Atom Transfer Radical Polymerization of Styrene Initiated by Polychloroalkanes and Catalyzed by CuCl/2,2′-Bipyridine: A Kinetic and Mechanistic Study

MATHIAS DESTARAC,* JEAN-MARIE BESSIERE, BERNARD BOUTEVIN

Laboratoire de Chimie Macromoléculaire, UPRES 5076, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l’école normale, 34296 Montpellier Cedex 5, France

Received 9 October 1997; accepted 26 May 1998

ABSTRACT: A series of polychloroalkanes, known as telogen agents for redox telomerization, were used as initiators for atom transfer radical polymerization (ATRP) of styrene using the heterogeneous CuCl/2,2′-bipyridine catalyst. In copper-catalyzed redox telomerization, the reactivity of RCCl3-type telogens is strongly influenced by the nature of the R group. In ATRP, the 2,2′-bipyridine ligand levels the activity of the catalytic system in such a way that all 1,1,1-trichloroalkanes are efficient initiators in ATRP, whatever the R group. The nature of this substituent influences the overall rate of polymerization through both the number of active sites per chain and the [Cu(I)]/[Cu(II)] ratio. By the combining of several analytical techniques, it is proved that some polychloroalkanes such as CCl3CO2CH3, CCl3CF3, or CCl4 are bifunctional initiators. Finally, a general mechanism of initiation is proposed. © 1998 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 36: 2933–2947, 1998

Keywords: atom transfer radical polymerization; styrene; initiation; polychloroalkanes; redox telomerization

INTRODUCTION

Living polymerization is one of the best methods leading to polymers with well-controlled architectures (predetermined molecular weights and chain end structures). Ionic controlled/living systems allow indefinite chain growth without transfer and termination reactions.1,2 However, their high sensitivity toward protic agents is a major drawback for their implementation.

Free-radical polymerization is a much more convenient process, authorizing a wide range of polymerization media and a great variety of monomers. However, because of a slow initiation and a high reactivity of active species, initiation, transfer, and termination reactions are concomitant during polymerization. Therefore, this process leads to ill-defined polymers with uncontrolled molecular weights and broad polydispersities.

Over the past few years, several approaches to controlled radical polymerization based on a reversible termination generated by nitroxide radicals,3–13 iniferters,14–17 and various organometallic derivatives18–21 were described. Among them, and as an extension of redox telomerization of an alkene with a (poly)haloalkane,22–24 leading to low molecular weight products—generally monoadducts—with a high selectivity, several authors25–43 developed transition metal catalyzed systems to control radical polymerization of various monomers.

Using dichlorotris(triphenylphosphine)ruthenium(II) chloride (RuCl2(PPh3)3) (a well-known
catalyst for redox telomerization coupled with a bulky Lewis acid, Sawamoto et al. reported “living” radical homo- and copolymerization of various methacrylates. More recently, they used nickel complexes to control radical polymerization of MMA. Organonickel(II) amine species \([\text{Ni}([\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2])\text{X}] (\text{X} = \text{Cl}, \text{Br}, \text{I})\) were described in the literature as being among the most effective complexes for redox telomerization of MMA with (poly)haloalkanes. Recently, Granel et al. used Ni-based catalysts to control radical polymerization of MMA and n-butyl methacrylate.

Copper complexes and more particularly copper(I) chloride are highly selective catalysts for redox telomerization. Julia et al. reported the considerable role played by 2,2'-bipyridine ligand in the activation of the copper(I) complex. Matyjaszewski et al. developed the transition metal catalyzed atom transfer radical polymerization (ATRP) process, based on a RX/CuX/2,2'-bipyridine and derivatives system (X = Cl, Br). First they described the controlled bulk polymerization of styrene initiated by an alkyl chloride and catalyzed by the heterogeneous CuCl/2,2'-bipyridine complex (CuCl/2Bpy). This complex was used by Percec et al. with arylsulfonyl chlorides as initiators. They both improved their systems using homogeneous copper complexes with 4,4'-dialkyl-2,2'-bipyridine ligands. More recently, Haddleton used (2-pyridinecarbaldehyde imine)copper(I) complexes to promote ATRP of MMA.

Redox telomerization leads to target products (from oligomeric halides RM\(_n\)X to the RMX monadduct, depending on the relative rates of deactivation—i.e. halogen atom transfer from the metal in its highest oxidation state to the growing chain—to propagation) which are unable to react with the metal catalyst to generate a new propagating radical. In all recent systems described above, RM\(_n\)X behave like dormant species (or “macrotelogens”) which can be repeatedly activated by the metal catalyst, leading to a succession of consecutive redox telomerizations.

Tri- and tetrahaloalkanes were extensively studied as telogens in redox telomerization (very few examples of dichlorinated, monobrominated, and monochlorinated active telogens were reported). Among them, polychloroalkanes were the most frequently used.

After a first communication, this paper is an extensive investigation of the use of polychloroalkanes to initiate ATRP of styrene catalyzed by CuCl/2Bpy.

**EXPERIMENTAL**

**Reagents**

Styrene was vacuum distilled from CaH\(_2\) before polymerization. 1-Phenylethyl chloride (ACROS), carbon tetrachloride, and chloroform were distilled before use. Methyl trichloroacetate (99%, Aldrich), 1,1,1-trichlorotrifluoroethane (99%, Aldrich), 1,1,1-trichloroethane (99+%, Aldrich), and 2,2'-bipyridine (99+%, Aldrich) were used as received. 4,4’-Di-(5-nonyl)-2,2'-bipyridine was synthesized according to the procedure described by Matyjaszewski and purified by column chromatography (ether/hexane, 1/10; yield, 28%). CuCl (98%, Aldrich) was purified by washing it with glacial acetic acid, absolute ethanol, and finally ether.

**Measurements**

Monomer conversion was determined by \(^1\)H-NMR. NMR spectra were recorded on a Bruker 200 MHz spectrometer. Molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) using a Spectra Physics instrument, a SP8801 pump coupled with a Shodex RE-61RI detector, and Phenogel columns (10\(^5\), 10\(^4\), 10\(^3\), 500 Å; eluent, THF, 30°C). Polystyrene standards were used to calibrate the columns.

**Polymerization**

A typical polymerization procedure is given as follows: To a 50 mL Schlenk flask are added 517 mg of 2,2'-bipyridine (3.3 mmol), 0.146 mL of 1-phenylethyl chloride (1.1 mmol), and 11 mL of styrene (96 mmol). The solution is first degassed by bubbling argon for 15 min. A 109 mg amount of CuCl (1.1 mmol) is then added. The flask is closed with a stopcock, and three pump–freeze–thaw cycles are then performed on the contents of each flask. The reaction mixture is kept under vacuum and immersed with vigourous stirring in an oil bath maintained at 130°C. After a certain time, the flask is cooled and opened and the polymer is characterized.
Initiator Synthesis

2,2,2-Trichloroethyl Pivalate (3)

A mixture composed of 20 g of 2,2,2-trichloroethanol (0.133 mol), 16.4 g of trimethylacetyl chloride (0.133 mol), and 0.254 g of *p*-toluenesulfonic acid monohydrate (1.33 mol) was stirred at room temperature for 24 h. We isolated a colorless liquid by distillation: CCl$_3$CH$_2$OCOC(CH$_3$)$_3$, 3 (yield 90%; bp 82°C/0.15 mmHg). $^1$H-NMR (CDCl$_3$): δ = 2.1 (s; 3H; CH$_3$), 5.4 (t; 1H; CH), 7.3–7.6 (m; 5H; phenyl). $^{13}$C-NMR (CDCl$_3$): δ = 20.3 (CH$_3$, 1C), 26.5 (CH$_2$, 1C), 51.5 (CCl$_3$, 1C), 62.0 (CH$_2$, 1C), 99.1 (CCl$_3$, 1C), 169.9 (C=O, 1C).

3,3,3-Trichloropropyl Acetate (4)

In a two-neck round-bottomed flask are added 20 g of 1-octene (0.178 mol) and 213 g of chloroform (1.78 mol) in the presence of 2.31 g (5.8 mmol) of di-(p-tert-butyldicarbonate). The reaction mixture is heated at 120°C. The distillation led to a colorless oil:

- CCl$_3$CH$_2$CHClPh, 9 (yield 48%; bp 80°C/0.15 mmHg). $^1$H-NMR (dmf-d$_7$): δ = 3.7 (m; 2H; CH$_2$), 5.4 (t; 1H; CH), 7.3–7.6 (m; 5H; phenyl). $^{13}$C-NMR (dmf-d$_7$): δ = 59.3 (CH, 1C), 62.7 (CCl$_3$CH$_2$, 1C), 97.4 (CCl$_3$, 1C), 128.3–141.1 (phenyl, 6C).

2,2,4,4,4-Pentachloromethyl Butyrate (10)

In a Carius tube were mixed 82.2 g (0.85 mol) of vinylidene chloride, 236.8 g (1.33 mol) of methyl trichloroacetate, and 8.8 g (8.45 mol) of acetonitrile for 22 h at 120°C. After cooling, we isolated the monoadduct (a colorless oil) by distillation: CCl$_3$CH$_2$CHClPh, 9 (yield 80%; bp 58°C/0.15 mmHg). $^1$H-NMR (dmf-d$_7$): δ = 4.05 (s; 3H; CH$_3$), 4.25 (s; 2H; CH$_2$). $^{13}$C-NMR (dmf-d$_7$): δ = 54.2 (CH$_2$, 1C), 63.6 (CH$_2$, 1C), 80.1 (CCl$_3$, 1C), 94.1 (CCl$_3$, 1C), 165.3 (C=O, 1C).

1,1,1-Trichlorononane (8)

The radical telomerization of 20 g of 1-octene (0.178 mol) and 213 g of chloroform (1.78 mol) was initiated by 0.71 g of di-(p-tert-butyldicarbonate) percarbonate (1.78 mmol). The reaction was performed under argon at 60°C for 10 h. A colorless oil was distilled: CCl$_3$CH$_2$(CH$_2$)$_6$CH$_3$, 8 (yield 52%; bp = 50°C/2 mmHg). $^1$H-NMR (CDCl$_3$): δ = 0.9 (t; 3H; CH$_3$), 1.3 (m; 10H; C$_9$H$_{12}$CH$_3$), 1.8 (m; 2H; CCl$_3$CH$_2$CH$_2$), 2.65 (2H; m; CCl$_3$CH$_2$).

$^{13}$C-NMR (dmf-d$_7$): δ = 14.4 (CH$_3$, 1C), 23.1–32.5 (C$_9$H$_{12}$CH$_3$, 6C), 55.4 (CCl$_3$CH$_2$, 1C), 101.3 (CCl$_3$, 1C).

1,1,1,3-Tetrachloro-3-Phenylpropane (9)

In a Carius tube, 2 g of ferric chloride hexahydrate (FeCl$_3$, 6H$_2$O) (7.5 mmol), 1.5 g of triethylamine chlorohydrate (11.25 mmol), and 1.6 g of benzoin (7.5 mmol) are dissolved in 60 g of acetonitrile, 78 g of styrene (0.75 mol), and 230 g of carbon tetrachloride (1.5 mol). The tube is sealed under vacuum and heated at 110°C for 40 h. After the opening of the tube, the reaction mixture is diluted in ether and successively washed with a HCl solution (10%), a saturated solution of Na$_2$CO$_3$, and water. After being dried with MgSO$_4$, the solution is filtered and the volatiles are evaporated. By distillation, we isolated a yellow oil: CCl$_3$H$_2$CHCIPh, 9 (yield 48%; bp 80°C/0.15 mmHg). $^1$H-NMR (dmf-d$_7$): δ = 3.7 (m; 2H; CH$_2$), 5.4 (t; 1H; CH), 7.3–7.6 (m; 5H; phenyl). $^{13}$C-NMR (dmf-d$_7$): δ = 59.3 (CH, 1C), 62.7 (CCl$_3$CH$_2$, 1C), 97.4 (CCl$_3$, 1C), 128.3–141.1 (phenyl, 6C).
under vacuum. A bright yellow oil is recovered by distillation: H\(_3\)CO\(_2\)CCl\(_2\)CH\(_2\)CHClPh, 11 (yield 47%; bp 176°C/25 mmHg). \(^1\)H-NMR (CDCl\(_3\)): \(\delta\) 3.2–3.6 (ABX; 2H; CH\(_2\)), 3.65 (s; 3H; CH\(_3\)), 5.25 (t; 1H; CH), 7.25–7.65 (m; phenyl; 5H). \(^1\)3C-NMR (CDCl\(_3\)): \(\delta\) 54.1 (CH\(_2\), 1C), 54.4 (CH\(_3\), 1C), 85.5 (CH, 1C), 82.2 (CCl\(_2\), 1C), 127.0–139.6 (phenyl, 6C), 165.6 (C=O, 1C).

**RESULTS AND DISCUSSION**

When used as telogens for redox telomerization, polychloroalkanes can be divided into two main categories: 1,1,1-trichloroalkanes; tetrachloroalkanes, including 1,1,1,3-tetrachlorocompounds resulting from the telomerization of an alkene with CCl\(_3\) and carbon tetrachloride itself.

**A. 1,1,1-Trichloroalkanes**

Redox telomerization catalyzed by copper salts with 1,1,1-trichloroalkanes as telogens has been widely studied (Table I). It has been clearly established in all cases that if the presence of a trichloromethyl group is necessary, the nature of its close environment is crucial. The polar effect of the R group in RCCl\(_3\)-type telogens is measured by its Taft constant \(s^*\), excluding all contributions from steric or resonance effects.\(^{59}\) An excellent correlation was found between the logarithm of the telogen’s reactivity and the Taft constant values \(s^*\) of the R group, for styrene\(^{60}\) and butadiene.\(^{61}\) More generally, as shown in Table I, activated telogens such as methyl trichloroacetate (CCl\(_3\)CO\(_2\)CH\(_3\)) or trichlorotrifluoroethane (CF\(_3\)CCl\(_3\)) lead to high yields, whereas chloroform or 1,1,1-trichloroethane (CCl\(_3\)CH\(_3\)) are regarded as “poor” telogens (they can be totally inactive toward monomer in some cases).

We reconsidered these telogens and many others as initiators in ATRP of styrene catalyzed by CuCl/2Bpy (Table II). Whatever the initiator, number-average molecular weights \(M_n\) increase with monomer conversion, with a slight down-
ward deviation from the theoretical profile for high conversions. Figure 1 represents the evolution of $M_n$ as a function of monomer conversion for methyl trichloroacetate (CCl₃CO₂CH₃) and 1,1,1-trichlorononane (CCl₃C₈H₁₇), known as the most and least active telogens in redox telomerization, respectively. A good correlation between theoretical (eq. 1 in Table II) and experimental $M_n$ at low monomer conversion for an initiation by 1,1,1-trichlorononane indicates that initiation is fast compared to propagation whatever the nature of the R group. Further evidence for fast initiation even for inactivated RCCl₃-type initiators was given by using an equimolar amount of 1-phenylethyl chloride (CH₃CH(C₆H₅)Cl) (1-PECl) and 1,1,1-trichloroethane (CCl₃CH₃) as an initiating system (Fig. 2). From results depicted in Figure 2, it appears that CCl₃CH₃ initiates polymerization much faster than 1-PECl.

Although initiation is fast whatever the initiator, the nature of the R group influences the overall rate of polymerization (Fig. 3 and Table III). Using an initiator bearing an electron-withdrawing R group (CO₂CH₃, C₆F₃) increases the overall rate of polymerization compared to 1-PECl (vide Table II.

**Table II.** ATRP of Styrene Initiated by 1,1,1-Trichloroalkanes and Catalyzed by CuCl/2Bpy {\([M]_0 = 8.7 \text{ M}, [\text{RCCl}_3]_0 = [\text{CuCl}]_0 = 0.1 \text{ M}, [\text{Ligand}]_0 = 0.3 \text{ M}, T = 130° \text{C}\)}

<table>
<thead>
<tr>
<th>R in RCCl₃</th>
<th>Initiator Code</th>
<th>$M_n$</th>
<th>$M_{n,SEC}$</th>
<th>$M_n/M_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃CO₂C</td>
<td>1</td>
<td>8500</td>
<td>7700</td>
<td>1.47</td>
</tr>
<tr>
<td>CF₃</td>
<td>2</td>
<td>8800</td>
<td>7500</td>
<td>1.42</td>
</tr>
<tr>
<td>(CH₃)₃C₂O₂CH₂</td>
<td>3</td>
<td>8600</td>
<td>7300</td>
<td>1.46</td>
</tr>
<tr>
<td>AcOC₂H₄</td>
<td>4</td>
<td>9000</td>
<td>7000</td>
<td>1.47</td>
</tr>
<tr>
<td>AcOC₃H₆</td>
<td>5</td>
<td>8600</td>
<td>6900</td>
<td>1.50</td>
</tr>
<tr>
<td>CH₃</td>
<td>6</td>
<td>8600</td>
<td>7300</td>
<td>1.71</td>
</tr>
<tr>
<td>H</td>
<td>7</td>
<td>8600</td>
<td>7100</td>
<td>1.40</td>
</tr>
<tr>
<td>CH₃(CH₂)₆CH₂</td>
<td>8</td>
<td>8600</td>
<td>7200</td>
<td>1.49</td>
</tr>
</tbody>
</table>

\[ M_n = \frac{[\text{M}]_0}{[\text{RX}]_0} \alpha_n \text{ (eq. 1) (} 0.9 < \alpha_n = \text{monomer conversion} < 1). \]

**Figure 1.** Evolution of $M_n$ with monomer conversion in bulk ATRP of styrene initiated by 1,1,1-trichloroalkanes and catalyzed by CuCl/2,2'-bipyridine {\([M]_0 = 8.7 \text{ M}, [\text{RCCl}_3]_0 = [\text{CuCl}]_0 = 0.1 \text{ M}, [\text{Ligand}]_0 = 0.3 \text{ M}, T = 130° \text{C}\)}.

**Figure 2.** Relative reactivities of 1,1,1-trichloroethane and 1-phenylethyl chloride as initiators for ATRP of styrene {\([\text{CCl}_3\text{CH}_3]_0/\text{[1-PECl]}_0/\text{[CuCl]}_0/\text{[2,2'-bipyridine]}_0/\text{[styrene]}_0 = 1/1/0.3/0.6/10 \text{ in toluene (50% vol.), } T = 130° \text{C}\). Conversions determined by GC using toluene as an internal standard.
Among all the initiators tested, methyl trichloroacetate is the most active followed by trichlorotrifluoroethane. On the contrary, 1,1,1-trichloroalkanes having no activating group in the α-position (1,1,1-trichlorononane (8) and 2,2,2-trichloroethyl pivalate (3)) promote slightly slower ATRP than 1-PECl. Contrary to redox telomerization, the presence of an activating substituent in the α-position to the trichloroethyl group (3) brought no additional activity to the system.

After having characterized the effect of the R group on the overall rate of polymerization, results reported in Table II show its nature has a negligible influence on $M_w/M_n$ values, even for low monomer conversions ($1.3 < M_w/M_n < 1.7$) for the chosen $[M_0]/[RCCl_3]_0$ ratio. To conclude this first part, 1,1,1-trichloroalkanes are active initiators in ATRP of styrene catalyzed by CuCl/2Bpy, whatever the R group.

Discussion

Although very simplified, authors generally come to an agreement that the ATRP mechanism relies on a fast equilibrium between dormant (polymeric halides) and active species (growing radicals) as shown in Scheme 1.

$$P_n - X + Cu(II)/2L \overset{k_{act}}{\rightarrow} P_n^* + Cu(II)Cl/2L \overset{k_{deac}}{\rightarrow} P_n$$

Scheme 1.

For an initiation by arylsulfonyl chlorides, $RC_6H_4SO_2Cl$, a mechanism comprising an additional stage of initiation has been proposed. Using active alkyl halides initiators regarded as “models” of dormant chains, the initiation is fast compared to propagation, and therefore, the initiation stage “disappears” from the kinetic scheme. Thus, the stationary concentration of growing radicals can be expressed as in eq. 3, assuming $[P_nX] = [RX]_0$.

$$K = \frac{k_{act}}{k_{deac}} = \frac{[P_n^*][Cu(II)X]}{[P_nX][Cu(II)]}$$

(2)

$$[P_n^*] = \frac{K[P_nX][Cu(II)]}{[Cu(II)X]}$$

(3)

$$R_p = k_p[M][P_n^*] = k_p\frac{K[RX]_0[Cu(II)]}{[Cu(II)X]}[M]$$

For an initiation by arylsulfonyl chlorides, $RC_6H_4SO_2Cl$, a mechanism comprising an additional stage of initiation has been proposed. A much faster rate of initiation than that of propagation has been reported, regardless of the nature of the R group. Therefore, identical to an initiation by alkyl halides, the only activation/deactivation reversible process determines the overall rate of polymerization.

Using $RCCl_3$-type initiators, the general mechanism is more complex and can differ according to...
the nature of the R group. After generation of the first oligomeric halide RCrlMnCl, two new potential initiators (both chain ends) are present in the system. The major problem is the lack of knowledge of the relative reactivities of the residual RCrlz-type initiator and both chain ends. Experimental results depicted in Figures 1 and 2 show that initiation is fast compared to propagation whatever the R group. A good correlation between \( M_n, \text{act} \) and \( M_n, \text{deter} \) determined for all initiators at low monomer conversion and also relatively low polydispersities are proof of a preferential activation of 1,1,1-trichloroalkanes before “macroinitiators” (chain ends). A greater activity of chain ends would result in an incomplete initiation with higher \( M_n \) than predicted and broader polydispersities.

Despite a fast initiation, inactivated 1,1,1-trichloroalkanes (3 and 8) induce slower polymerization than 1-PECl. This can be explained by a higher equilibrium constant of initiation \( K_{eq} \) —defined in Scheme 4—responsible for the generation of a high concentration of radicals in the early stages of polymerization (Fig. 2). In this case, termination is favored (second order) compared to propagation (first order). Therefore, coupling reactions occur and contribute to the buildup of an excess of deactivating species (CuCl2/2Bpy) that tends to slow down the polymerization. Of course, because of the much higher initial concentration of chains \((\approx [RCrlz]_0)\) than that of deactivator, it has a minor effect on the control of molecular weights; on the other hand, it substantially affects kinetics of polymerization (eq. 3).

Considering 1-PECl promotes a fast initiation compared to propagation in the aforementioned conditions, the equilibrium constant \( K \) determines kinetics of ATRP. So, some of the \( \alpha \)-activated 1,1,1-trichloroalkanes, promoting faster ATRP than 1-PECl, undoubtedly affect \( K \) values. These kinetic results led us to consider that some of the \( \alpha \)-activated 1,1,1-trichloroalkanes certainly act as multifunctional initiators. In order to check these assumptions, ATRP of styrene was initiated by monoadducts bearing both RCrlz—\( R = \text{Cl included} \) and \( -\text{CH(ClC}_6\text{H}_5)\text{Cl} \) groups. Before that, ATRP of styrene initiated by CCl4 was studied in detail.

B. Tetrachloroalkanes

Among tetrachloroalkanes, carbon tetrachloride has been the most widely used telogen in redox telomerization (Table IV). In almost all cases, its reaction with an alkene \( \text{CH}_2=\text{CXY} \) catalyzed by a copper salt leads to the following monoadduct:

\[
\text{X} \\
\text{CCl}_4 - \text{CH}_2 - \text{C} - \text{Cl} \\
\text{Y}
\]

As mentioned before, the ability of a trichloromethylated end group to be activated by the metal catalyst in redox telomerization pushed many authors to use CCl4 as a promoter of bistermolecularization (Scheme 2). \( \alpha,\omega\)-Bis(monoadducts) are exclusively obtained in a two-step reaction. However, under certain conditions (monomer in excess), “false adducts \( n = 2 \)” \( (\alpha,\omega\)-bis(monoadducts)) have been characterized during the first step. \( \text{CCl}_4 \) acts as an initiator that promotes a fast initiation compared to propagation.

In order to shed light on the behavior of \( \text{CCl}_4 \) during the initiation stage, we used it at different concentrations in ATRP of styrene catalyzed by CuCl2/2Bpy (Fig. 4). Results reported in Figure 4 and relatively low polydispersities obtained whatever the concentration conditions \( 1.35 < \frac{M_n}{M_n} < 1.5 \) show \( \text{CCl}_4 \) acts as an initiator that promotes a fast initiation compared to propagation.

In our concern to determine the functionality of \( \text{CCl}_4 \) and \( \alpha \)-activated 1,1,1-trichloroalkanes, we investigated ATRP of styrene initiated by several monoadducts, choosing a \[\frac{[M]_0}{[\text{initiator}]_0}\] ratio equal to 10. Results reported in Table V show that the chosen monoadducts are efficient initiators for ATRP of styrene. An excellent correlation between theoretical (eq. 1) and experimental number-average degree of polymerization \( DP_n \) and polydispersities comprised between 1.28 and 1.40 are characteristic of a good control. Moreover, we checked by GC and SEC analysis that no residual trace of initiator is present at total monomer conversion. In order to analyze terminal functionalities of these oligomers, samples were purified and characterized by \( ^{13}\text{C-NMR} \) spectroscopy.

Initiator Functionality

Carbon atoms bonded to chlorine substituents resonate in frequency ranges characteristic of the number of bonded chlorine atoms. Independently
of the closest substituents, three characteristic zones have been defined\textsuperscript{45,62}:

90 < \( \delta < 100 \) ppm for \( \text{CCl}_3\text{CH}_2\text{CHR} \)

75 < \( \delta < 90 \) ppm for \( -\text{RCHCH}_2\text{CCl}_2\text{CH}_2\text{CHR} \)

55 < \( \delta < 70 \) ppm for \( -\text{CH}_2\text{CHRCl} \)

When ATRP is initiated by CCl\textsubscript{4} (Fig. 5a), only two kinds of carbon atoms bearing chlorine atoms are present. Thanks to a \( ^{13}\text{C}-\text{NMR} \) analysis of 9 and 1-PECl, the signal at \( \delta = 97 \) ppm has been attributed to the CCl\textsubscript{3}CH\textsubscript{2} chain end and the two close signals at \( \delta = 62 \) and 63 ppm to the monochlorinated carbon atom \( -\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{Cl} \) (two diastereoisomers). Using 9 (Fig. 5b) as an initiator gave an identical spectrum. Thus, no characteristic signal of a difunctional initiation (in the 75–90 ppm range) could be detected. Such a result would mean that the polymerization occurs via a selective activation of the monochlorinated chain end. This hypothesis seems improbable considering the much faster initiation by 1,1,1-trichloroalkanes compared to that of 1-PECl (Fig. 2). Therefore, a difunctional initiation is expected. Another method based on \( ^1\text{H}-\text{NMR} \) spectroscopy helped us to determine the mechanism of initiation.

Table IV. Redox Telomerization of Various Monomers with Tetrachloroalkanes Catalyzed by Copper Salts

<table>
<thead>
<tr>
<th>Telogen</th>
<th>Monomer</th>
<th>Catalyst</th>
<th>Product</th>
<th>Yield</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl\textsubscript{4}</td>
<td>Ethyl acrylate</td>
<td>Cu\textsuperscript{I}/Cu\textsuperscript{II} ( n = 1 )</td>
<td>60</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>MMA</td>
<td>Cu\textsuperscript{I}/Cu\textsuperscript{II} ( n = 1 )</td>
<td>90</td>
<td>45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butadiene</td>
<td>CuCl\textsubscript{2} ( n = 1 )</td>
<td>80</td>
<td>61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinylidene chloride</td>
<td>Cu\textsuperscript{I}/Cu\textsuperscript{II} ( n = 1 )</td>
<td>90</td>
<td>63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,5-Hexadiene</td>
<td>Cu\textsuperscript{I}/Cu\textsuperscript{II} ( n = 1 )</td>
<td>77</td>
<td>72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diallyl ether</td>
<td>Cu\textsuperscript{I}/Cu\textsuperscript{II} ( n = 1 )</td>
<td>low</td>
<td>73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Divinylbenzene</td>
<td>CuCl</td>
<td>Bismonoadduct</td>
<td>100</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>Allyl methacrylate</td>
<td>CuCl</td>
<td>Bismonoadduct</td>
<td>73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>CuCl</td>
<td>( n = 1 )</td>
<td>74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl undecenyl</td>
<td>Cu\textsuperscript{I}/Cu\textsuperscript{II} ( n = 1 )</td>
<td>65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTFE</td>
<td>CuCl\textsubscript{2}</td>
<td>Mainly ( n = 1 )</td>
<td>75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Menthyl acrylate</td>
<td>CuCl\textsubscript{2} ( n = 1 )</td>
<td>76</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Menthyl methacrylate</td>
<td>CuCl\textsubscript{2} ( n = 1 )</td>
<td>76</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrafluoroethylene</td>
<td>CuCl\textsubscript{2}</td>
<td>Telomers</td>
<td>77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>CuCl\textsubscript{2} ( n = 1 )</td>
<td>95</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCl\textsubscript{3}CH\textsubscript{2}CH(X)Cl</td>
<td>Methyl acrylate</td>
<td>CuCl</td>
<td>Only</td>
<td>&lt;30</td>
<td>69</td>
</tr>
<tr>
<td>Allyl chloride</td>
<td>CuCl</td>
<td>( \alpha,\omega)-bismonoadduct</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allyl alcohol</td>
<td>CuCl</td>
<td>Only</td>
<td>&lt;30</td>
<td>69</td>
<td></td>
</tr>
</tbody>
</table>
1H-NMR spectra of polystyrene synthesized by ATRP using a RCl/CuCl initiating system exhibit a broad signal between 4.25 and 4.55 ppm characteristic of the terminal proton, \( \text{CH}(_2\text{C}_6\text{H}_5)\text{Cl} \) (Fig. 6). According to a mono- or difunctional initiation, \( M_n \) values can be calculated by 1H-NMR in the following way (\( I \) = peak integration):

\[
\langle M_n \rangle_{\text{NMR}} = \frac{I(\text{C}_6\text{H}_5\text{Cl})/5}{I(\text{CH}(\text{C}_6\text{H}_5)\text{Cl})} \times M_0
\]

if monofunctional \hspace{1cm} (4)

\[
\langle M_n \rangle_{\text{NMR}} = \frac{I(\text{C}_6\text{H}_5)/5}{I(\text{CH}(\text{C}_6\text{H}_5)\text{Cl})/2} \times M_0
\]

if difunctional \hspace{1cm} (5)

[styrene]_0/[CCl]_0 ratios equal to 10, 20, and 30 were used to prepare well-defined polystyrene samples. At complete monomer conversion, products were purified and analyzed by 1H-NMR, GPC, and elemental analysis (Table VI). Results depicted in Table VI show a good correlation between \( \langle M_n \rangle_{\text{num}} \) difunc and both \( M_n\text{GPC} \) and \( M_n\text{el} \) for the highest [styrene]_0/[CCl]_0 ratios (entry 3). However, the number of phenylethyl chloride terminal moieties per chain is always slightly less than 2, because of a high overall rate of polymerization compared to that of the two consecutive initiation steps. Therefore, by this method, the difunctional initiation by CCl₄ has been clearly established.

Despite the conditions used to run \(^{13}\text{C}-\text{NMR}\) analysis of the oligostyrene samples (high number of scans, long delay times—cf. Fig. 5a,b), the central —CCl₂— quaternary carbon signal could not be seen on the spectra, presumably because of its much longer relaxation time compared to that of terminal carbon atoms.

As for ATRP initiated by 10 (Fig. 5c), the absence of a signal around 80 ppm proves that the initiation occurs by a favored activation of the dichloromethylated end group of the initiator. Moreover, the presence of a broad signal centered at 95.1 ppm shows that the trichloromethylated end of the initiator is poorly affected during initiation. In redox telomerization, a similar selective activation of the dichloromethylated end of 10 used as a telogen has been reported. Finally, when ATRP of styrene is initiated by 11 (Fig. 5d), the absence of a signal at 82.1 ppm shows that the initiator has been fully consumed by its dichloromethylated end. After the creation of a first oligomeric halide (first redox cycle), it can be assumed that propagation occurs on at least two sites per chain according to the mechanism shown in Scheme 3. Considering that haloisobutyric acid is more efficient initiators than 1-phenylethyl halides, the carbon atom bearing both chlorine and the methyl ester group (structure B, Scheme 3) is a potential initiating site. In other terms, methyl trichloroacetate and some other \( \alpha \)-activated 1,1,1-trichloroalkanes are presumably trifunctional initiators. This point is still under investigation in our laboratory. Here again, if present, the central carbon atom could not be characterized because of a much longer relaxation time than that of terminal carbon atoms (Fig. 5d).

C. General Discussion

When ATRP of styrene is initiated by polychloroalkanes, the mechanism of initiation is complex and differ according to the initiator used. In every case, the first activation process leads to the following oligomeric halide:

\[
\text{RCl}_2\text{CH}_2\text{CH}(_2\text{C}_6\text{H}_5)\text{Cl}
\]

Afterward, relative reactivities of both RCl₂—CH₂CH(C₆H₅)— and —CH₂CH(C₆H₅)Cl ends de-
fine the mono- or bifunctional character of the initiation. A combination of several analytical techniques and the use of “models” of the intermediate shed light on the mechanism of the initiation stage.

Figure 5. $^{13}$C-NMR analysis of styrene oligomers described in Table V (J-Mod). Initiation by (a) CCl$_4$, (b) 9, (c) 10, and (d) 11. Conditions: solvent dmf-$d_7$; delay time, 5 s; number of scans, between 6000 and 7000.
By the combining of 1H-NMR spectroscopy, GPC measurements, and elemental analysis, a difunctional initiation by CCl₄ was determined. This important result can be interestingly compared to that of Boutevin et al.⁶⁹ for the study of redox telomerization of several monomers (methyl acrylate, allyl alcohol, allyl chloride) with their own monoadducts with CCl₄ as new telogens. In all cases, only the trichloromethylated ends were proved to be activated (Scheme 2). Despite the doubling of initiating sites compared to 1-PECl, similar $k_p^{app}$ values have been measured (Fig. 3, Table III). This can be explained by a balancing effect between the decrease of the $[P_n]/[P_nX]$ ratio and the concomitant increase of $[Cu(II)]/[Cu(I)]$ (eq. 2). Here again, a high concentration of radicals at the beginning of the reaction induces coupling reactions and the formation of

![Figure 6. 1H-NMR spectrum of polystyrene initiated by CCl₄ (sample described in Table VI, entry 2).](image)

**Table V.** ATRP of Styrene Initiated by CCl₄ and Various Monoadducts and Catalyzed by CuCl/2,2'-Bipyridine ([M]₀/[Initiator]₀ = 10, [CCl₄]₀/[CuCl]₀ = 1/3[Ligand]₀, 50 vol % in Xylene, $T = 130°C$)

<table>
<thead>
<tr>
<th>Initiator</th>
<th>$DP_{n,th}$</th>
<th>$DP_{n,SEC}$</th>
<th>$M_w/M_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>10</td>
<td>10</td>
<td>1.30</td>
</tr>
<tr>
<td>CCl₄CH₂CHCl</td>
<td>9.4</td>
<td>10</td>
<td>1.40</td>
</tr>
<tr>
<td>H₂CO₂CCl₂CH₂CCl₃</td>
<td>9.5</td>
<td>10.7</td>
<td>1.28</td>
</tr>
<tr>
<td>H₂CO₂C—Cl₂—CH₂CHCl</td>
<td>9.5</td>
<td>10.9</td>
<td>1.27</td>
</tr>
</tbody>
</table>
copper(II) species (when CCl₄ initiates, the reaction mixture turns green after a few seconds whereas the solution remains brown—characteristic of the copper(I) complex—throughout the polymerization for an initiation by 1-PECl). Also, the parallel between reactivities of “conventional” initiators (CCl₃CH₂R·1-PECl) (Fig. 2) and “macrorinitiators” (CCl₃CH₂CH(C₆H₅)O·OCH(C₆H₅)Cl) (Table VI) is noteworthy.

α-Activated 1,1,1-trichloroalkanes (CCl₃CO₂CH₃, CCl₃CF₃) induce faster polymerizations than CCl₄. Therefore, a—at least—bifunctional initiation could be strongly assumed for these initiators. ¹³C-NMR analysis (Fig. 5d) and kinetic results (Fig. 3) enabled us to show that methyl trichloroacetate, CCl₃CO₂CH₃ (as well as presumably CCl₃CF₃), acts as a—at least—bifunctional initiator. By using adduct 11, the preferential activation of the dichloromethylated end before the monochlorinated end has been proved (Fig. 5d). In this case, the kinetic scheme becomes complex, comprising an initiation stage followed by consecutive propagation stages, each one of them differing in their active species concentration [Pₙ]. Moreover, according to the initiator used, different rates of initiation result in the irreversible generation of variable concentration of copper(II) species. Effects of the initiator on both the number of active sites per chain and [Cu(II)]/[Cu(I)] ratio explain the fractional values of k_p²²²²²²²²²²/CCL₃CO₂CH₃)k_²²²²²²²²²²(1-PECl) (≈ 1.4) and k_p²²²²²²²²²²/CCL₃CF₃)k_²²²²²²²²²²(1-PECl) (≈ 1.2) (Table III) for the chosen temperature and concentration conditions. Finally, considering initiation is fast compared to propagation whatever the initiator (Figs. 1 and 2) and through results depicted in Figure 5, the following reactivity order can be defined:

RCCl₃ > ~CH₂CCl₂CO₂CH₃ > ~CH₂CCl₃ > ~CH₂—CH—Cl

To conclude, this series of results enabled us to define a general reaction scheme for the initiation of ATRP of styrene by polyhaloalkanes (Scheme 4).

**CONCLUSION**

We investigated polychloroalkanes as initiators in ATRP of styrene catalyzed by CuCl/2Bpy. Whatever the initiator, both kinetics and chain structures depend on the relative reactivities of several potential initiation sites. Even 1,1,1-trichloroalkanes regarded as “poor” telogens for redox telomerization are efficient initiators for bulk ATRP of styrene. It has been shown that carbon tetrachloride, methyl trichloroacetate, and also certainly other α-activated 1,1,1-trichloroalkanes act as—at least—bifunctional initiators. The nature of the R group influences the overall rate of polymerization by affecting the [Cu(I)]/[Cu(II)] ratio as well as the functionality of the initiator.

The electron-donating 2,2′-bipyridine ligand by its complexation with copper(I) chloride increases

---

**Table VI.** Molecular Weight Measurements of Polystyrene Samples Initiated by CCl₄: Application to the Determination of the Initiator Functionality

| [M]₀/|RX|₀ | Mₙ,bi | Mₙ,GPC | Mₙ,calc | Mₚ/Mₙ | (Mₐ,mono) | (Mₐ,bi) |
|---|---|---|---|---|---|---|---|
| 10 | 1000 | 1170 | 1295 | 1.26 | 790 | 1440 |
| 20 | 2225 | 2440 | 2700 | 1.35 | 1630 | 3120 |
| 30 | 3265 | 3520 | 3640 | 1.38 | 1990 | 3830 |

*a* (DFₐ)₂ = \( \frac{142 - 154(\% \text{Cl})}{104(\% \text{Cl})} \), (DFₐ)₃ = \( \frac{154(\% \text{Cl}) - 12}{96 - 104(\% \text{Cl})} \).

Mₐ,calc calculated from the average of these two values.

---

**Scheme 3.** Mechanism of CuCl/2Bpy-catalyzed ATRP of styrene initiated by 11.
the activity of the catalyst by both increasing its solubility and stabilizing the metal in its high oxidation state, therefore facilitating the formation of active species. Consequently, it tends to level the activity of the catalytic system compared to redox telomerization.

$^{13}$C-NMR spectroscopy has been shown to be a useful tool to analyze terminal functionalities of oligomeric chains. From this analysis and kinetic results, we defined a reactivity order relating to the activation process. Finally, choosing appropriate initiators, new groups (acetate, tert-butyl, trifluoromethyl...) that may be useful for further chemical modifications or labeling were introduced at chain ends.

This survey enabled us to draw a parallel between redox telomerization and ATRP. Through all of the results mentioned in this paper, ATRP appears to be an extension of redox telomerization. Only by use of an appropriate ligand such as 2,2'-bipyridine can a dead telomer be reinitiated, leading to a controlled polymerization process.

The CNRS/Elf Atochem France Research Group is gratefully acknowledged for financial support of this research.

REFERENCES AND NOTES

42. C. Granel, Ph. Dubois, R. Jérôme, and Ph. Teyssié, Macromolecules, 29, 8576 (1996).