Polymer Bulletin 10, 157-161 (1983)

**Polymer Bulletin**

# Synthesis of Macromers of Vinylchloride and Vinylidene Chloride from Telomers

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## ABSTRACT

New macromers are prepared from monofunctional telomers of vinylidene chloride and vinylchloride obtained by redox catalysis or by means of radical initiators. Especially, model graft copolymers are obtained upon copolymerising these telomers with acrylic compounds.

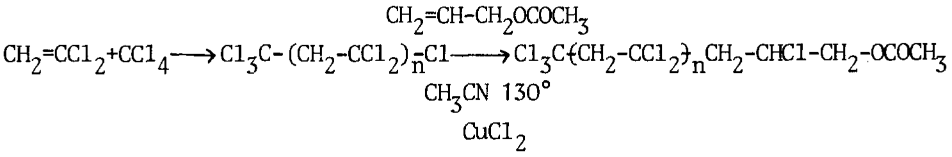
## INTRODUCTION

Recently, the synthesis of macromers has been developing fast, specially because macromers can be used to prepare graft copolymers with specific properties. Synthetic methods include the polymerization with cationic initiators (Kennedy, 1980 ; Sierra Vargas et al, 1980 ; Asami et al., 1980 ; Goethals, 1981) or by anionic deactivation (Milkovich, 1980) by selfcondensation of a monoadduct of divinylbenzene onto a substituted diamine (Tsuruta, 1980) or starting from a functional polymer upon which a polymerizable group is grafted (Graetz, 1980). The latter method consists in preparing the polymer chain by free radical polymerization in the presence of a difunctional (Yamashita et al., 1981) or of a monofunctional

(Thompson et al., 1968 ; Waite, 1971 ; Ito et al., 1980) transfer agent. Actually, this is a telomerization reaction similar to those we have studied : through telomerization involving redox catalysis we have obtained telomers of butadiene (Anthoine et al., 1978), chlorotrifluoroethylene (Battais et al., 1979), vinylchloride (Boutevin et al., 1982 a) and hydroxyethylacrylate (Boutevin et al., 1982 b), trichloracetic acid or its derivatives being used as telogens. We have obtained monofunctional oligomers, too, by bistelomerization from $CF_2{=}CFCl$ upon $CCl_4$, where upon the adduct was reacted with another monomer carrying an alcohol or an acid function (Boutevin et al., 1982 b) ; Boutevin et al., 1982 c). Finally, the telomer was functionalized by reacting it with oleum, whereupon the trichloromethyl end groups became to carboxylic acid functions (Boutevin et al., 1976). Until now, we had obtained macromers only in the latter case (Boutevin et al., 1982 d). The aim of the present work is to disclose the synthesis of macromers originating from the telomerization reaction of vinylidene chloride or vinyl chloride.

## RESULTS AND DISCUSSION

We have first prepared macromers of vinylidene chloride ($CV_2$). The reaction of $CV_2$ with carbon tetrachloride in boiling acetonitrile, in the presence of $CuCl_2$, gave telomer 1, the polymerization degree of which varies from 1 to 15 according to the conditions. Compound 1 was reacted afterwards with allyl acetate in the presence of $CuCl_2$ to yield telomer 2. The latter, once hydrolysed in methanol in the presence of $H_2SO_4$, gave alcohol 3. Thereafter the telomer is fitted with an end standing polymerizable unsaturation upon reaction with acrylic acid. Thus we got macromers of type 4 (n=1) from telomer 1 and 6 from telomer 5 (n=2).

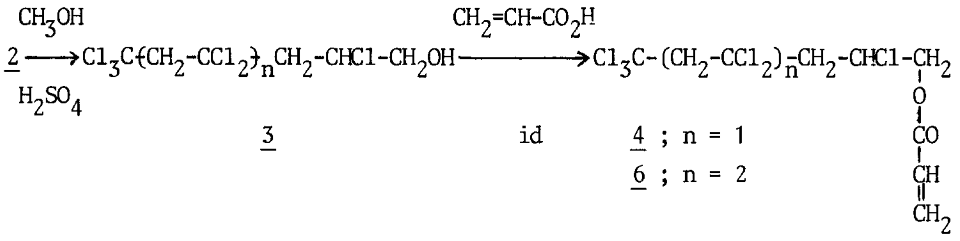


$$CH_2{=}CCl_2+CCl_4 \longrightarrow Cl_3C-(CH_2-CCl_2)_n-Cl \xrightarrow[CH_3CN\ 130^\circ,\ CuCl_2]{CH_2=CH-CH_2OCOCH_3} Cl_3C(CH_2-CCl_2)_nCH_2-CHCl-CH_2-OCOCH_3$$

1 ; n = 1

5 ; n = 2

2



$$\underline{2} \xrightarrow[H_2SO_4]{CH_3OH} Cl_3C(CH_2-CCl_2)_nCH_2-CHCl-CH_2OH \xrightarrow{CH_2=CH-CO_2H} Cl_3C-(CH_2-CCl_2)_n-CH_2-CHCl-CH_2-O-CO-CH=CH_2$$

3　　id　　4 ; n = 1　6 ; n = 2

In a second step, we have studied the macromers deriving from vinylchloride (CV). We have prepared monofunctional telomers of CV, to start with.

The telomerization of CV with $CCl_4$ by redox catalysis, gives compounds exhibiting the general formula : $Cl-(CHCl-CH_2)_n-CCl_3$, the first term of which (for n = 1) is compound 7. By acid hydrolysis the latter telomer does not give the expected saturated carboxylic acid, but rather a product resulting from its dehydrohalogenation, 8 $ClHC=CH-CO_2H$. We had therefore to introduce the end standing acid (or alcohol) function either by bistelomerization (as for $CV_2$) or by telomerizing the CV with compounds such as $Cl_3C-CO_2CH_2CH_2OH$, $Cl_3C-CH_2CHCl-CO_2H$ and $Cl_3C-CH_2-CHCl-CH_2CO_2H$ (Boutevin et al., 1982 e). However, these telomerization reactions are carried out with a redox catalyst, $FeCl_3$ that exhibits a rather high transfer constant (about 80) and the reaction yields only compounds with a low degree of polymerization. In order to obtain $10 < \overline{DP}_n < 50$ which would correspond to macromers for which $1000 < \overline{M}_n < 5000$ we have used thioglycolic acid and the corresponding alcohol as telogens. Free radical initiation was used, AIBN being the initiator. The transfer constants of the telogens used is close to one. The reaction was carried out in acetonitrile, at 65° C, for 16 hours. Results are shown in table 1.

The functional polymer chains 9 and 10 and compound 11 as well were reacted under suitable conditions with unsaturated compounds fitted with antagonist functions (acrylic or methacrylic chloride for OH terminated telomers, glycidyl methacrylate for COOH terminated telomers), to yield the corresponding macromers, carrying end standing (meth)acrylic ester functions. The products 12, 13, 14 and 15 are listed in table 2.

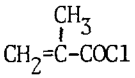
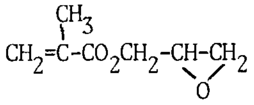
TABLE 1

Telomerization of vinylchloride with thiols

| Telogen | Mole ratio $\frac{\text{(Telogen)}}{\text{(Monomer)}}$ | $\overline{M}_n$ GPC | Compound |
|---|---|---|---|
| $HS-CH_2-CO_2H$ | 0,25 | 2 200 | 9 |
|  | 0,50 | 1 400 |  |
| $HS-CH_2-CH_2OH$ | 0,20 | 2 400 |  |
|  | 0,60 | 1 000 | 10 |

TABLE 2

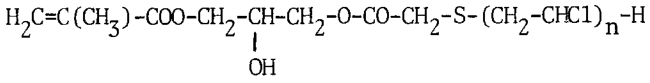
Macromers of vinylchloride

| Telomer | $CH_2=CHOCOCl$ |  $CH_2=\overset{CH_3}{C}-COCl$ |  $CH_2=\overset{CH_3}{C}-CO_2CH_2-CH-CH_2$ (epoxide, O) |
|---|---|---|---|
| Conditions of the reaction | In the THF at 0° C in the presence of pyridine |  | In the THF at 60° C with dimethyllaurylamine |
| 11 | 12 | 13 | - |
| 10 | - | 14 | - |
| 9 | - | - | 15 |

12 $H_2C=CH-O-CO-O-CH_2-CH_2-O-CO-CCl_2-(CH_2-CHCl)_n-Cl$

13 $H_2C=C(CH_3)-CO-O-CH_2-CH_2-O-CO-CCl_2-(CH_2-CHCl)_n-Cl$

14 $H_2C=C(CH_3)-COO-CH_2-CH_2-S-(CH_2-CHCl)_n-H$

15 

$H_2C=C(CH_3)-COO-CH_2-\underset{OH}{CH}-CH_2-O-CO-CH_2-S-(CH_2-CHCl)_n-H$

Macromers were characterized by G.P.C. for the measure of their molecular mass, by infrared spectroscopy to detect the insaturations and to check for the simultaneous disappearance of the initial acid or alcohol functions. Finally the macromers were copolymerized with standard monomers.

A detailed study of this work is presently being carried out and will be reported in a subsequent paper.

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*Accepted May 14, 1983*

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