INHIBITION OF THE TETRAFLUOROETHYLENE POLYMERIZATION REACTION

ESPERIDIANA A.B. DE MOURA, FELICITAS M. WIRKNER, ADEMAR B. LUGÃO; Comissão Nacional de Energia Nuclear CNEN/IPEN-SP, Cidade Universitária, Travessa R, nº 400, CEP:05508-900, São Paulo, Brazil

ABSTRACT

The polymerization of gas-phase tetrafluoroethylene (TFE) through gamma-irradiation induction of free radicals was inhibited by terpene hydrocarbons. The experiments demonstrated that inhibition was established by addition of as little as 0.1%(w/w) of terpinolene; in the absence of terpenes, formation of polymeric blocks took place, with occurrence of an induction-period and the acceleration phenomenon.

INTRODUCTION

Tetrafluoroethylene (TFE), an important monomer for the synthesis of polymers such as polytetrafluoroethylene and copolymers and the perfuoropolyethers of great industrial value, is a very unstable compound. TFE undergoes spontaneous polymerization through a higly exothermic reaction (ΔH=-41Kcal/mol)[1] with formation of polymeric blocks that obstruct ducts and valves, and is also capable of initiating the explosive disproprotionation reaction. Since TFE autopolymerization takes place via a free radical mechanism, it can be inhibited by addition of terpene hydrocarbons which act as radical scavengers.

The present study was undertaken to analyse the efficiency of dipentene, terpinolene and α-pinene as free-radical scavengers for inhibition of gas-phase TFE polymerization.

EXPERIMENTAL PROCEDURES

Tetrafluoroethylene monomer used produced at the CNEN/IPEN-SP laboratories. Polymerization assays were carried out in a stainless-steel reactor vessel (10 ml capacity) containing pressure and temperature sensor devices and a safety system. The polymerization reaction was induced by gamma-rays from a Co^{60} source.The scavenging efficiency of terpenes as investigated by comparing the outcome of polymerization with or without addition of these hydrocabons at initial pressures of 1-11 Kgf/cm^2abs and temperatures of 22-26°C, under a 108-448 Gy/hr dose rate; postpolymerization was carried out at room temperature.

RESULTS AND DISCUSSION

Figure 1 illustrates pressure variation as a function of time of irradiation. When the assays were carried out in the presence of 0.1% or 1.0% terpene (curves 2 and 4), the pressure remained constant thus demonstrating absence of a polymerization reaction. Conversely, when no terpene was added (curves 1, 3 and 5), an induction-period was observed, followed by an acceleration phase caused by the formation of "hot spots" and the gel effect.

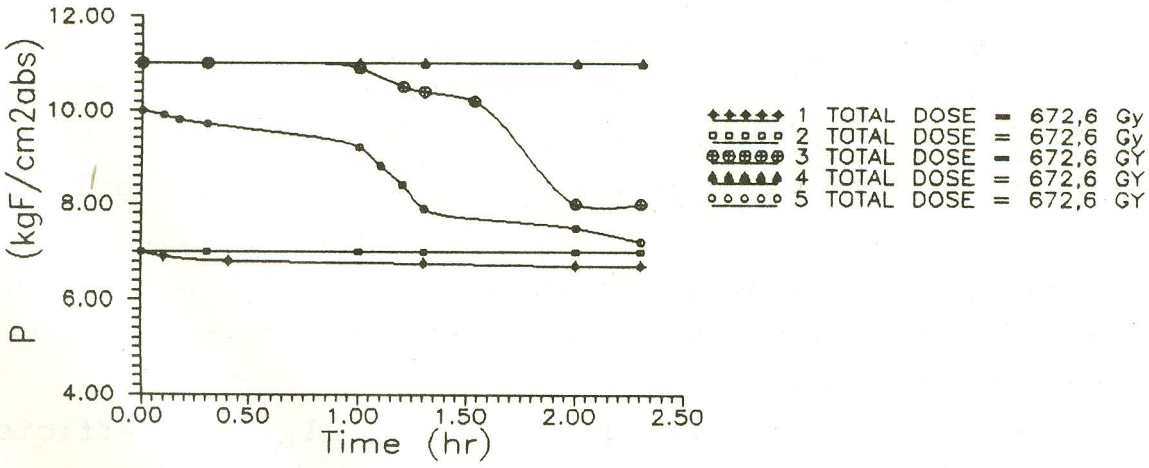

FIGURE 1

The data on efficieny of terpenes as inhibitors of gas-phase TFE polymerization are summarized in Table 1. Results show that, after a postpolymerization period of 66 hours, no conversion was detected for reactions run in the presence of the scavengers tested, for terpene concentrations ranging from as little as 0.1% to 1.0%. On the other hand, control reactions run without inhibitors reached high conversion values after much shorter postpolymerization periods, which varied depending on radiation dose.

TABLE 1

Pressure KgF/cm²abs	IR Temp. (°C)	Total dose(Gy)	Postpolym. Time (hr)	Terpene add. (%,w/w)	Conversion[a] (%)
4	24	544.0	23	---	20
4	26	544.0	66	0.1-1%Mixt.	---
4	26	544.0	66	0.1-1%Terpin	---
5	23	448.4	24	---	16
5	22	443.5	66	1.0%Terpin.	---
6	23	170.1	23	---	9
11	23	672.6	1.5	---	29.2
11	23	672.6	66	1.0%Terpin.	---

[a] %Conversion = $(P_o - P)/P_o$ X 100.[2]

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