



## USE OF IONIZING RADIATION FOR THE STUDY OF THE STABILIZATION OF TETRAFLUOROETHYLENE

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### ABSTRACT

TFE is highly unstable. It can easily go through an explosive disproportionation reaction under polymerization. The present work proposes the use of ionizing radiation for the study of monomer stability by inducing the polymerization and disproportionation reactions. Radiation was used to promote the initiation of TFE polymerization with and without inhibitors. Inhibitors and TFE were irradiated by  $\gamma$ -rays from  $^{60}\text{Co}$ . Small explosions with polymerization were observed yielding oligomer and polymer plus byproducts. It was shown that the initiation was completely inhibited by the addition of 0.1% of  $\alpha$ -pinene, dipentene, terpinolene or its mixture 1:1:1. In conclusion, radiation is a safe, reliable and easily controllable method to study TFE stabilization.

### KEYWORDS

Irradiation, tetrafluoroethylene, explosion, stabilization, polymerization, disproportionation

### INTRODUCTION

Tetrafluoroethylene (TFE) is the monomer for the production of a family of fluorinated polymers, elastomers, inks and fine chemicals. The fluorinated polymers are a very important class of materials with improved thermal and chemical inert properties; however they are very expensive and they are used only when the performance in aggressive conditions is the key issue. The high price of fluorinated polymers comes mainly from the cost of the fluorine. However, as TFE is highly unstable, it undergoes polymerization easily through an explosive reaction; so the safety of TFE handling is of paramount importance for this industry, with its effect on the production costs. Moreover, the polymerization can occur even during monomer manufacture, plugging tubes, columns and reactors (Carlson, P.D.; Schmiegel, W., 1980). Early in the 60's, Tabata had introduced the radio-induced polymerization as more controllable process for PTFE production (Tabata, Y. et al 1967). Dietrich studied the TFE stabilization by the addition of compounds with ethylene, acetylene and aldehydes links. He showed that they could stabilize TFE for long term and the best results were achieved with terpenes, mostly with liquid TFE (Dietrich, M.A.; et al 1946). The present work studies the use of radiation to test the monomer stability by inducing the polymerization reactions.

### METHODOLOGY

TFE was produced at our group laboratories by pyrolysing chlorodifluoromethane in a Pt tube at 700 to 900°C. The pyrolysis products were purified by solvent extraction and fractional distillation. The purity was higher than 99.9% as checked by CG/DCT. Special care was taken for  $\text{O}_2$  removal by repeating TFE freezing and  $\text{O}_2$  purge in vacuum to perform stabilization tests and to store TFE at ambient temperature and pressure of 4 kgf/cm<sup>2</sup>. The tests were conducted using 2 polymerization reactors with 237mL and 74mL capacity, for gaseous and liquid TFE, respectively. The reactors were equipped with pressure and temperature transducers and rupture disk and safety valve for security. The

temperature and pressure were in the range of  $-78^{\circ}\text{C}$  to  $24^{\circ}\text{C}$  and 1 to  $47\text{kgf/cm}^2$ , respectively. The total doses were between 100 and  $800\text{kGy}$  and the pos-polymerisation time between 0 and 70 hr. After irradiation and pos-polymerization, the gaseous products were analyzed by CG/DCT and the PTFE was checked for crystallization enthalpy by DSC, using DSC-50 from Shimadzu. The number average molecular weight was calculated using the expression in eq. [1]. This equation relates the number average molecular weight with the crystallization enthalpy of the PTFE. Further details can be found in the group's previous paper (Moura *et al.*, 1997)

$$M_n = 2,1 \times 10^{10} \Delta H_c^{-5,16} \quad [1]$$

where:  $M_n$  = number average molecular weight of PTFE;  
 $\Delta H_c$  = crystallization enthalpy(cal/g)

### RESULTS AND DISCUSSION

Figure 1 shows the results of TFE pressure as a function of total dose for irradiation of pure gaseous TFE. The experiments showed that the TFE polymerization always occurred without terpenes, independently of total dose and time of post-polymerization. It also showed an induction period at the early stages of irradiation, followed by oscillation in the internal pressure of the reactor and finally a decrease of the pressure. The pressure decrease was higher at higher pressure, i.e., load density, as expected.

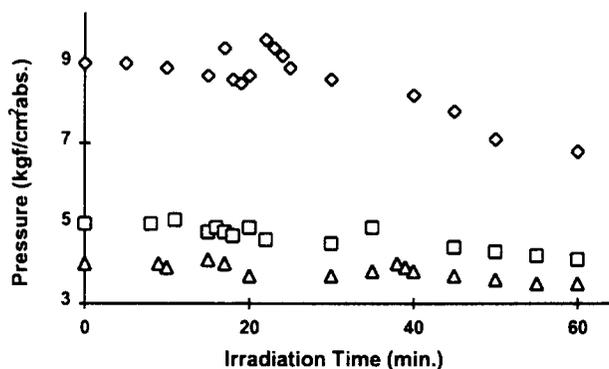


Figure 1. Internal pressure of pure TFE in gaseous phase as a function of irradiation time.

The radiation-induced polymerization of pure TFE in liquid phase showed an induction time, followed by the acceleration effect and some small explosions. The acceleration effect occurred for all tested temperatures during irradiation and pos-polymerization. Its intensity, measured as pressure increase per second, was higher at lower initial temperature, particularly, at  $-78^{\circ}\text{C}$  and  $-23^{\circ}\text{C}$ , as strong explosions occurred. Some experiments showed a very fast disproportionation reaction occurring with a violent explosion and destroying the rupture disk projected for bursting at  $50\text{kgf/cm}^2$ . Figure 2a, 2b and 2c show the acceleration effect and the speed of the TFE disproportionation reactions, resulting in violent explosions for TFE irradiated at load density of  $0.5\text{g/ml}$  and at initial temperatures of  $-76^{\circ}$ ,  $-64^{\circ}$  and  $21^{\circ}\text{C}$ .

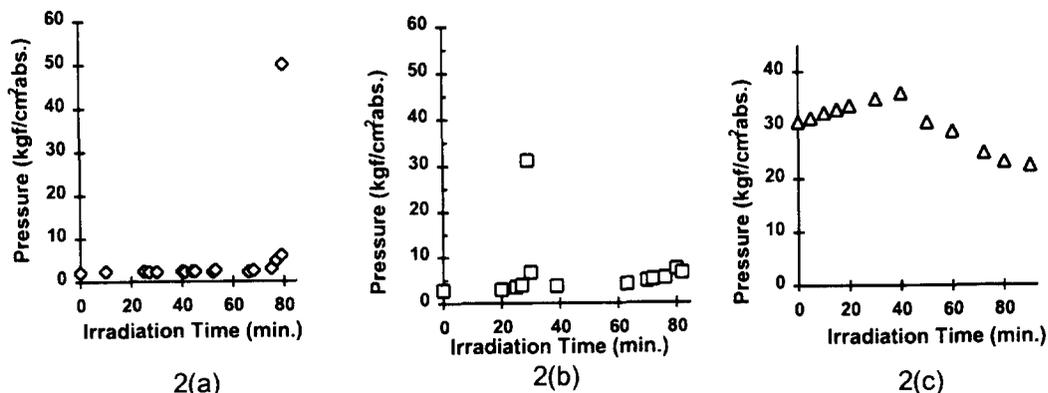


Figure 2. Acceleration effect and the speed of the TFE disproportionation reactions for TFE

From figure 2(a) and 2(b) for the reactions at  $-76^{\circ}$  and at  $-64^{\circ}\text{C}$ , respectively, it is possible to follow the remarkable acceleration effect for both and resulting in violent explosion at initial temperature of  $-76^{\circ}\text{C}$ . Nevertheless, figure 2(c) showed that the reaction at  $21^{\circ}\text{C}$  was easily controllable. This result was completely unexpected and can be explained by accepting that at  $21^{\circ}\text{C}$  the reactor had a much smaller amount of liquid phase. This small amount of liquid TFE was not enough to induce the acceleration effect. However, a more plausible explanation could be based on the initial solubility of TFE in PTFE before the formation of a hot spot, i.e., the initial bulk polymer formed is still relatively cold and under these circumstance a lot of TFE is soluble and is available for further reaction.

The samples of TFE with terpenes showed almost no change of temperature and pressure during irradiation and post-polymerization, for all tested terpenes even at 0.1% concentration. The behavior of TFE polymerization with 0.1% terpenes was showed in figure 3a, 3b, 3c and 3d.

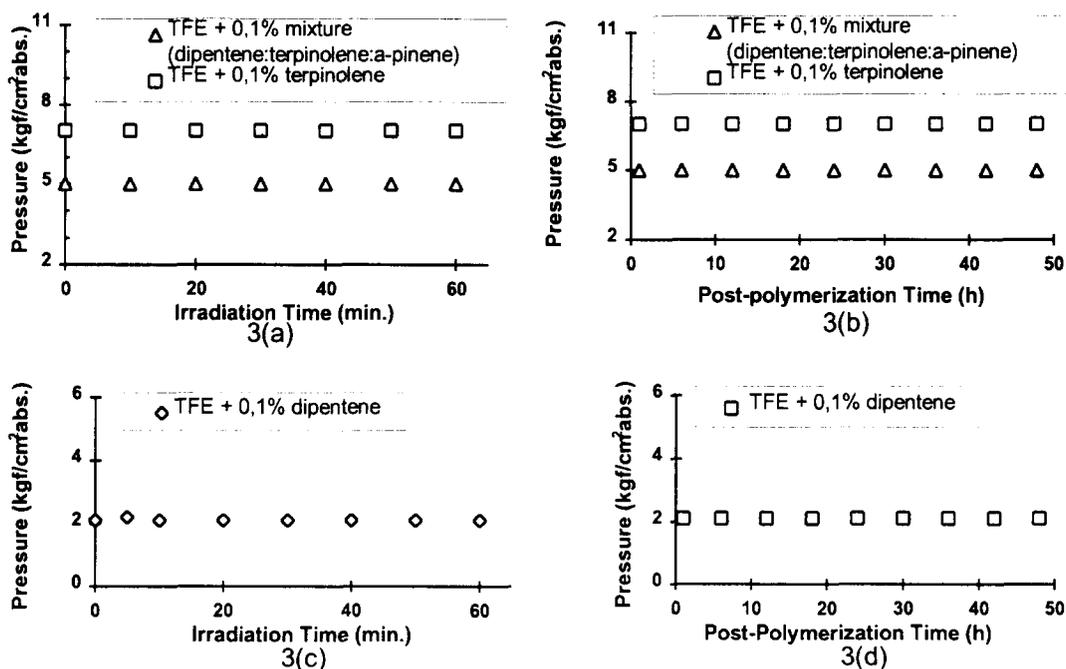
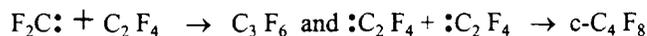


Figure 3. The behavior of TFE polymerization with 0.1% terpenes.

The gas chromatography analysis of the irradiated and non converted TFE without terpenes showed the yield of very low molecular weight products,  $C_3F_6$  and  $c-C_4F_8$ , from the following secondary reactions (the primary radiolysis species of TFE are  $F_2C\cdot$ ,  $\cdot C_2F_3$ ,  $\cdot C_2F_4$ ):



The CG analysis of the irradiated TFE with terpenes showed no changes in the chromatogram. The PTFE produced by the radiation-induced polymerization of pure TFE showed very low molecular weight, around  $10^5$  Da as calculated by crystallization enthalpy. However, some samples showed molecular weight of  $10^6$  Da, close to that of the commercial samples. The very low molecular weight was already expected as the reaction proceed always in very hot regions. The high molecular weight formed was surprising and was not explained so far. One explanation for the high molecular weight polymer could be the presence of small amounts of terpenes, resulting in some beneficial effect, for instance, reducing the termination rate, or even initiation during irradiation.

### CONCLUSION

The polymerization reaction of TFE was completely inhibited by the addition of 0,1% of  $\alpha$ -pinene, dipentene, terpinolene or its mixture 1:1:1. For the pure monomer, the polymerization reaction proceeded. The acceleration reaction step and small explosions with polymerization were observed yielding gaseous products, oligomer and polymer for samples of low temperatures. PTFE usually showed a low molecular weight of  $10^5$ , but for some samples reached  $10^6$ . The use of ionizing radiation showed itself as a safe, reliable, easily controllable method to study monomer stabilization in particular the TFE stabilization. However, under the experimental conditions, it was not possible to study the kinetics of the inhibition as the reaction was the type Yes/No. The high molecular weight produced was an indication that very small amounts of stabilizers can have a measurable effect in the polymer properties and so on the reaction kinetics. Further studies should be conducted in this subject.

### ACKNOWLEDGMENT

We thank Célia M. Napolitano, M.Sc from Institute for Energy and Nuclear Research - IPEN/CNEN-SP, for constructive criticisms of this paper. We are also grateful to Angela Regina Mattos de Castro for her continuous support and encouragement. This work was partially funded by the Navy Technology Center - CTM/SP.

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