

PYROLYSIS GAS-CHROMATOGRAPHIC STUDIES OF HOMOPOLYMERS AND COPOLYMERS OF CHLOROTRIFLUOROETHYLENE WITH VINYLIDENE FLUORIDE AND METHYL METHACRYLATE

M. Rizvi¹, A. Munir², S. Zulfiqar¹ and M. Zulfiqar¹

¹Department of Chemistry, Quaid-i-Azam University, Islamabad

²Pakistan Atomic Energy Commission, Islamabad

Abstract

Homopolymers of chlorotrifluoroethylene (CTFE), vinylidene fluoride (VDF) and methyl methacrylate (MMA) and their copolymers were studied by PGC/IR with regard to the separation and identification of the degraded products and clarification of the degradation mechanism. Besides monomers, HCl, CO₂, C₂H₂, HF, C₅H₁₀O₂, C₃F₅Cl and dimers are the observed pyrolysis products. Mechanisms for different degradation reactions have also been studied.

Keywords: degradation reactions, polymers, pyrolysis gas chromatography

Introduction

For the development of a heat-stable and chemical-resistant polymer, it is desirable to have detailed information on the degradation reactions and on the mechanism of these reactions. Thermal degradation techniques are among the oldest approaches for the study of the structure and degradation patterns of polymers [1]. PGC can be put to excellent use in the structural analysis of the thermal degradation products of different polymers [2-4]. The complexity of many polymeric systems favours the use of pyrolytic methods for the analysis of polymers. The thermal decomposition is quick and easy to perform, and the products provide a good guide to the identity of the polymers.

Fluoro and chlorofluoro polymers have the potential to withstand a variety of stringent conditions because of their high thermal stability and excellent chemical resistivity. The homopolymer of CTFE is insoluble in common solvents and is amorphous, while PMMA has lesser thermal stability and low chemical resistivity. The copolymerization of CTFE monomer with vinylidene fluoride or methyl methacrylate improves the physico-chemical properties to a great extent [5]. In the present investigation, homopolymers of CTFE, VDF, MMA and two copolymers each of CTFE-VDF and CTFE-MMA have been studied by means of PGC/IR techniques, following the usual procedures, to elucidate the degradation reactions and mechanisms.

Experimental

The polymerization procedures for the synthesis of homopolymers and different copolymer compositions, i.e. 30:1 and 1:4 for CTFE:VDF and 12:1 and 1:4 for CTFE:MMA, have been reported elsewhere [6].

Table 1 Operating conditions and characteristics

Column operating conditions	
Carrier gas	Helium
Flow rate	25 ml min ⁻¹
Column packing	Silicon OV-17 2% Uniport HP 60/80
Oven temp.	40°C
Detector	TCD
Injection temperature	150°C
Detector temperature	150°C

The PGC studies were carried out on a Hitachi 63-80 gas-chromatograph equipped with a Hitachi KP-1 pyrolyser. A series of columns were tested to achieve the maximum resolution of the degraded products. It was found that the OV-17 column gave the best results in general. However, the first peak, which consisted of gaseous products, could not be resolved with this column and hence it was separated with the help of a Porapak S column. Other parameters, such as column temperature, rate of flow of carrier gas, etc., were also optimized (Table 1). 1-2 mg polymer samples were pyrolysed for 20 s at 350, 500 and 700°C and then chromatographed. The relative peak area of each peak reflects the true relative concentration of that component. This was ascertained by calibrating the procedure with known standards. The products were also identified by comparison with the retention times of pure compounds under identical conditions. Since two different compounds can have the same retention time in GC, IR spectroscopy was used as the supporting technique for product identification. All the peaks were collected one by one in a specially designed micro-collector. This unit was fitted to the outlet of the thermal conductivity detector (TCD) of the GC instrument.

Results and discussion

Pyrolysis of PCTFE

Pyrograms of PCTFE at 350, 500 and 700°C are shown in Fig. 1(a-c). The pyrolysis of PCTFE at 350°C gives three products, identified as CTFE (monomer), SiF₄ and C₃F₅Cl. Similar results are obtained on degrading the CTFE polymer at 500°C. At 700°C, only CTFE and SiF₄ are found. This can be ex-

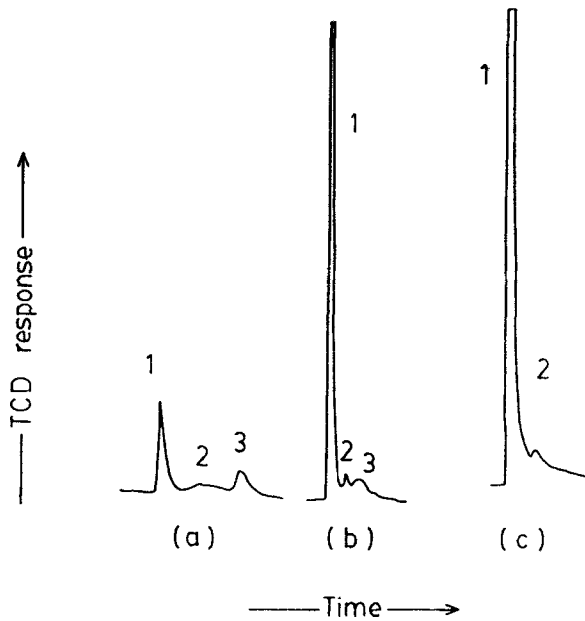
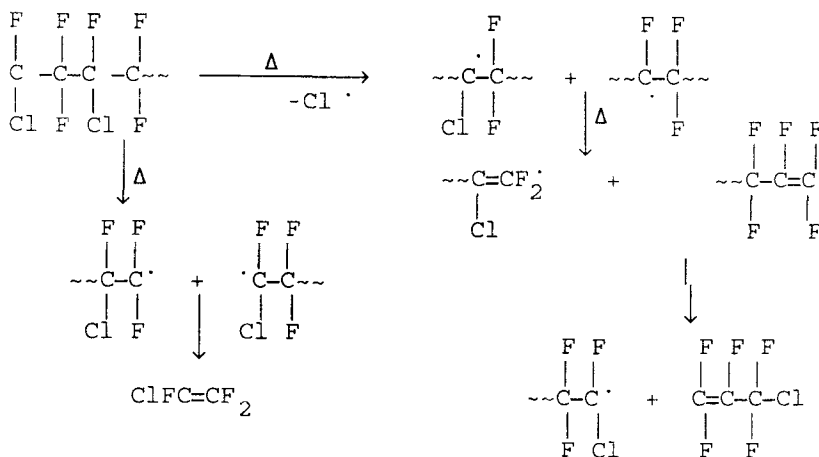


Fig. 1 Pyrograms of PCTFE at (a) 350°C; (b) 500°C and (c) 700°C

plained by the fact that, at higher temperature, the conditions are very drastic and thus the thermal energy required for bond dissociation can easily be acquired from the surroundings. Hence, degradation via chain unzipping is the most favoured reaction, resulting in the formation of monomer. This is supported by the presence of a higher concentration (99.59%) of CTFE monomer during pyrolysis. A plausible mechanism for the degradation reaction is depicted in Scheme 1.



Early removal of Cl radical initiates the reaction at low temperatures. At higher temperature, main chain scission takes place, leading to the formation of monomer.

In the IR spectra, the products show the absorption characteristics of CTFE (1797, 1341, 1220, 1062, 690 and 545 cm^{-1}), SiF_4 (1020 cm^{-1}) and $\text{C}_3\text{F}_5\text{Cl}$ (1176, 854, 1780, 1334, 1220, 1075 and 935 cm^{-1}) [6]. $\text{C}_3\text{F}_5\text{Cl}$, which is formed by Cl atom attack, is observed only at 350 and 500°C. SiF_4 is believed to be formed by the reaction of fluoro polymers with glass [7].

Pyrolysis of PVDF

Figure 2(a-c) shows pyrolysis curves of PVDF. In this case, the first peak is further separated by a Porapak S column. Two peaks are observed, which are identified as CO_2 (2300 cm^{-1}) and SiF_4 (1020 cm^{-1}). The second peak has two triplets, at 1600 and 800 cm^{-1} , indicating the presence of VDF monomer (1740, 1626–1600, 1316, 1292, 940 and 818–748 cm^{-1}). It is further observed that the formation of VDF monomer is higher at a low temperature of pyrolysis. This may be due to the fact that at higher temperatures a different degradation reaction, leading to HF formation predominates. The third peak is due to the formation of a dimer of VDF. The fourth peak at 350°C and the third peak at 500 and 700°C have not been identified.

HF is the most favoured degradation products, as observed by the higher amounts of SiF_4 . HF formation further leads to the introduction of unsaturation

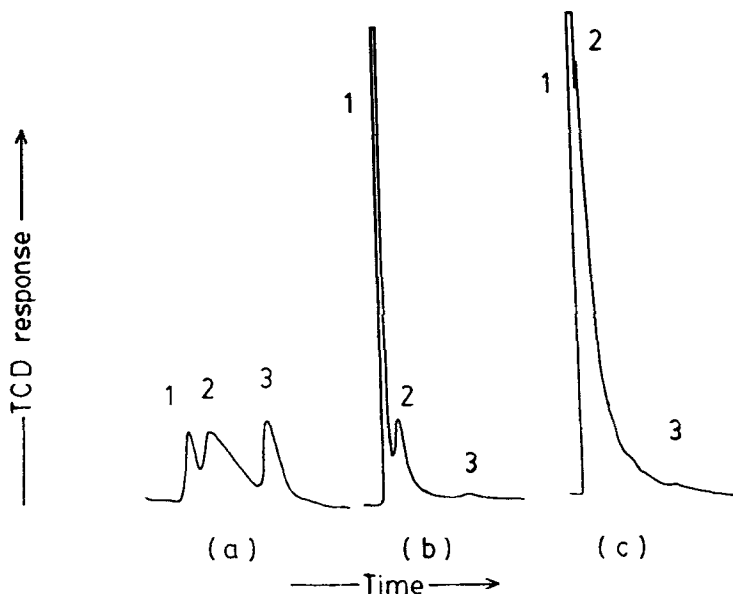
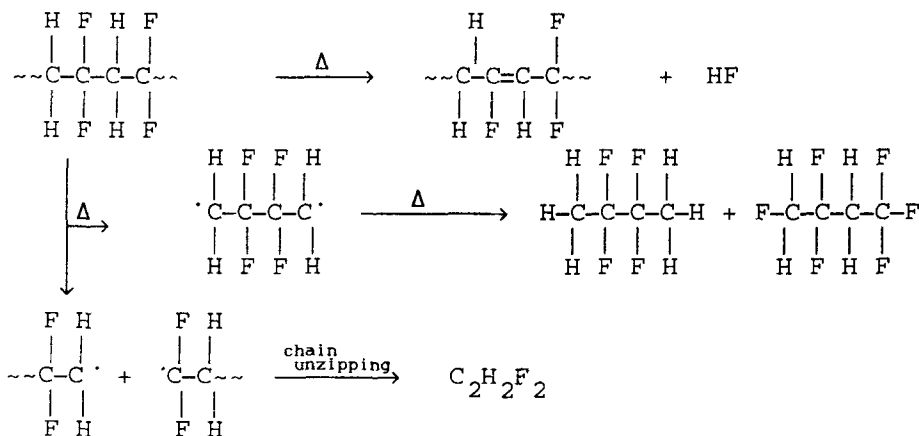


Fig. 2 Pyrograms of PVDF at (a) 350°C; (b) 500°C and (c) 700°C

in the polymer backbone. Hydrogen abstraction or rearrangement gives rise to the dimer. As a result of backbone homolysis, the VDF monomer is formed.



Pyrolysis of PMMA

The results of degradation of PMMA are shown in Fig. 3(a-c). The pyrolysis of PMMA at 350°C gives three peaks. On further separation of the first

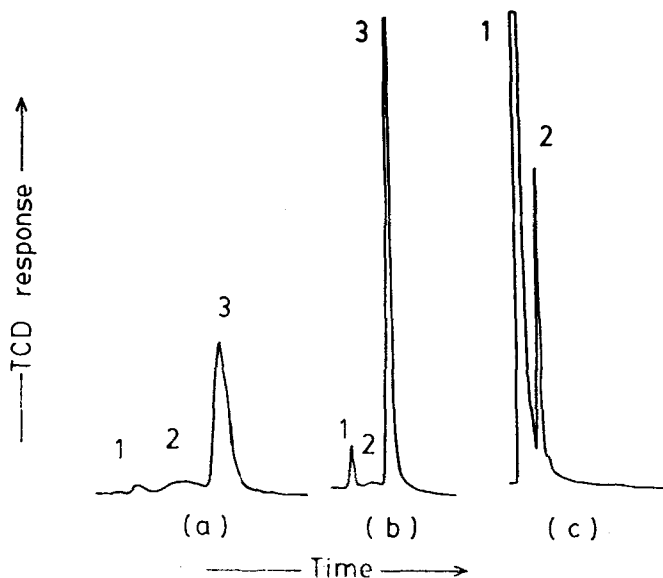
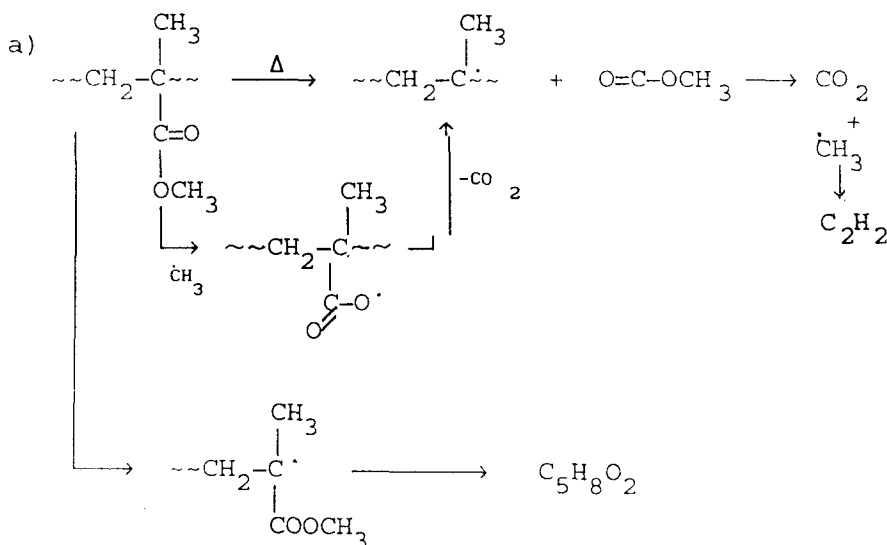
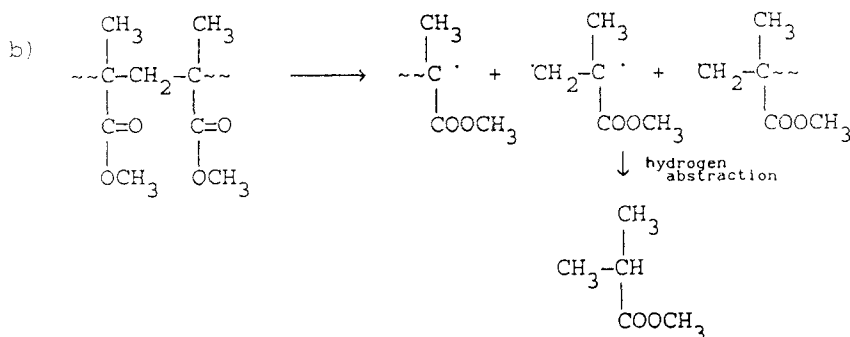


Fig. 3 Pyrograms of PMMA at (a) 350°C; (b) 500°C and (c) 700°C

peak on a Porapak S column, CO_2 (2300 cm^{-1}) and C_2H_2 ($3010, 2990, 1750, 1380, 1220$ and 750 cm^{-1}) are observed. The second peak is identified as $\text{C}_5\text{H}_{10}\text{O}_2$, with IR absorptions found at $2990, 2900, 1750, 1470, 1350, 1280\text{--}1090, 1000, 900, 820$ and 750 cm^{-1} . The third peak consists mainly of monomer, i.e. $\text{C}_5\text{H}_8\text{O}_2$ ($2990, 2900, 1720, 1620, 1450, 1320, 1220, 1000, 810, 650$ and 325 cm^{-1}). The gaseous mixture of CO_2 and C_2H_2 is formed from the fragmentation of MMA units. This fact is supported by the higher percentages of these products as the degradation temperature is increased. Chain unzipping, either by initiation from the disproportionate chain end or by main chain scission, contributes to monomer formation [9]. Intermolecular rearrangement and hydrogen abstraction gives methyl isobutyrate (Scheme 3). At 500°C , similar results are obtained, with the indication of higher rates of fragmented products. This trend reaches its maximum at 700°C . Only two peaks are observed. The first peak, with $>91\%$ concentration, comprises gaseous products such as CO_2 and C_2H_2 . The second peak is that of MMA monomer.

The mechanism of PMMA degradation shows similar trends to those reported in previous studies [8]. Part (a) of Scheme 3 shows the most plausible route for the fragmentation of MMA. Formation of CO_2 takes place by the removal of COOCH_3 radical. The CH_3 radical may take part in the formation of C_2H_2 by reaction with other methyl radicals. Monomer formation involves the established route of chain unzipping, initiated either from the unsaturated chain ends or by the random chain scission of polymer backbone [9]. Formation of methyl isobutyrate is depicted in part (b).





Pyrolysis of copolymer of CTFE-VDF

The pyrolysis of the 30:1 and 1:4 CTFE-VDF compositions at 350, 500 and 700°C gives higher amounts of gaseous products. For the copolymers, the first peak increases as the temperature is raised from 350 to 700°C. This peak is separated by the Porapak S column into five peaks, as shown in Fig. 4(a). HCl (3020–2800 cm^{-1}), CO_2 , CTFE, SiF_4 and VDF are identified. The second peak for the composition 30:1 is due to the formation of $\text{C}_3\text{F}_5\text{Cl}$ [6], whereas for the composition 1:4 the second peak is due to VDF monomer. The concentration of this peak decreases markedly as the pyrolysis temperature is increased. It is further observed that the amount of SiF_4 increases as the composition of the copolymer is changed from a CTFE-VDF ratio of 30:1 to 1:4. This indicates that HF formation is facilitated and the reaction with glass is favoured. We were unable to identify the third peak. The simplest route to monomer formation is via chain cleavage by homolysis. HF and HCl are produced as a result of new bond formation between neighbouring hydrogen with either fluorine or chlorine atoms.

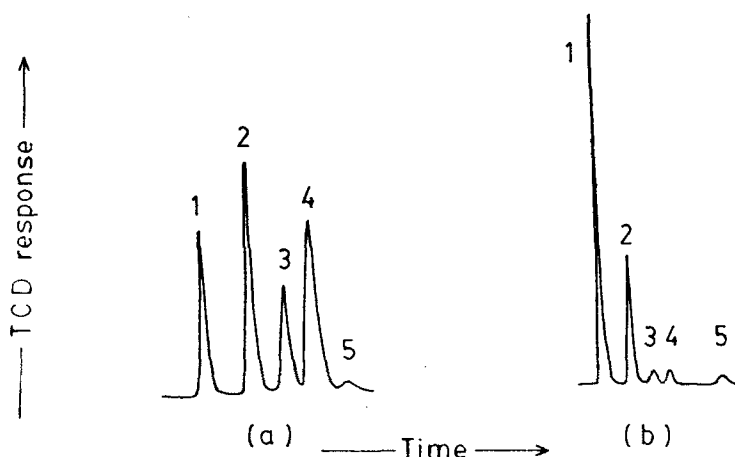


Fig. 4 Pyrograms of first peak separated by Porapak S, (a) CTFE-VDF, (b) CTFE-MMA

Pyrolysis of copolymers of CTFE–MMA

Copolymers with CTFE–MMA ratios of 12:1 and 1:4 were used for pyrolysis studies at different temperatures. For the copolymer composition 12:1, the first peak is identified as a mixture of HCl, CO₂, C₂H₂ and CTFE monomer, as resolved by the Porapak S column, illustrated in Fig. 4(b). A small amount of SiF₄ is also detected as part of the first peak. The second peak is due to methyl isobutyrate. The third peak is that of MMA monomer. A major increase in concentration of such fragmented products of MMA as CO₂ and C₂H₂ on increase of the pyrolysis temperature indicates the effect of higher temperature. For the CTFE–MMA composition 1:4, higher amounts of MMA monomer are observed. The degradation reactions leading to different products are similar to those for the homopolymers.

Conclusions

PGC leads to the establishment of a plausible degradation reaction route. For both homopolymers and copolymers, it is shown that chain unzipping is the predominant mechanistic route of thermal degradation leading to the formation of greater amounts of monomer. The higher electronegativities of chlorofluoro units incorporated in the copolymer chain seem to promote the reaction of random scission of the polymer main chain.

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Zusammenfassung — Mittels PGC/IR wurden Homopolymere von Chlorotrifluorethylen (CTFE), Vinylidenfluorid (VDF) und Methylmethacrylat (MMA) und deren Kopolymere in Bezug auf die Trennung und Identifizierung der Abbauprodukte und auf die Klärung des Abbaumechanismus untersucht. Außer den Monomeren wurden HCl, CO₂, C₂H₂, HF, C₅H₁₀O₂, C₃F₃Cl und Dimere als Pyrolyseprodukte beobachtet. Mechanismen für verschiedene Abbaureaktionen wurden ebenfalls untersucht.