, were placed in an ampoule which, then, was cooled with ice–water, flushed with nitrogen gas, and sealed. The ampoule was set in an oil bath thermostated at 50° without stirring for a fixed time of polymerization. Then it was cooled again with ice–water, opened, and added with excess methanol to deposit a copolymer which then was filtered, washed repeatedly with methanol, and dried under reduced pressure to constant weight. Copolymers were obtained as white powder.

**Reagents and Instruments.** Reagent grade commercial α,α,α,α′,α′,α′-hexachloro-*p*-xylene, sulfur monochloride, sulfuryl chloride, and anhydrous aluminum chloride were used without further purification. Styrene as comonomer and benzene, tetrahydrofuran, cyclohexane, etc., as solvent were purified by an individual conventional method.

Instruments employed in this work were as follows: X-ray diffractometer of Rygaku Denki Corp., spectrophotometer of Hitachi Model 123, molecular weight apparatus (vapor pressure osmometer) of Hitachi Perkin-Elmer Model 115, Yanagimoto microdeterming apparatus for elements Model MX-3, and nmr spectrometer of Nippon Denshi Corp. Model C-60HL.

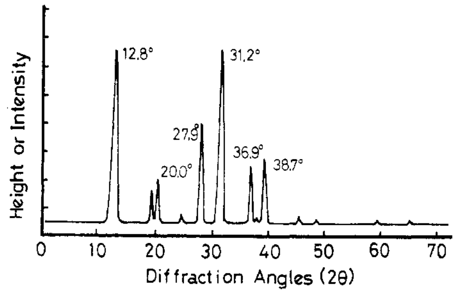

Figure 2. X-Ray diffraction powder pattern of crystalline HCX.

## Results and Discussion

Preparation of α,α,α,α′,α′,α′,2,5-octachloro-*p*-xylene was carried out by a modified perchlorination method of Ballester, *et al.*[9] The milder reaction condition was adopted so as to make the reaction time shorter (from 9 hr[9] to 5 hr) because the reaction for this purpose is not a perchlorination but a partial chlorination. Then, α,α,α,α′,α′,α′,2,5-octachloro-*p*-xylene, instead of perchloro-*p*-xylene, was obtained successfully in a fairly good yield.

Preparation of HCX by a gas-phase dechlorination of α,α,α,α′,α′,α′,2,5-octachloro-*p*-xylene on copper net was carried out in reference with the procedure of Gilch for preparation of TCX from α,α,α,α′,α′,α′-hexachloro-*p*-xylene.[5] Since an outline of his apparatus has not been obtained, an apparatus for this preparation was designed after our own style. In some preliminary runs the reaction conditions of Gilch for TCX[5] were found to be good also for the HCX preparation. Although the yield of HCX isolated as monomer was only about 20%, it is believed that the amount of HCX generated by dechlorination was higher, since a significant amount of poly(HCX) deposited as white powder form or brittle and transparent film form along the walls of the apparatus between the monomer collector and the generator. Therefore, if appropriate improvements on the procedure are realizable, the yield of HCX as a monomer state could be increased much more.

When ultraviolet absorption maxima of HCX in cyclohexane solution are compared with corresponding ones of TCX, a bathochromic shift by about 10 nm is observed in each corresponding maximum.[10] HCX obtained as yellow needle crystals was found to be kept without any change for a long time below 0°. At room temperature, it changes gradually to white powder which is regarded as poly(HCX) from its elemental analysis and its insolubility in organic solvents. At elevated temperatures above 100° it reacts explosively to the similar white powder. The temperature (below 0°) at which HCX can be kept safely without polymerization is higher than that for TCX (below −10°),[8] so HCX appears to be more stable than TCX even qualitatively.

The change observed in HCX crystal for its standing at room temperature was examined in detail by using an X-ray diffractometer in order to follow the rate of solid state polymerization of HCX. Since poly(HCX) obtained as white powder was found not to give any X-ray diffraction profile, indicating that the powder is completely in the amorphous state, the height (or intensity) of the X-ray diffraction profile must correspond to the amount of crystal fraction in the probe. Therefore, the change in the heights of X-ray diffraction profile is considered to afford a decrease in the amount of crystalline HCX in the probe. The heights of six X-ray diffraction profiles at diffraction angles of 12.8, 20.0, 27.9, 31.2, 36.9, and 38.7° were measured at each 6-hr interval. The results obtained are shown in Figure 3. It is clear in Figure 3 that all six plots of heights at each diffraction angle *vs.* time of standing give straight

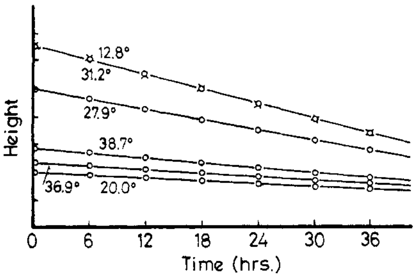

**Figure 3.** Relationship between the height of the X-ray diffraction profiles of the HCX monomer at various diffraction angles and the time of standing in the solid state polymerization of HCX.

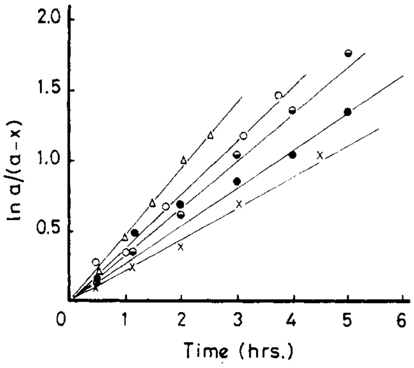

**Figure 4.** First-order rate plots of HCX polymerization in benzene solution at various temperatures: (△) 50° (1.83 × $10^{-2}$ mol/l.), (○) 45° (1.73 × $10^{-2}$ mol/l.), (◒) 40° (1.60 × $10^{-2}$ mol/l.), (●) 35° (1.63 × $10^{-2}$ mol/l.), (×) 30° (1.80 × $10^{-2}$ mol/l.). The initial concentration of HCX is indicated in parentheses.

lines. These six straight lines intersect each other at the one point where the height and the time of standing are 0.9 and 66 hr, respectively. The intensity of background of crystalline HCX is about 0.5 as shown in Figure 2. In the course of its standing, crystalline HCX changes gradually to amorphous poly(HCX) and simultaneously the intensity of background was found to increase little by little with the time of standing. This increase in intensity of the background thus is reasonably considered to correspond to an increase in fraction of amorphous poly(HCX) in the probe and all crystalline monomer of HCX is concluded to be consumed after 66 hr of standing at room temperature.

Straight lines in Figure 3 indicate the reaction order of the spontaneous solid state polymerization of HCX to be zero. This zero reaction order can be understood easily if the effective monomer concentration in solid state is taken into account. That is, when an active site moves into a crystal in the course of the polymerization, the number of HCX monomers around the active site and also eligible to the polymerization is considered to be constant and a polymer chain already formed does not influence the number because it always exists just behind the active site and is excluded from the crystal of HCX. In addition, if formation of the active site in unit volume is independent of an amount of HCX monomer in unit volume, this zero reaction order can be reasonably explained. There remains, however, still another unsolved problem on the mechanism of formation and disappearance of an active site in the polymerization.

Kinetic behavior of spontaneous polymerization of HCX in benzene solution was investigated. Measurement of the amount of HCX monomer remaining in each experimental run was carried out spectrophotometrically by using the absorbance at 360 nm. Reasons why the spectrophotometrical method was employed were as follows: bromine addition of HCX was found not to take place quantitatively, the amount of HCX used in each experimental run was much less when weighing the polymer accurately, and the molar extinction coefficient of the absorption of HCX at 360 nm is as large as 5.19 × $10^4$.

Results at various temperatures are shown in Figure 4 where rates of the solution polymerization are evidently of the first order with respect to monomer concentration. These apparent first-order rate constants at various temperatures were obtained as follows; 5.56 × $10^{-5}$ $\sec^{-1}$ at 30°, 7.17 × $10^{-5}$ $\sec^{-1}$ at 35°, 7.33 × $10^{-5}$ $\sec^{-1}$ at 40°, 10.32 × $10^{-5}$ $\sec^{-1}$ at 45°, and 13.33 × $10^{-5}$ $\sec^{-1}$ at 50°. The Arrhenius plot of these rate constants gives a good straight line and its slope permits the apparent activation energy of the polymerization of HCX to be calculated as 8.23 kcal/mol.

The polymerization behavior of QM in toluene solution was reported by Errede, *et al.*[3] The apparent first-order rate constant of the polymerization at −78° was found to be 9 × $10^{-6}$ $\sec^{-1}$ and the apparent activation energy of the polymerization is 8.7 kcal/mol. From both values, the temperature at which an apparent first-order rate constant of polymerization of QM in toluene solution is 5.56 × $10^{-5}$ $\sec^{-1}$ is calculated to be −61°. On the other hand, the temperature of the polymerization of HCX with the same rate constant was found to be as high as 30°. It is, therefore, obvious that QM is much more reactive than HCX, in other words, HCX is a much stabler monomer than QM.

It is of interest that both values of the apparent activation energy of polymerization of QM and HCX are almost the same and this fact suggests that these polymerizations both proceed through the same mechanism.

In addition, Errede, *et al.*,[3] pointed out in their paper on polymerization of QM in toluene solution at −78° that the first-order reaction rate plot of the logarithm of the monomer concentration *vs.* time of polymerization gave an almost straight line, in a strict meaning actually a curve with a slope decreasing little by little with the time of polymerization. A ratio of rate constant of consumption of polymerization active sites (termination) to that of propagation was calculated from analyses of the variation in the slope to be 0.452. In the case of the polymerization of HCX, we attempted to obtain such a curve with decreasing slope in the first-order reaction rate plot, but the attempt was in vain except for giving a straight line because experimental values of concentration of HCX monomer remaining in a series of experimental runs showed some scatter as seen in Figure 4. One of the conceivable causes of the scatter probably exists in the way of charging monomer into an ampoul, because Errede, *et al.*, pointed out that polymerization active sites are created when the solution of QM comes into contact with a warmer surface, such as the pipet wall surface, above the level of the cold liquid.[3] Further experiments are being carried out using different procedures of charging monomer in order to obtain the curve.

HCX copolymerizes spontaneously with various vinyl compounds such as St, isoprene, vinyl acetate, acrylonitrile, and methyl methacrylate to give copolymers containing both monomer units.[11] Copolymers obtained are not soluble in any organic solvent except for the HCX–St copolymer prepared in the monomer feed of excess St. Here, the result of copolymerization of HCX with St is reported, and other copolymerizations will be reported elsewhere.

The results of copolymerizations of HCX with St are summarized in Table I. The copolymer of run number HS-1 is soluble in organic solvents such as benzene and chloroform, though copolymers of other runs are not soluble in any organic solvent. In addition, the copolymer of HS-1 melts without decomposition at a temperature between 220 and 250°, while other copolymers do not melt even at 350°

**Table I**
**Results of Copolymerization of HCX with St[a]**

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Copolymers | | | | | |
| | Monomer feeds | | | | Conversion, % | | Elemental analyses, % | | | |
| Run no. | HCX, mmol | St, mmol | St, mol % | Yield, mg | Both monomers | HCX | C | H | Cl | St unit, mol % |
| HS-1 | 0.412 | 5.00 | 92 | 52.8 | 7.1 | 31.3 | 45.76 | 2.72 | 51.87 | 48.5 |
| HS-2 | 0.405 | 2.00 | 83 | 26.5 | 5.6 | 17.3 | 42.10 | 2.98 | 55.95 | 39.3 |
| HS-3 | 0.395 | 1.00 | 72 | 58.4 | 23.7 | 40.0 | 41.00 | 2.01 | 57.18 | 36.1 |
| HS-4 | 0.397 | 0.50 | 56 | 21.9 | 11.8 | 16.0 | 37.24 | 2.15 | 60.97 | 25.0 |
| HS-5 | 0.401 | 0.25 | 38 | 50.6 | 32.5 | 37.2 | 36.35 | 2.33 | 62.37 | 21.7 |
| HS-6 | 0.398 | 0.10 | 20 | 27.2 | 20.0 | 20.9 | 34.08 | 1.88 | 64.90 | 13.6 |

[a] Solvent, benzene. Temperature of polymerization, 50.0°. Time of polymerization, less than 1 hr.

**Table II**
**Influence of Oxygen on the Copolymerization of HCX with St[a]**

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | Copolymers | | | |
| | | | Elemental analyses, % | | | |
| Run no. | Remarks in process of monomer charging | Yield, mg | C | H | Cl | HCX, mol % |
| HS-12 | Perfect degassing | 34.3 | 44.73 | 2.68 | 52.15 | 52.9 |
| HS-13 | Perfect degassing and introduction of pure $O_2$ | 37.0 | 44.34 | 3.26 | 52.04 | |
| HS-14 | No degassing under air | 37.9 | 44.24 | 3.11 | 52.11 | |

[a] Process of monomer charging: the solution A was made by dissolving 250 mg of HCX in 30 ml of benzene and the solution B was made by mixing 2 ml of styrene and 8 ml of benzene. Solution A (8 ml) and 2 ml of solution were placed into ampoules. The molar percentage of St in the monomer feed was 94.2.

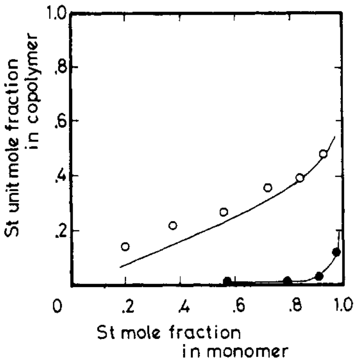

**Figure 5.** Composition diagram of the copolymerization of HCX with St. (○) Experimental value, solid line; calculated line in the theoretical equation using $r_1$(HCX) = 3.0 and $r_2$(St) = 0.02; and (●) results of copolymerization of TCX with St.

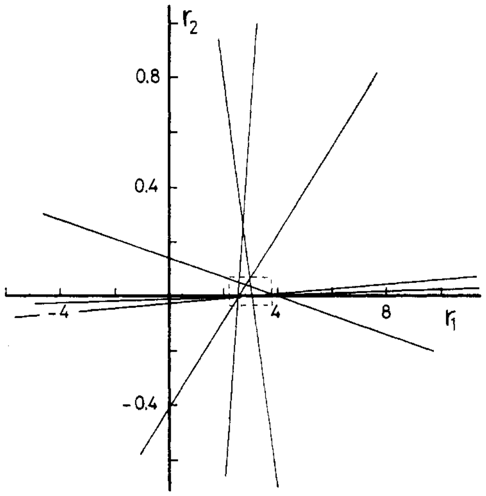

**Figure 6.** Diagram of $r_1$ *vs.* $r_2$ in application of the integral form of the theoretical equation of copolymerization to the copolymerization of HCX ($M_1$) with St ($M_2$).

and begin to stain to brown above 250°. Compositions of copolymers were determined by elemental analyses in which combustion of samples was found to be carried out quantitatively but only carbon and chlorine contents were employed for calculation of the composition of copolymers because hydrogen content is very low and suffers from serious experimental error.

An influence of oxygen on this copolymerization was studied and the results are summarized in Table II. The results indicate that oxygen does not affect the copolymerization at all.

The composition diagram of copolymerization of HCX with St is shown in Figure 5 where experimental points do not serve such meaningful points as in the composition diagram of common vinyl copolymerization because the conversion of polymerization could not be controlled below a few per cent in the present experimental runs. It has not yet been concluded definitely that this copolymerization can be treated with the theoretical equations of common vinyl copolymerization.[12-14] Nevertheless, these equations were applied to this copolymerization. Results of the application of the integral forms[12] of these equations to this copolymerization are shown as the diagram of monomer reactivity ratios, $r_1$ *vs.* $r_2$, in Figure 6 where reasonably limited values of $r_1$ and $r_2$ are obtained as follows: $r_1 = 3 \pm 0.8$ ($M_1$ = HCX) and $r_2 = 0.02 \pm 0.05$ ($M_2$ = St). This fairly good accommodation of the theoretical equations with this copolymerization suggests that this copolymerization could proceed through a similar mechanism for common vinyl copolymerization. Furthermore, corroborating experimental evidences, however, are necessary to establish this postulate because behaviors of homopolymerization of HCX and QM appear to be considerably different from that of common vinyl polymerization as pointed out earlier and also behavior of this copolymerization is remarkably different from that of common vinyl copolymerization as described

**Table III**
**Results of Copolymerization of HCX with St Started with 92.3 mol % of St in Feed**[a]

| | | | Copolymers | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Conversion, % | | | | | |
| Run no. | Time of polymn, min | Yield, mg | Both monomers | HCX | Cl content, % | St unit content, mol % | Solution viscosity, $\eta_{sp}/c$ | mol wt $\times 10^{-4}$ |
| HS-7 | 30 | 177.7 | 7.8 | 22.4 | 54.52 | 43.3 | 0.235 | 0.82 |
| HS-8 | 60 | 296.3 | 11.7 | 34.4 | 52.41 | 47.8 | 0.342 | 1.02 |
| HS-9 | 100 | 399.5 | 17.6 | 44.9 | 51.59 | 49.4 | 0.377 | 1.12 |
| HS-10 | 150 | 442.1 | 19.5 | 48.8 | 51.09 | 50.3 | 0.351 | 1.25 |

[a] Temperature of polymerization, 50.0°. Solution viscosity, 30.0°; solvent, benzene. Molecular weight, by vapor pressure osmometer; solvent, benzene. Monomer charging; 10 ml of St was mixed with 50 ml of benzene and, then, 10 ml of the resulting St solution and 450 mg of HCX were placed in an ampoule which was cooled with ice–water, flushed with nitrogen gas, and sealed.

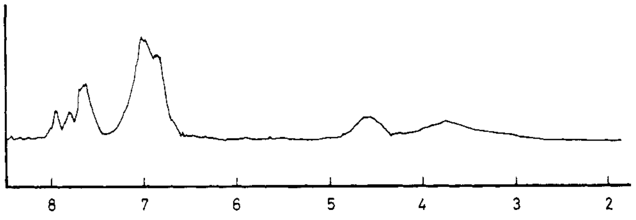

**Figure 7.** The nmr spectrum of the copolymer of HCX with St (run number HS-7).

later. Anyhow, those two monomer reactivity ratios may be useful to figure the composition behavior of this copolymerization.

In addition, the composition diagram of the copolymerization of TCX with St[8] is shown in Figure 5. It is obvious in Figure 5 that HCX copolymerizes much better with St than TCX does. Copolymerization of QM with St was reported to give no copolymer but the homopolymer of QM.[4] It is, then, evident that cross propagation between the QM derivatives and St takes place frequently in the increasing order of QM, TCX, and HCX (whereas homopolymerization of the QM derivatives proceeds rapidly in the decreasing order of QM, TCX, and HCX.). Their spontaneous homopolymerizations and copolymerizations are expected to proceed through the free-radical active site because their monomer and also their polymers just after polymerization carry paramagnetic character.[3,6] It is, therefore, concluded that radical affinity of the QM derivatives decreases in the order of QM, TCX, and HCX, the affinity of QM is too high to compare with that of St, and the affinity of HCX comes close to that of St but still higher than that of St.

In Figure 7 is shown a nmr spectrum of the copolymer of run number HS-7 in chloroform-*d*. Absorptions at δ 7.5–8 and 6.7–7.2 ppm are assigned to protons on the benzene nucleus of the HCX unit and to protons on the phenyl group of the St unit, respectively. Two broad absorptions at δ 3.7 and 4.6 ppm are assigned to methylene and methine protons of the St unit, respectively. The methylene and methine protons of common poly(St) were reported to absorb at δ 8.5 and 8.2 ppm, respectively,[15] and then, these absorptions in the figure are considered to shift to the lower field. The shift observed in absorptions of methylene and methine protons of the St unit in the copolymer is reasonably explained to take place due to the electron-withdrawing effect of the just neighboring dichloromethylene group when the St unit is sandwiched between two HCX units in the copolymer. It may be concluded from both results of the nmr spectrum and the composition of the copolymer that the copolymers obtained from high St monomer feed as 92 mol %, that is, the copolymers of HS-1 and HS-7 are real alternating copolymers of HCX with St.

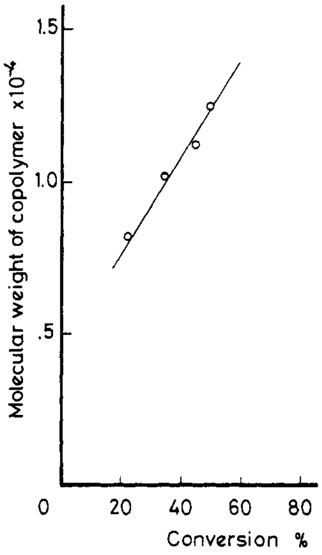

**Figure 8.** Relationship between the molecular weight of the copolymer and the conversion of polymerization in the copolymerization of HCX with St started in high St monomer feed as 92.3 mol %.

In Table III are summarized the result of the time–conversion behavior of the copolymerization of HCX with St started with high St monomer feed such as 92.3 mol %. A drift of St unit content of the copolymers with conversion of polymerization can be observed as like that in common vinyl copolymerization but here its magnitude may be regarded even roughly as small as negligible. In the copolymerization of the special monomer feed, conversion of polymerization is thought to be calculated in the base of the consumed amount of HCX monomer better than in the base of those of both monomers, because a monomer reactivity ratio of HCX is much higher than that of St ($r_1 \gg r_2$), variation in HCX monomer concentration with the time of polymerization is much larger than that in St monomer concentration, and both HCX and St monomer are consumed equivalently. A relationship[16] between conversion of polymerization, according to the above concept, and molecular weight of copolymers is shown in Figure 8 where the molecular weight of copolymers is found to increase with conversion of polymerization and the degree of the increase is fairly large. The relationship is not observed in common vinyl radical polymerization. It may be postulated from the relationship that this copolymerization proceeds partially through the stepwise addition mechanism, in other words it carrys a somewhat living character.

Finally, if this copolymerization and the homopolymerizations of QM and HCX are assumed to take place under a similar mechanism, it may be proposed in summary of the behavior of the copolymerization of HCX with St, the behavior of homopolymerization of QM,[3] and the paramagnetic character of the QM derivatives[3,6] that the propagation in those polymerizations may be very close to a radical coupling type and stepwise reaction between the polymer active site and the biradical of the QM derivatives. In the copolymerization of HCX with St, a polymer active site with the terminal unit of HCX is considered to react with St *via* the common mechanism of the radical addition to the carbon–carbon double bond and, then, the resulting polymer active site reacts with HCX *via* the radical coupling mechanism. If the copolymerization does not start in high St monomer feed, the former polymer active site reacts with HCX *via* the latter mechanism to yield the homopolymer of HCX or copolymers with the predominant HCX unit content. The latter polymer active site reacts exclusively with HCX because of the great difference in reactivity of both monomers. The latter step of radical coupling is considered to play an important role in this copolymerization.

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# Organometallic Polymers. XXX. Synthesis and Copolymerization of η$^6$-(2-Phenylethyl methacrylate)tricarbonylchromium with Organic Monomers

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ABSTRACT: The monomer η$^6$-(2-phenylethyl methacrylate)tricarbonylchromium (PEMATC) was synthesized and copolymerized in ethyl acetate solutions at 70° with acrylonitrile, methyl methacrylate, and styrene using azobisisobutyronitrile (AIBN) as the free-radical initiator. The reactivity ratios of each of the comonomer pairs were determined using the integral form of the copolymer equation on copolymerizations to higher yields. $M_1$ is defined as the organometallic monomer. The ratios were: PEMATC–styrene $r_1 = 0.04$, $r_2 = 1.35$; PEMATC–acrylonitrile $r_1 = 0.07$, $r_2 = 0.79$; PEMATC–methyl methacrylate $r_1 = 0.09$, $r_2 = 1.19$. A classic $r_1$, $r_2$ determination using low conversion polymerizations, at several different $M_1{}^0/M_2{}^0$ ratios, gave reactivity ratios very close to those stated above. Microgel formation and binodal gel permeation chromatograms were frequently observed in the high conversion runs, but such processes had little effect on the reactivity ratios since the low conversion runs were free of these complications. *Q–e* maps were prepared for the PEMATC copolymerizations, but no values of *Q* or *e* could be assigned to PEMATC which were consistant for all the copolymerizations. The copolymerization behavior of PEMATC was compared to the related monomers η$^6$-(2-phenylethyl acrylate)tricarbonylchromium and η$^6$-(benzyl acrylate)tricarbonylchromium. PEMATC readily homopolymerized in ethyl acetate at 70° to give homopolymers with $\bar{M}_n$ values of 15,000–20,000. Thermal decomposition of PEMATC polymers resulted in a slow destruction of the η$^6$-benzenetricarbonylchromium units, both in air and under nitrogen, with the formation of CO, insoluble polymers, and chromium oxides dispersed in the polymers.

The synthesis of polymers[2–4] containing organometallic monomers and investigations of their properties[2a,5,6] have recently accelerated in scope. The radical-initiated vinyl addition homopolymerization and copolymerization of a variety of organometallic monomers, such as η$^6$-styrenetricarbonylchromium,[7] vinylcyclopentadienylmanganese tricarbonyl,[2a,8] vinylferrocene,[9] η$^6$-(benzyl acrylate)tricarbonylchromium,[10] ferrocenylmethyl acrylate[11,12] and methacrylate,[11,12] and 2-ferrocenylethyl acrylate[13] and methacrylate[13] have now been well established.

Only a few organochromium monomers have been synthesized and polymerized. These include η$^6$-styrenetricarbonylchromium,[7] η$^6$-(benzyl acrylate)tricarbonylchromium,[10] and η$^6$-(2-phenylethyl acrylate)tricarbonylchromium.[14] η$^6$-(Benzyl acrylate)tricarbonylchromium has been homopolymerized and copolymerized with both styrene and methyl acrylate to give high molecular weight polymers.[10] η$^6$-Styrenetricarbonylchromium has been readily copolymerized with styrene ($r_1 = 0$, $r_2 = 1.39$) and methyl acrylate ($r_1 = 0$, $r_2 = 0.75$), but it would not homopolymerize.[7] η$^6$-(2-Phenylethyl acrylate)tricarbonylchromium has been copolymerized with styrene, methyl acrylate, acrylonitrile, and 2-phenylethyl acrylate using AIBN initiation.[14]

Polymers containing η$^6$-(aryl)tricarbonylchromium units are of interest because the thermal decomposition of this moiety within a polymer film might lead to the deposition of chromium metal or chromium oxides within that film in molecular sized units. Also these polymers could be of potential use as chromium catalysts.

## Results and Discussion

η$^6$-(2-Phenylethyl methacrylate)tricarbonylchromium (hereafter PEMATC) was prepared by the route shown in eq 1. η$^6$-(2-Phenylethanol)tricarbonylchromium was syn-