THERMOLYSIS OF CHLORINE CONTAINING ACYCLATE POLYMERS (U) MASSACHUSETTS UNIV AMHERST DEPT OF POLYMER SCIENCE AND ENGINEER. V L RAO ET AL. JUN 87
OFFICE OF NAVAL RESEARCH
Contract N00014-86-K-0345
R&T Code 413C028
Technical Report No. 4

Resist Polymers IX.
Thermolysis of Chlorine Containing Acrylate Polymers

by

V.L. Rao, P.K. Dhal, G.N. Babu and James C.W. Cnien

Prepared for Publication
in the

Journal of Polymer Degradation and Stability

University of Massachusetts
Department of Polymer Science and Engineering
Amherst, MA 01003

June 1987

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited
Resist Polymers IX. Thermolysis of Chlorine Containing Acrylate Polymers

V.L. Rao, P.K. Dhal and G.N. Babu*
Polymer Research Laboratory,
Indian Institute of Technology,
Powai, Bombay 400 076, INDIA

and

James C.W. Chien,
Department of Polymer Science and Engineering,
University of Massachusetts,
Amherst, MA 01003

*Present Address: 3M Research Center
St. Paul, MN 55144
ABSTRACT

The thermal degradation of poly(chloroethyl methacrylate) (PCEMA), poly(trichloroethyl methacrylate) (PTCEMA), poly(methyl- α-chloroacrylate) (PMCA) and their copolymers with methyl methacrylate (MMA) have been investigated. Both ester decomposition and main chain scission occurs for the chloroalkyl methacrylate polymers with the former playing the dominant role. In contradistinction, HCl elimination and aromatization prevail over other processes for PMCA. The thermolysis results are compared with radiolysis results.
INTRODUCTION

Photolithography has been pushed to its limits by the ever increasing demand for higher sensitivity and contrast in the manufacturing of VLSI devices. Electron beam lithography looms as one of the techniques to pack more circuitry into a smaller area. This has renewed academic as well as practical interests in the radiation chemistry of resist polymers, in particular the role of chemical structures and steric configuration in affecting susceptibility toward radiolysis. Since poly(methyl methacrylate) is the industry standard for positive E-beam resists, there have been several extensive studies on the effect of substituents in acrylate polymers on the radiation sensitivity toward chain scission and crosslinking. Fluorine and chlorine containing substituents tend to increase scission yield by radiation as has been found for polymers and copolymers of methyl-α-chloroacrylate,\textsuperscript{1-3} methyl-α-fluoroacrylate,\textsuperscript{4} haloalkyl-α-chloroacrylate,\textsuperscript{5,6} and haloalkyl methacrylates.\textsuperscript{7}

Thermal degradation of a resist is as important as its radiation sensitivity. This is because there are several thermal treatments during the manufacturing of VLSI devices, and the requirement for thermal stability is increasing for higher temperatures. This makes it necessary to make parallel studies of a polymer resist candidate for both radiolysis and thermolysis processes. The results would also benefit the understanding of the mechanisms of degradation by heat and by radiation. In our
two previous papers, the thermolysis of fluoro and chloro methacrylates were reported. In this paper we present the results of thermal degradation of homopolymer and copolymers of α-chloroacrylate and comparison with previously published radiolysis results.

EXPERIMENTAL

The synthesis of 2-chloroethyl methacrylate (CEMA) 2,2,2-trichloroethyl methacrylate (TCEMA) and methyl-α-chloroacrylates and their polymerizations were as given previously. Thermal pyrolysis was determined by thermogravimetric analysis using a Perkin-Elmer thermobalance in N₂ atmosphere, and the pyrolysates identified by GC-MS.

RESULTS AND DISCUSSION

Poly(trichloroethyl methacrylate) (PCEMA). TGA curve of PCEMA (Figure 1) shows its weight loss to begin at 250°. At 265°, 307°, 327° and 348° the wt. losses are 10, 30, 50 and 70%, respectively. The maximum decomposition rate was found to be 314° and decomposition is complete at 445°. These thermal behaviors are reproducible except the onset decomposition temperature is different for independently prepared samples of the same polymer possibly due to residual monomer and solvent.

Figure 2 is the pyrogram of PCEMA; the pyrolysis products identified by MS are summarized in Table I. The most abundant
non-chlorinated products are $\text{CO}_2$ and acetaldehyde. Among the chlorinated products are vinyl chloride, ethyl chloride and monomer (CEMA). The formation of vinyl chloride may be attributed to the decomposition of ester groups through a six membered ring intermediate involving $\beta$-hydrogen atoms,$^{11}$

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{C=O} \\
\text{CH}_2 & \quad \text{OH} \\
\text{H} & \quad \text{H} \\
\text{CH} & \quad \text{CH}_3 \\
\text{Br} & \quad \text{CO}_2
\end{align*}
\]

This process also produces $\text{CO}_2$. The concerted mechanism shown above might be promoted by the acidic $\beta$-hydrogen and is consistent with the thermolysis results of halopenated methacrylate polymers i.e. poly(2-bromoethyl methacrylate)$^9$ and poly(2-fluoroethyl methacrylate).$^8$

The production of monomer is accounted for on the basis of random scission of main chains followed by depolymerization.
The propagating radical I may undergo intra and intermolecular reactions resulting in the liberation of ethyl chloride as shown in equations 3 and 4,
Formation of chloroethyl radicals is favoured over chloromethyl radicals because of the stability of the former.\textsuperscript{12}

Production of low concentration of acetaldehyde may result from either one of the following degradation mechanisms. Intra and intermolecular reactions shown in equations 3 and 4 may produce acetaldehyde. However, in order for the acetaldehyde to be formed from $\gamma$-lactone it involves the scission of three carbon-carbon bonds and acquisition of two hydrogen atoms which is deemed improbable. A more plausible source of acetaldehyde may be the chloroethyl radical produced by the intramolecular perception in equation 5.
This reaction sequence has been proposed for the pyrolysis of poly(2-fluoroethyl methacrylate).\(^8\)

**Methyl Methacrylate-chloroethyl Methacrylate Copolymers.** The pyrogram of poly(72 MMA-co-28 CEMA) is shown in Figure 3. The pyrolysis products of the copolymer are CO\(_2\), acetaldehyde, vinyl chloride and methyl methacrylate (Table II). The abundance of MMA monomer liberated is not unexpected considering that the copolymer contains large blocks of MMA interspersed with CEMA units. On the other hand, it is difficult to explain at this juncture why the CEMA monomer was not seen in the copolymer degradation which was found in the pyrolysis of PCEMA. The other pyrolysis products are the same for the homopolymer and copolymer.

The radiolysis of poly(13 MMA-co-87 CEMA) differs from the thermolysis of poly(78 MMA-co-22 CEMA) mainly in the production
of HCl and CH₃Cl by high energy radiation. Dissociative electron capture followed by hydrogen abstraction is undoubtedly the process leading to HCl. Similar phenomenon was observed for γ-irradiated poly(bromoethyl methacrylate), but not in the case of poly(fluoroethyl methacrylate) presumably due to the strong C-F bond. Radiolysis also produces ClCH₂⁻ radical to form CH₃Cl upon hydrogen abstraction. Both radiolysis and thermolysis of poly(MMA-co-CEMA) produces CO₂, propene and ethyl chloride which implies ester decomposition occurs in both cases, but not necessarily through the same mechanism.

Poly(2,2,2-trichloroethyl methacrylate) (PTCEMA). TGA of PTCEMA showed two stages of weight loss (Fig. 4). The onset of decomposition was at 195⁰ followed by rapid decomposition until 225⁰, but slowed down between 225⁰ and 275⁰. The remaining material degraded rapidly above 275⁰. The initial stage of degradation was presumably due to dissociation of the bulky CCl₃ group which can account for 40% weight loss.

The pyrogram of PTCEMA is given in Figure 5 and the products of decomposition are summarized in Table III. The principal products are CO₂, propene, vinyl chloride and vinylidene chloride. The absence of monomer among the pyrolysates suggests that ester decomposition is an important pathway for the degradation, probably facilitated by the polar CCl₃ groups and stability of the Cl₃C⁻ radical. The molecular elimination of
vinyl chloride via a transition state proposed for PCEMA (eqn. 1) is not available to PTCMA which is devoid of β hydrogen. The actual amount of vinyl chloride found is very small (Figure 5); it is probably the result of secondary reactions.

The major pyrolysis product is vinylidene chloride. It is most likely to be produced by the elimination of the stable \( \text{CCl}_3\text{CH}_2\cdot \) radical facilitated by the electron withdrawing effect of the \( \text{CCl}_3 \) group.

Decarboxylation and subsequent processes can produce the other products.
A similar decomposition mechanism had been proposed for poly(trifluoroethyl methacrylate).\textsuperscript{8}

Though dichloroacetaldehyde was not found among the pyrolysates of PTCEMA, it was separated and identified in the thermal decomposition of TCEMA/MMA copolymer (\textit{vide infra}). This signals the following reaction course,

\begin{align*}
\text{propene} + \cdots \text{CH} = \text{C} \cdots + \cdots \text{C} \\
\text{CO}_2\text{CH}_2\text{CCl}_3 + \text{CO}_2\text{CH}_2\text{CCl}_3
\end{align*}

\begin{equation}
(7)
\end{equation}

It seems that chloral should be formed but not detected in the thermolysis of PTCEMA by a plausible mechanism.
We can only speculate that chloral may undergo C-Cl bond cleavage and the \( \cdot \text{CCl}_2\text{CHO} \) radical abstracts a hydrogen atom to provide a second possible source for the formation of dichloroacetaldehyde.

Irradiation of PTCEMA\(^7\) gave CO, CO\(_2\), HCl, CH\(_3\)Cl, chloroform and various other minor products. CO\(_2\) was the only product common to radiolysis and thermolysis. Whereas ester decomposition predominates in the latter, dissociative electron capture producing Cl\(\cdot\) and Cl\(_3\)C\(\cdot\) radicals seems to dominate in the former. Radiolysis apparently does not produce significant amounts of CCl\(_3\)CH\(_2\)\(\cdot\) radical which would have lead to vinylidene chloride according to eq. 6 but it was not found.

The pyrogram of poly(76 MMA-co-24 TCEMA) is illustrated in Figure 6; the pyrolysis products listed in Table IV. They are as one would expect, i.e. MMA plus the pyrolysates of TCEMA unit. In addition there was dichloroacetaldehyde formed as discussed above. The fact that it is not observed in the decomposition of the homopolymer may be attributed to the steric hindrance of the
CCl₃ group inhibiting the formation of cyclic transition states postulated in eqs. 9 and 10.

**Fig. 7 Poly(methyl-α-chloroacrylate).** The TGA curve (Figure 7) showed PMCA to be appreciably more stable than PCEMA or PTCEMA. Even though weight loss commences at 225° and degradation was relatively rapid initially, it slows down considerably 32% decomposition. At 265°, 295°, 360° and 420° the weight losses are 10, 30, 50 and 70%. About 20% of the polymer remained even at 475°. Since PMCA contains 34% of H + Cl, it appears that the initial thermolysis is the elimination of HCl. The residues not decomposed at 475° are carbonaceous char. If dehydrochlorinations convert the backbone carbon atoms to charry products, they would amount to 20% in agreement with the TGA data. Therefore the thermolysis processes for PMCA are distinctly different from the other two polymers with Cl in the pendant groups.

In order to find supporting evidences, PMCA was heated to 175° and IR spectra was obtained. A weak olefinic band at 1625 cm⁻¹ was found as expected. The formation of the first olefinic group is known¹³ to promote the further elimination of adjacent HCl as in the thermal decomposition of poly(vinyl chloride). One might anticipate similar processes of HBr elimination would be even easier for poly(methyl-α-bromoacrylate).¹⁴ That this was found not to be the case⁹ may be due to the fact that dehydrochlorination is a chain reaction but dehydrobromination is
not. Apparently, the bromine atom is less reactive and prefers the reaction forming CH$_3$Br.

The pyrogram (Figure 8 and Table V) showed that CH$_3$Cl instead of HCl was one of the major products. This may be rationalized by the acidolysis of PMCA. An alternative explanation is that HCl reacts in the column and was not eluted and that CH$_3$Cl was instead formed by lactonization or crosslinking,

\[
\begin{align*}
\text{PMCA} & \xrightarrow{\text{acidolysis}} \text{CH}_2=\text{CH}_2 + \text{CH}_3\text{Cl} \\
\text{Cl} \quad \text{O} \quad \text{C} \quad \text{O} \\
\text{Cl} & \quad \text{C} = \text{O} \\
\text{Cl} & \quad \text{H}_2\text{C} = \text{C} = \text{H}_2
\end{align*}
\]

The fact that a lactone group was not found in the IR of degraded PMCA tends to favor the first explanation rather than the latter.

Production of monomer might have resulted from random scission of main chains. This is conceivable considering the high polarization of C-C main chain bond by the chlorine atom attached to one of the carbons. It is recalled that thermolysis
of PMBA did not yield any monomer.

The pyrogram of poly(62 MMA-co-38 MCA) (Figure 9) showed that it differs from that homopolymer of MCA (Figure 8) only in that MMA is produced instead of MCA (Table VI). However, because of the similarity in retention times of the two monomers, it is not easy to separate small amounts of MCA from MMA.

The products of radiolysis and pyrolysis data of PMCA suggests that a similar degradation mechanism is operative in both the processes. The principal difference is in the monomer formation. The chain terminal radical, which is believed to be involved in the unzipping process leading to monomer at the higher temperatures of thermal degradation, not not observed at ambient temperature in radiolysis. Any monomer produced can not diffuse away in the solid polymer and it may repolymerize because of the propagation-depropagation equilibrium

\[ P_n^* \rightarrow P_{n-1}^* + M^* \]  \hspace{1cm} (11)

Acknowledgement

This work was supported in part by a grant from the Office of Naval Research.
References


Figure Captions

Figure 1 TGA of PCEMA.

Figure 2 Pyrogram of PCEMA.

Figure 3 Pyrogram of poly(78 MMA-co-22 CEMA).

Figure 4 TGA of PTCEMA.

Figure 5 Pyrogram of PTCEMA.

Figure 6 Pyrogram of poly(76 MMA-co-24 TCEMA).

Figure 7 TGA of PMCA.

Figure 8 Pyrogram of PMCA.

Figure 9 Pyrogram of poly(62 MMA-co-38 MCA).
Table I. Pyrolysates of PCEMA

<table>
<thead>
<tr>
<th>Peak</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO₂</td>
</tr>
<tr>
<td>2</td>
<td>Propene</td>
</tr>
<tr>
<td>3</td>
<td>Vinyl Chloride + Acetaldehyde</td>
</tr>
<tr>
<td>4</td>
<td>Ethyl chloride</td>
</tr>
<tr>
<td>5</td>
<td>Unidentified</td>
</tr>
<tr>
<td>6</td>
<td>CEMA</td>
</tr>
</tbody>
</table>
Table II. Pyrolysates of Poly(78 MMA-co-22 CEMA)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>2</td>
<td>Propene</td>
</tr>
<tr>
<td>3</td>
<td>Vinyl chloride + Acetaldehyde</td>
</tr>
<tr>
<td>4</td>
<td>Ethyl chloride</td>
</tr>
<tr>
<td>5</td>
<td>MMA</td>
</tr>
</tbody>
</table>
Table III. Pyrolysates of PTCEMA

<table>
<thead>
<tr>
<th>Peak</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO₂</td>
</tr>
<tr>
<td>2</td>
<td>Propene</td>
</tr>
<tr>
<td>3</td>
<td>Vinyl chloride</td>
</tr>
<tr>
<td>4</td>
<td>Vinyldene chloride</td>
</tr>
<tr>
<td>5</td>
<td>Unidentified</td>
</tr>
<tr>
<td>Peak</td>
<td>Compounds</td>
</tr>
<tr>
<td>------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>1</td>
<td>CO₂</td>
</tr>
<tr>
<td>2</td>
<td>Propene</td>
</tr>
<tr>
<td>3</td>
<td>Vinyl chloride</td>
</tr>
<tr>
<td>4</td>
<td>Vinylidene chloride</td>
</tr>
<tr>
<td>5</td>
<td>Dichloroacetaldehyde</td>
</tr>
<tr>
<td>6</td>
<td>MMA</td>
</tr>
<tr>
<td>Peak</td>
<td>Compounds</td>
</tr>
<tr>
<td>------</td>
<td>----------------</td>
</tr>
<tr>
<td>1</td>
<td>CO₂</td>
</tr>
<tr>
<td>2</td>
<td>Propene</td>
</tr>
<tr>
<td>3</td>
<td>CH₃Cl</td>
</tr>
<tr>
<td>4</td>
<td>Monomer (MCA)</td>
</tr>
</tbody>
</table>
Table VI. Pyrolysates of Poly(62 MMA-co-38 MCA)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO₂</td>
</tr>
<tr>
<td>2</td>
<td>Propene</td>
</tr>
<tr>
<td>3</td>
<td>CH₃Cl</td>
</tr>
<tr>
<td>4</td>
<td>MMA</td>
</tr>
</tbody>
</table>