Telomerization of acrylic acid with mercaptans: Part 2. Kinetics of the synthesis of star-shaped macromolecules of acrylic acid

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Abstract: The telomerization of acrylic acid with a polyfunctional transfer agent initiated by 2,2’-azobisisobutyronitrile, was first investigated in an organic medium (THF) at 65°C. Transfer constants (C_T) for three mercaptans, ethylene glycol bis(thioglycolate), trimethylolpropane tris(2-mercaptoacetate) and pentaerythritol tetrakis(3-mercaptopropionate) of about 6.1, 6.3 and 7.3, respectively, were determined. From these results, it followed that a well-defined star poly(acrylic acid) could not be synthesized via telomerization of acrylic acid in THF. Nevertheless, the same study was performed with the tetrafunctional transfer agent in water/THF mixtures. This work emphasized that the nature of the solvent plays an important role in determining the transfer constant. Thus, the value of C_T for the tetrafunctional transfer agent decreased from 7.3 in THF to 1, the ‘ideal’ case for telomerization (C_T = 1), for the mixture of solvents water/THF (80%, 20%, v/v). With this route, it seems that acrylic acid star-shaped macromolecules could be synthesized via telomerization.

Keywords: acrylic acid; polyfunctional transfer agent; telomerization; kinetic transfer constant; solvent effect

INTRODUCTION

Over 50 years ago, Flory¹ and Stockmayer² reported statistical and experimental studies on polymerization systems that give polymers containing substantial chain branching. Nowadays, star-shaped macromolecules have gained more and more interest; many polymers that possess extensive chain branching are called hyperbranched polymers.³ However, these polymers mimic but do not duplicate the perfect branching found in dendrimers.⁴ This concept of star-shaped macromolecule synthesis is interesting and our aim was to apply it to the polyelectrolyte area by performing the telomerization of acrylic acid (AA).

Since the discovery of the principle of chain transfer in free radical polymerization,⁵⁻⁷ this phenomenon has been applied in polymer science, in particular for regulating the polymer length.⁸⁻¹³ The regulators are monofunctional reagents with a high transfer reactivity. The most efficient are the mercaptans which fulfil the condition of high transfer reactivity. While the effect of monofunctional components has been investigated comprehensively, very little attention has been devoted to the use of transfer agents containing two or more active groups endowed with comparable reactivity. In principle, the use of such compounds seems contradictory: chain transfer reduces chain length, but the coupling of two or more chains produces an increase in molecular mass.⁹ Ullisch and Burchard¹⁰ investigated this kind of compound from a theoretical point of view by means of the cascade theory. The authors concluded from their theoretical study that the formation of star-branched polymers can be obtained in free-radical telomerization by using polyfunctional transfer agents having a transfer constant, C_T, close to one (Fig 1).

The present work reports the telomerization of AA by this class of transfer reagents in order to determine their transfer constants. Many studies have been devoted to the telomerization of this monomer with various telogens. Among the most used telogens alkyl halides such as RCl₂ or RBr₃,¹¹,¹² mercaptans¹³⁻¹⁸ or fluorinated mercaptans¹⁹,²⁰ may be noted. How-

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ever, the telomerization of AA with a polyfunctional transfer agent has not been reported.

In a previous report related to the telomerization of AA with thioglycolic acid, we found a significant effect of the solvent on the $C_T$ value. A transfer constant equal to 1 (the ‘ideal’ case for telomerization) was reached by using a mixture of water/THF (80%, 20%, v/v).

In the present article we report the telomerization of AA with di-, tri- or tetrafuctional transfer reagents in order to determine the influence of both the mercapton functionality and the nature of the solvent on the $C_T$ value of this kind of compound.

**EXPERIMENTAL**

**Materials**

*Acrylic acid*. Reagent grade product (Aldrich) was distilled under reduced pressure to remove the inhibitor.

*Tetrahydrofuran*. Reagent grade product (SDS) was refluxed for more than 24 h over sodium, stored under an atmosphere of nitrogen and distilled before use.

*2,2'-Azobisisobutyronitrile*. Reagent purity grade product (Aldrich) was recrystallized twice from cold methanol, dried under vacuum at room temperature and stored under an atmosphere of nitrogen at $-4^\circ$C.

*Ethylene glycol bis thioglycolate, trimethylolpropane tris(2-mercaptoacetate) and pentaerythritol tetrakis(3-mercaptopropionate)*. Reagent grade products (Aldrich) were used without further purification.

*Water*. Deionized (Millipore) and degassed water was used.

**Analytical techniques**

$^1$HNMR spectra were recorded using a Bruker AC 200 with trimethylsilyl as internal reference and dimethyl sulfoxide (DMSO) as deuterated solvent.

**Telomerization**

Telomerizations were carried out in a 50-ml two-necked flask, equipped with stirrer, rubber septum and condenser connected to a nitrogen inlet or vacuum system. After degassing, the required amounts of reagents were charged, by syringe, through the septum. The telomerization of acrylic acid was carried out at 65°C both in tetrahydrofuran (THF) or water/THF mixtures under an atmosphere of nitrogen. The initial mole ratio between transfer agent and monomer ([RSH]$_i$/[M]$_0$) was 0.05. In all the experiments the initiator concentration was $1.4 \times 10^{-2}$ mol$^{-1}$ and the monomer concentration $1.4$ mol$^{-1}$.

In a standard reaction 5 g ($6.94 \times 10^{-2}$ mol) of acrylic acid, 0.42 g ($8.6 \times 10^{-4}$ mol) of pentaerythritol tetrakis(3-mercaptopropionate) and 45 ml of THF were charged into a nitrogen-flushed flask. Then the liquids were degassed twice by consecutive freezing, evacuation and thawing. Finally 0.114 g ($6.9 \times 10^{-4}$ mol) of 2,2'-azobisisobutyronitrile (AIBN) in 1 ml of THF was added using a nitrogen-flushed syringe.

**Telomerization kinetics**

All the kinetics have been studied by following the changes in monomer and telogen concentrations. Each reaction was monitored by sampling and each aliquot was quenched in ice in order to stop the reaction.

**Telogen conversion**

The telogen conversion of each sample was determined by means of iodine titration against a $2 \times 10^{-3}$ N iodine solution prepared from iodine standard solution (0.1029 N). The telogen concentration is given by the relation at equilibrium:

$$[RSH]_t = \frac{V_{eq}(t) \times [RSH]_0}{V_{eq}(0)}$$

**Monomer conversion**

Different analytical methods of recording monomer conversion have been tested such as FT-IR, GC or $^1$HNMR. We have used $^1$HNMR using DMSO-$d_6$ as deuterated solvent. Each sample was analyzed by comparing the integration ratio of the three vinyl protons integration of the monomer ($H1$) to that of the methine proton of the polymer ($H2$) as shown in Fig 2.

The rate of conversion ($z$) was calculated with the relation:

$$\alpha = \frac{H2}{H1^3 + H2}$$

**RESULTS AND DISCUSSION**

The control of polymer architecture through the use of a polyfunctional chain transfer agent in free radical polymerization was investigated both theoretically and experimentally by Ullisch and Burchard. They studied the polymerization of styrene in the presence of a tetrafuctional transfer agent, PETTMP, and found that the $C_T$ of this mercaptan to be 58. In contrast, Di Silvestro et al. studied the telomerization of methyl methacrylate with the same tetrafuctional transfer agent and found a $C_T$ of 0.64. These results underline a difference of reactivity with the telogen between these two classes of monomers.

In our laboratory Bechkhok et al. studied the telomerization of styrene with monofunctional transfer agents, thioglycolic acid and perfluorohexylethanol, and found $C_T$ values of 7.5 and 12.3, respectively. The authors claimed that these very high values are observed with mercaptans for all monomers bearing electron-donating groups and may be pre-
dicted by the Alfrey and Price Q-e system. This explanation confirmed Ullisch and Burchard and Yuan and Di Silvestro’s results since styrene is an electron-donating monomer and methyl methacrylate is an electron-accepting monomer.

Thus, in the first part of this work we proposed to investigate the telomerization of AA, which is an electron-accepting monomer, with a polyfunctional transfer reagent so as to determine the transfer constant of this reaction.

Transfer constant determination

For radical polymerization of vinyl monomers (M) in the presence of a conventional chain-transfer agent (XY), the mechanisms are described by the following eqns ((1) – (6)). For the radical telomerization using an initiator I₂, such as a diazoic compound, we have:

Initiation  \[ I_2 \xrightarrow{k_i} 2I^- \]  

\[ \text{(1)} \]

\[ \Gamma^- + XY \rightarrow IY + X^- \]  

\[ \text{(2)} \]

\[ X^- + M \rightarrow XM^- \]  

\[ \text{(3)} \]

Propagation  \[ XM^- + nM \xrightarrow{k_p} XM_{n+1}^- \]  

\[ \text{(4)} \]

Chain transfer  \[ XM_n^- + XY \xrightarrow{k_{n-t}} X(-M)_n^-Y + X^- + M \]  

\[ \text{(5)} \]

Termination  \[ XM_n^- + XM_p^- \xrightarrow{k_{n-t}} \text{Polymer} \]  

\[ \text{(6)} \]

There are several methods of determining the transfer constant \( (C_T = k_i/k_p) \) of the transfer agent (XY). The first and most widely used one is given by Mayo. This method requires a plot of the inverse of \( (\bar{DP}_n)^{1/2} \) as a function of \( R = \frac{[XY]}{[M]} \). The slope of the straight line gives the value of \( C_T \).

\[ \frac{1}{(\bar{DP}_n)^{1/2}} = C_T \frac{[XY]}{[M]} \]  

\[ \text{(7)} \]

The main drawback of this method is that it is applicable only for rates of conversion of less than 10%. Other methods have been proposed that take the conversion rate into account. For this purpose, O’Brien and Gornick have linked the transfer agent consumption with the monomer conversion in order to determine the value of \( C_T \).

\[ \ln \frac{[XY]}{[X]} = C_T \ln \frac{[M]}{[M_0]} \]  

\[ \text{(8)} \]

Thus, by plotting \( \ln \frac{[XY]}{[X]} \) versus \( \ln \frac{[M]}{[M_0]} \), \( C_T \) can be determined from the slope of the line obtained. This method was applied to the telomerization of AA in the presence of the telogens described below.

The telomerization of AA was performed under nitrogen, in THF at 65°C, in the presence of AIBN as initiator. Three different transfer agents, ethylene glycol bis thioglycolate (EGBTN) (Fig 3, 1), trimethylolpropane tris(2-mercaptoproacetate) (TMPTMA) (2) and pentaerythritol tetras(3-mercaptopropionate) (PETTMP) (3) have been investigated.

Each reaction was monitored by sampling, and each aliquot was quenched in ice to stop the reaction. The monomer (M) and telogen (T) conversions were determined, respectively, with \(^1\)HNMR using DMSO as the internal standard and iodine titration as explained in the experimental section.

From the change of each monomer and telogen

\[ \text{Synthesis of star-shaped macromolecules of acrylic acid} \]
concentration in the course of their telomerization, the slopes of the straight lines $\ln \frac{[T]}{[T]_0}$ versus $\ln \frac{[M]}{[M]_0}$ led to the determination of $C_T$ values.

Figure 4 shows the linear relationship between $\ln \frac{[T]}{[T]_0}$ and $\ln \frac{[M]}{[M]_0}$ for each telogen, the slope of which gives a $C_T$ value of 7.3 for the tetrafunctional, 6.3 for the trifunctional and 6.1 for the difunctional telogen. In Part 1 of this work we reported a $C_T$ value of 3.2 for a monofunctional transfer agent. Thus, we have found an increase of the value of $C_T$ with increasing the mercaptan functionality. However, no satisfactory chemical explanation could be proposed for this fact.

In the introduction we stated that the formation of star-branched polymers could be obtained by free radical polymerization using polyfunctional transfer agents having a transfer constant $C_T$ not far from 1 and this was represented in Fig 1. All the results showed an average $C_T$ value largely superior to one. Consequently, the formation of star-shaped macromolecules by AA telomerization in THF is not possible.

In Table 1, we have listed the $C_T$ values for different radical telomerizations of vinyl, acrylic and methacrylic monomers. These data require several comments. At first we can see that the styrenic monomer presents the highest transfer constant value. This result confirms Bechkok’s explanation for monomer-bearing electron-donating groups.

Methyl methacrylate (MMA) and AA are both electron accepting monomers so that according to Bech kok et al. these two monomers are likely to be telomerized with mercaptans. In practice, we have observed that only MMA satisfied the requirement of a $C_T$ value close to one. We have shown in a previous report that the AA consumption is too slow compared with that of the telogen. So, we endeavored to find conditions that increased the value of $k_p$ relative to that of $k_r$. Thus, we had exhibited the solvent effect on the $C_T$ value obtained for the telomerization of AA with thiglycolic acid; a $C_T$ value equal to one, ‘ideal’ case of telomerization was reached for a solvent mixture water/THF (80%, 20%, v/v).

In the next part of this paper we describe the application of these results to the telomerization of AA with polyfunctional transfer agents.

Effect of solvent on the transfer constant
It is important to remember that $C_T$ value is, by definition, equal to the ratio $k_c/k_p; k_c$ and $k_p$ are, respectively, the rate constants of the chain transfer reaction and the propagation reaction. In consequence, a variation of the numerator or denominator directly modifies the transfer constant value.

Figure 3. Structures of ethylene glycol bi thioglycolate (EGBTG, 1), trimethylolpropane trimethylolpropane tris (2-mercaptoacetate) (TMPTMA, 2) and pentaerythritol tetrakis (3-mercaptopropionate) (PETTMP, 3).

Figure 4. Free radical telomerization of acrylic acid with EGBTG, TMPTMA and PETTMP in THF at 65°C. Plot of $\ln \frac{[T]}{[T]_0}$ versus $\ln \frac{[M]}{[M]_0}$ for each telogen.
Several general observations can be deduced from the results of kinetic studies on aqueous polymerizations, carried out in detail by Dainton et al. and applied here. The monomers studied were usually of a type that exhibited solubility in both aqueous and non-aqueous solvents, allowing comparisons between solvent systems. The results obtained showed that these monomers had the ability to undergo polymerization to high molecular weight in aqueous media, the degree of polymerization obtained being substantially greater than was obtained in organic media. This is partly due to the fact that water possesses a chain transfer constant of virtually zero. In addition, other factors, such as the existence of polymer–water interactions, which produce a strongly bound hydration shell may help to protect the propagating radical centre and hinder termination. Moreover, the ability of water to have a significant effect on $D_N$ is found even in systems that are essentially non-aqueous but to which traces of water have been added.

Many studies have been performed on the effect of the solvent in free radical polymerization, Gal’Perina et al. studied this for the acrylic acid polymerization (see Table 2). As can be seen from their results, the $k_p/\sqrt{K_a}$ ratio was found to decrease in going from aqueous media to organic media in agreement with our previous work.

We have found it interesting to apply this phenomenon in order to study the effect of the solvent on the $C_T$ value during the telomerization of AA with a tetrafunctional transfer agent. Thus our work was centred on the study of AA telomerization with PETTMP in different solvents (THF, water, THF/water mixtures).

As before, we have investigated the radical telomerization of AA with PETTMP in a mixture of solvent (water/THF) in the presence of AIBN as initiator. For instance, Table 3 shows the changes of monomer and telogen concentration for the telomerization of AA with PETTMP using a water/THF mixture (80%, 20%, v/v) as solvent. As expected, these results show a similar consumption of monomer and telogen. This confirms our previous results and indicates that a $C_T$ value of one could be reached for the telomerization of AA with PETTMP by using a mixture of water/THF (80%, 20%, v/v) as solvent.

The decrease of $C_T$ value in this medium is clearly demonstrated in Fig 5 and Table 4. Both results confirm that water enhances acrylic acid polymerization. Thus, it is possible to synthesize well-defined star poly(acrylic acid) by telomerization of AA with PETTMP using a judicious mixture of solvents.

### Table 2. Ratio of propagation rate constant over square of termination rate constant ($k_p/\sqrt{K_a}$) for free radical polymerization of acrylic acid

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$T(°C)$</th>
<th>$k_p/\sqrt{K_a}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>WATER</td>
<td>29</td>
<td>2.02</td>
<td>38</td>
</tr>
<tr>
<td>Formamide</td>
<td>29</td>
<td>0.42</td>
<td>38</td>
</tr>
<tr>
<td>DMSO</td>
<td>29</td>
<td>0.11</td>
<td>38</td>
</tr>
<tr>
<td>THF</td>
<td>65</td>
<td>0.48</td>
<td>21</td>
</tr>
<tr>
<td>$f_{\text{water}} = 0.1$</td>
<td>65</td>
<td>0.54</td>
<td>21</td>
</tr>
<tr>
<td>$f_{\text{water}} = 0.3$, $f_{\text{THF}} = 0.7$</td>
<td>65</td>
<td>1.06</td>
<td>21</td>
</tr>
<tr>
<td>$f_{\text{water}} = 0.5$, $f_{\text{THF}} = 0.5$</td>
<td>65</td>
<td>1.56</td>
<td>21</td>
</tr>
<tr>
<td>$f_{\text{water}} = 0.8$, $f_{\text{THF}} = 0.2$</td>
<td>65</td>
<td>2.09</td>
<td>21</td>
</tr>
<tr>
<td>Water</td>
<td>65</td>
<td>2.48</td>
<td>21</td>
</tr>
</tbody>
</table>

### Table 3. Free radical telomerization of acrylic acid with PETTMP in water/THF mixture (80%, 20%, v/v) at 65°C

<table>
<thead>
<tr>
<th>$t$(min)</th>
<th>$[\text{AA}]_i/[\text{AA}]_o$</th>
<th>$[\text{PETTMP}]_i/[\text{PETTMP}]_o$</th>
<th>$\ln[\text{AA}]_i$</th>
<th>$\ln[\text{PETTMP}]_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>0.28</td>
<td>0.25</td>
<td>1.27</td>
<td>1.39</td>
</tr>
<tr>
<td>45</td>
<td>0.22</td>
<td>0.21</td>
<td>1.5</td>
<td>1.37</td>
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<tr>
<td>60</td>
<td>0.18</td>
<td>0.16</td>
<td>1.73</td>
<td>1.86</td>
</tr>
<tr>
<td>90</td>
<td>0.10</td>
<td>0.10</td>
<td>2.21</td>
<td>2.26</td>
</tr>
<tr>
<td>120</td>
<td>0.08</td>
<td>0.07</td>
<td>2.46</td>
<td>2.63</td>
</tr>
<tr>
<td>150</td>
<td>0.04</td>
<td>0.045</td>
<td>3.18</td>
<td>3.09</td>
</tr>
<tr>
<td>180</td>
<td>0.035</td>
<td>0.032</td>
<td>3.34</td>
<td>3.43</td>
</tr>
</tbody>
</table>

**CONCLUSION**

In the present work, a study of the kinetics of acrylic acid telomerization have shown that, in an organic solvent, the $C_T$ value is too high ($C_T \approx 7$) to synthesize a well-defined star polymer. However, by using water
as a co-solvent, the transfer constant presented a decrease from 7 in THF to a value of one, the ‘ideal’ case of telomerization, for a mixture of solvents water/THF (80%, 20%, v/v). Thus a thermal influence of water on the polymerization of acrylic acid kinetic was also demonstrated.

Finally, the results of this study indicate that telomerization could be an effective way to synthesize an acrylic acid star-shaped macromolecule.

REFERENCES