# Concentration Dependence of the Termination Rate Constant During the Initial Stages of Free Radical Polymerization

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ABSTRACT: The concentration dependence of the segmental diffusion coefficient of the polymeric chain ends and the termination rate constant in the initial stages of polymerization have been calculated by considering the effect of polymer concentration on the overall dimensions of the polymer coils. The expressions obtained for concentration dependence predict that both the segmental diffusion coefficient and the termination rate constant initially increase as the polymer concentration increase from zero. This initial increase is more when the molecular weight of polymer is high and/or when the polymerization is carried out in a "good" solvent. The concentration dependence of the termination rate constant has been tested against experimental data and close agreement has been found between calculated termination rate constants and those experimentally obtained.

The conversion level in free radical polymerization of vinyl monomers can be divided into three stages. An initial stage in which the rate of polymerization decreases; an intermediate stage in which the rate of polymerization increases (the "gel effect"); and a final stage in which, monomer being depleted or the reaction mixture approaching its glass transition point, the rate falls to zero. Also as a consequence of these changes in the rate of polymerization, the molecular weight of the polymer product may change; when chain transfer reactions do not play any significant role, the molecular weight of polymer changes inversely with the changes in the rate of polymerization. On the other hand, when chain transfer reactions control the chain length, the molecular weight of polymer is not affected by the change in conversion rate and only the overall rate of polymerization presents an anomalous behavior.

The effect of increasing conversion on the intermediate and later stages of the polymerization reaction have been studied for some time. The cause of the acceleration of the polymerization rate often observed in intermediate stages of polymerization has been shown to be due to the decrease in the rate at which polymeric radicals react with each other.[1] Although many theoretical discussions have been presented on the effect of conversion on the intermediate and later stages of polymerization reaction, among which the theory recently developed in our laboratory[2] should be particularly mentioned, the information about the effect of conversion on the initial stages of polymerization is almost nil.

A rate decrease in the initial stages of methyl methacrylate (MMA) polymerization has been reported by Hayden and Melville.[3] One year later North and Reed[4] experimentally showed that the decrease in the rate, as the conversion in initial stages of (MMA) polymerization increases, is a direct consequence of an increase in the termination rate constant. They also showed that this initial increase of the termination rate constant is more when the molecular weight of polymer is high and/or when the polymerization is carried out in a good solvent.

The only theoretical treatment for the effect of conversion on the termination rate constant in the initial stages of polymerization has also been proposed by North and Reed.[4] They related the termination rate constant by an empirical equation to the conversion using intrinsic viscosity and the second virial coefficient as parameters. However, they did not consider the concentration dependence of the linear expansion factor, $\alpha$,[5-10] and the effect of that on the conversion dependence of the termination rate constant.

The present work is concerned with a theoretical treatment of the effect of conversion on the termination rate constant in initial stages of polymerization based on the effect of the concentration on polymer–solvent interaction. The resulting expression predicts that the termination rate constant should increase with conversion to some extent and that this initial increase is more when the molecular weight of the polymer is high and/or when a "good" solvent is used.

## Theory

Experimental evidence indicates that the termination reaction in the initial stages of polymerization is controlled by segmental diffusion of chain ends.[4] The segmental diffusion coefficient of a chain end located a distance $s$ from the center of mass of polymer molecule, having $N$ monomer units, as a function of $s$ and size of the polymer molecule has been derived previously.[11] The result, which is obtained by considering the effect of concentration on diffusion coefficient, is given by

$$D(s,\alpha) = D^* \left[1 - \left(1 - 4\left(\frac{2N_0}{3\pi}\right)^{1/2} \frac{1}{\alpha N^{1/2}}\right) \times \exp\left(\frac{-9s^2}{2\alpha^2 \langle h^2 \rangle_0}\right)\right] \tag{1}$$

where $\alpha$ is the linear expansion factor (a decreasing function of the polymer concentration), $\langle h \rangle_0{}^2$ is the mean-square end-to-end distance of unperturbed chain, $N_0$ is the flexibility parameter,[11] and $D^*$ is given by[12]

$$D^* = \frac{k_B T}{\zeta}\left(\frac{\mathrm{d} \ln a}{\mathrm{d} \ln C}\right) = \frac{k_B T}{\zeta_0}\left[\frac{1 + 2\Gamma_2 C + \ldots}{1 + k_s C + \ldots}\right] \tag{1a}$$

where $\zeta_0$ is the friction coefficient of the polymer chain when placed separately in the solvent, $k_B$ is the Boltzmann constant, $a$ and $C$ are the activity and the concentration of polymer respectively, $\Gamma_2$ is the thermodynamic parameter depending on polymer–solvent interactions as obtained from the second virial coefficient of osmotic pressure, and $k_s$ is the hydrodynamic coefficient. It has been suggested that $k_s$ is proportional to the intrinsic viscosity $[\eta]$.[13]

$$k_s = 1.6[\eta] \tag{1b}$$

Considering only small values of the concentration we have

$$D^* = \frac{k_B T}{\zeta_0}\left(\frac{1 + 2\Gamma_2 C}{1 + 1.6[\eta] C}\right) \tag{1c}$$

Introducing eq 1c in eq 1 gives

$$D_c(s,\alpha) = \frac{k_B T}{\zeta_0}\left[\frac{1 + 2\Gamma_2 C}{1 + 1.6[\eta] C}\right]\left[1 - \left(1 - 4\left(\frac{2N_0}{3\pi}\right)^{1/2} \times \frac{1}{\alpha N^{1/2}}\right) \exp\left(\frac{-9s^2}{2\alpha^2 \langle h \rangle_0{}^2}\right)\right] \tag{2}$$

The diffusion of a free radical chain end out of the polymer coil into a region where reaction with another such end can take place is a function of the dimension of the polymeric coil. In a thermodynamically "good" solvent, any increase in the total polymer concentration will be reflected in a decrease of this dimension. The immediate effect of this will be to increase the segmental concentration gradient across which polymer chain end diffusion takes place. Therefore the segmental diffusion coefficient and the specific rate constant of the termination reaction controlled by the segmental diffusion process will be increased. These increases are a direct result of the effect of polymer concentration on the dimensions of the polymer coils due to the polymer–solvent interaction. The effect of concentration on the diffusion coefficient in eq 2 is not only through the concentration dependence of $\alpha$ but is also through the term $(1 + 2\Gamma_2 C)/(1 + 1.6[\eta]C)$.

Several workers have attempted to calculate the concentration dependence of $\Gamma_2$ and $\alpha$.[5–10] Fixman[8,9] predicts that $\alpha$ initially decreases to less than unity as the concentration increases from zero then passes through a minimum as the concentration increases to a value given by

$$C^* = \frac{K^*}{(\langle h\rangle_0{}^2/M)^{3/2}M^{1/2}} \tag{3}$$

(where $K^*$, for a given polymer–solvent system, is constant) and then increase to a value near unity as the molar concentration of polymer tends to unity. Similarly, Yamakawa[10] has worked out a perturbation theory for $\alpha$ predicting that $\alpha$ initially decreases with increasing $C$ according to the relation

$$\alpha = \alpha_0 \exp[-0.725 \times 10^{23}(\langle h\rangle_0{}^2/M)^{3/2}M^{1/2}Z\phi_2(Z/\alpha_0{}^3)C] \tag{4}$$

where

$$\phi_2(Z/\alpha^3) = 1 - [1 - \exp(-5.731Z/\alpha^3)]/5.731Z/\alpha^3 \tag{4a}$$

Here, $\alpha_0$ is the linear expansion factor at zero polymer concentration and $Z$ is the interaction parameter.

In a good solvent the second virial coefficient, $\Gamma_2$, initially increases rapidly with $C$ then levels off with further increase in $C$ (the volume fraction of polymer always being less than about 0.1). Such behavior has been observed,[9] and the following equations[10] satisfactorily correlate the sparse data available.

$$\Gamma_2 = 9.12 \times 10^{23}(\langle h\rangle_0{}^2/M)^{3/2}M^{1/2}ZH(C,Z/\alpha^3) \tag{5}$$

where

$$\begin{aligned} H(C,Z/\alpha^3) = {} & \exp[-5.731Z/\alpha^3 + 1.824 \\ & \times 10^{24}(\langle h\rangle_0{}^2/M)^{3/2}M^{1/2}ZC\phi_1(Z/\alpha^3)] + \phi_2(Z/\alpha^3) \\ & + 1.824 \times 10^{24}(\langle h\rangle_0{}^2/M)^{3/2}M^{1/2}ZC\phi_3(Z/\alpha^3) \end{aligned} \tag{5a}$$

$$\begin{aligned} \phi_1(Z/\alpha^3) = {} & [1 - \exp(-1.664Z/\alpha^3)] \\ & \times [1 - \exp(-5.731Z/\alpha^3)]/5.731Z/\alpha^3 \end{aligned} \tag{5b}$$

$$\begin{aligned} \phi_3(Z/\alpha^3) = {} & [\exp(-5.731Z/\alpha^3)] \\ & \times [\sinh(5.731Z/\alpha^3) - 5.731Z/\alpha^3] \Big/ \left(\frac{5.731Z}{\alpha^3}\right)^2 \end{aligned} \tag{5c}$$

and

$$\alpha_0{}^2 = 0.541 + 0.459(1 + 6.04Z)^{0.46} \qquad \alpha_0 \leqslant 1.5 \tag{5d}$$

Considering the effect of concentration on the linear expansion factor $\alpha$ and substituting for $s$ the mean radius of coil $(\langle s\rangle_0{}^2)^{1/2}$, the change in segmental diffusion coefficient is then given by

$$\frac{D_C(\langle s\rangle_0,\alpha)}{D_0(\langle s\rangle_0,\alpha_0)} = \left[\frac{1 + 2\Gamma_2 C}{1 + 1.6[\eta]C}\right] \times \left\{\frac{1 - \left(1 - 4\left(\frac{2N_0}{3\pi}\right)^{1/2}\frac{1}{\alpha N^{1/2}}\right)\exp\left(-\frac{3}{4\alpha^2}\right)}{1 - \left(1 - 4\left(\frac{2N_0}{3\pi}\right)^{1/2}\frac{1}{\alpha_0 N^{1/2}}\right)\exp\left(\frac{-3}{4\alpha_0{}^2}\right)}\right\} \tag{6}$$

A combination of eq 4 to 6 gives the full effect of polymer concentration on the segmental diffusion coefficient.

The specific rate constant for the termination reaction controlled by the segmental diffusion process, which has been previously derived,[11] is given by

$$K_t = 8\pi \times 10^{-3}N_{AV}RD^*[(\alpha_A\alpha_B)^{-1.3}]\left[1 - 0.37(\alpha_A\alpha_B)^{-0.37} \times \left\{1 - 4\left(\frac{2N_0}{3\pi}\right)^{1/2}(\alpha_A\alpha_B)^{-1/2}(N_AN_B)^{-1/4}\right\}\right] \tag{7}$$

where $N_{AV}$ is the Avogadro's number and $R$ is the distance at which two chain ends react with each other.

As eq 7 shows, the termination rate constant is a decreasing function of the size of two reactants. The extension of the polymer chain in solution, a direct consequence of the magnitude of solvent–polymer interaction $\alpha$, can effect the termination rate constant. For a given polymer–solvent system $\alpha$ increases with molecular weight of the polymer, and for a given polymer with fixed molecular weight $\alpha$ is greater when a good solvent is used. Given that the extension of a polymer chain in solution is greater for a higher value of $\alpha_0$, the observed dependence of the termination rate constant upon polymer concentration can be regarded as evidence of a size dependence of the termination rate constant.

Considering the effect of polymer concentration on $\alpha$, the change in termination rate constant can be written as eq 8,

$$\frac{K_t}{K_{t0}} = \left[\frac{1 + 2\Gamma_2 C}{1 + 1.6[\eta]C}\right]\left(\frac{\alpha_A\alpha_B}{\alpha_{0A}\alpha_{0B}}\right)^{-1.3}\left[\frac{1 - 0.37(\alpha_A\alpha_B)^{-0.37}\left\{1 - 4\left(\frac{2N_0}{3\pi}\right)^{1/2}(\alpha_A\alpha_B)^{-1/2}(N_AN_B)^{-1/4}\right\}}{1 - 0.37(\alpha_{0A}\alpha_{0B})^{-0.37}\left\{1 - 4\left(\frac{2N_0}{3\pi}\right)^{1/2}(\alpha_{0A}\alpha_{0B})^{-1/2}(N_AN_B)^{-1/4}\right\}}\right] \tag{8}$$

where $K_{t0}$ is the specific rate constant for termination between two polymeric radicals A and B at infinite dilution.

Equation 8 along with eq 4 and 5 predict that the termination rate constant, in the initial stages of polymerization, undergoes an initial increase as the polymer concentration increases from zero ($\alpha$ decreases but $\Gamma_2$ increases). This initial increase is not predicted when the molecular weight of polymer is low ($\alpha_0 \simeq 1$) or when the polymerization is carried out in a poor solvent.

## Discussion

The concentration dependence of the segmental diffusion coefficient and the termination rate constant in initial stages of polymerization can be fully described by eq 6 and 8, respectively. These two equations must be solved numerically along with eq 4 to 5d.

The complete specification of eq 6 and 8 requires the knowledge of two parameters. The constant $(\langle h\rangle_0{}^2/M)^{1/2}$ (only a function of temperature) can be evaluated by light scattering or low-angle x-ray scattering. The flexibility parameter $N_0$ can be obtained as described previously.[11] Knowing the constant $(\langle h\rangle_0{}^2/M)^{1/2}$, for a given molecular weight of polymer mole-

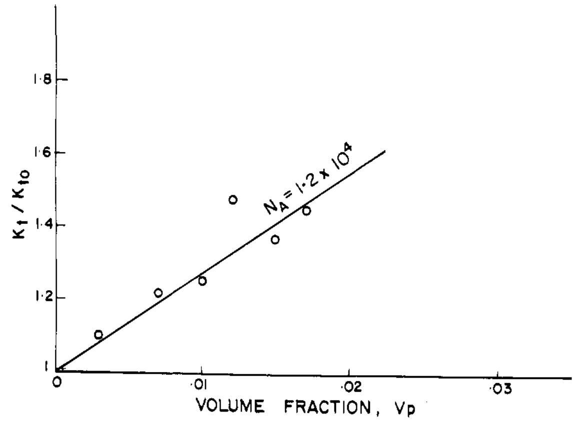

**Figure 1.** $K_t/K_{t0}$ against volume fraction of PMMA formed at 30 °C: (○) experiment 4; Solid line predicted by present model using $N_A = 2N_B$

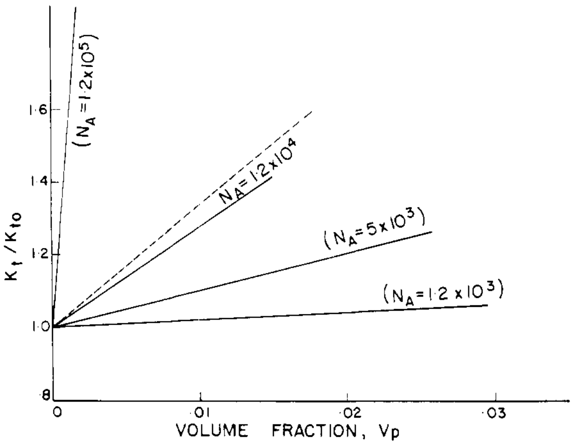

**Figure 2.** Concentration dependence of termination rate constant of PMMA at 30 °C for several chain lengths of PMMA ($N_A = 2N_B$) and in different solvents: (- - -) ethyl acetate; (—) MMA.

cule, $\alpha_0$ can be calculated by using the Mark-Ouwink-Flory[14] relationship for intrinsic viscosity

$$[\eta] = KM^b = \Phi(\langle h\rangle_0^2/M)^{3/2}\alpha_0^3$$

$$\Phi = 2.5 \times 10^{21}([\eta] \text{ in dl/g})$$

where $K$ and $b$ are the Mark–Houwink constants. The interaction parameter $Z$ can be evaluated by using the calculated value of $\alpha_0$ in eq 5d. Then by using eq 4, 5, 6, and 8 the dependencies of the segmental diffusion coefficient and the termination rate constant on the polymer concentration can be obtained.

The development described above has been tested against experimental data reported by North and Reed[4] for the polymerization of MMA. Figure 1 shows a comparison between the experimental and predicted termination rate constant vs. conversion of MMA to PMMA. (All relevant parameters used in this calculation are listed in Table I.) The calculated effect of molecular weight of polymer and the effect of solvent on the concentration dependence of the termination rate constant are shown in Figure 2. Figure 2 demonstrates that the dependence of $K_t$ on conversion is more when the molecular weight of polymer is high and/or when the solvent is good.

**Table I**
**Parameters of MMA Polymerization**

| Parameter | | Ref |
|---|---|---|
| $N_0$ | 4.84 | 11, 14 |
| $(\langle h\rangle_0^2/M)^{1/2}$, cm | $0.68 \times 10^{-8}$ | 18 |
| d ln $\langle h^2\rangle_0/\text{d}T$, deg$^{-1}$ | $0.1 \times 10^{-3}$ | 15 |
| $K$, ml/g | $6.75 \times 10^{-3}$ (PMMA in MMA) | 16 |
| $b$ | 0.72 (PMMA in MMA) | 16 |
| $\left[\dfrac{\langle h\rangle^2\text{EA}}{\langle h^2\rangle\text{MMA}}\right]^{1/2} = \dfrac{2.36}{2.33}$ | | 4 |

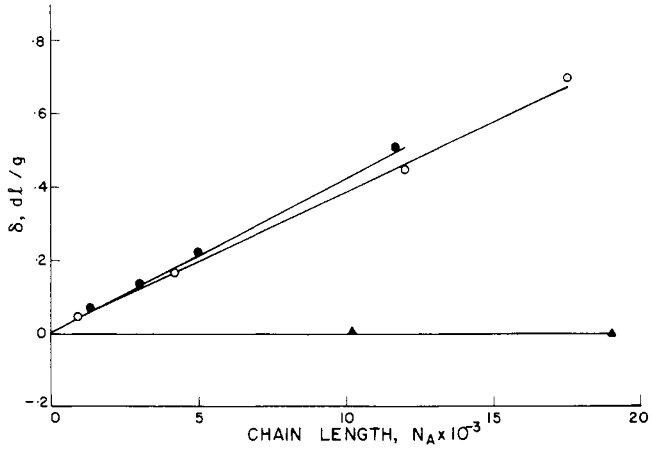

**Figure 3.** Calculated dependence of $\delta$ on the degree of polymerization of terminating PMMA radicals for experimental data of ref 4: (○) MMA at 30 °; (●) MMA at 50 °C; (▲) 50% diethyl ether at 30 °C. (Solid lines predicted by present model.)

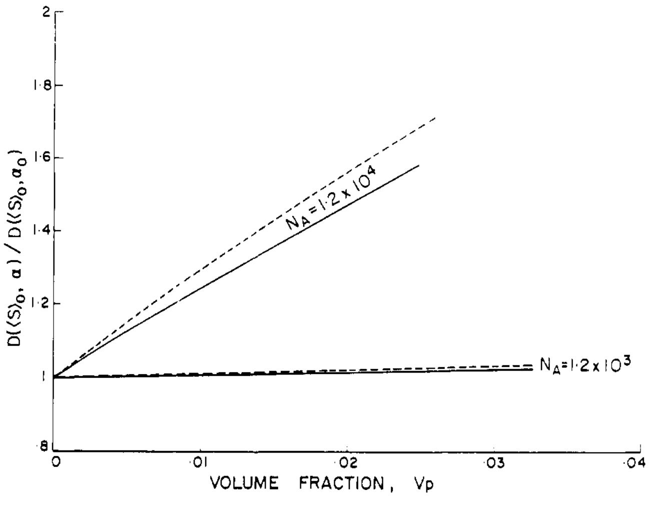

**Figure 4.** The effect of polymer concentration on the segmental diffusion coefficient of PMMA at 30 °C in: (- - -) ethyl acetate; (—) MMA.

It can be seen from Figures 1 and 2 that at very low conversions the concentration dependence of termination rate constant is linear and therefore eq 8 can be simplified to:

$$K_t/K_{t0} = 1 + \delta C \text{ if } C < C^* \qquad (9)$$

where

$$\delta = B(\langle h\rangle_0^2/M)^{3/2}M^{1/2}Z \qquad (9a)$$

and $B$ for low polymer concentration is a constant.

The dependence of $\delta$ on the molecular weight of polymer is shown in Figure 3 along with experimental data. Figure 3 shows that $\delta$ increases directly with $\alpha_0$, i.e., with a higher molecular weight or better solvent.

The concentration dependence of the segmental diffusion coefficient of chain ends for different molecular weights of PMMA and different solvents is shown in Figure 4. It can be seen from this Figure that $D$ increases with concentration to some extent and this initial increase depends on the size of the polymeric radicals.

Some comment must be made concerning molecular weight 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

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

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.

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# Preparation and Polymerization of α,α,α′,α′-Tetrachloro-2-cyano-*p*-xylylene

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ABSTRACT: α,α,α′,α′-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 2–3 × $10^{-3}$ 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–α,α,α′,α′,2,5-hexachloro-*p*-xylylene(HCX), and CTCX–α,α,α′,α′-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, α,α,α′,α′-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 α,α,α′,α′,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-