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Graft Polymerization of a Polymer Matrix: Grafting of Tetrafluoroethylene

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ABSTRACT

Graft polymerization of tetrafluoroethylene on polyethylene preirradiated by γ-rays from a cobalt-60 source at -196°C has been investigated in the region of PE devitrification. A calorimetric technique made it possible to establish that 1.5-2% of monomer dissolves in the amorphous regions of PE at low temperatures. Efficient grafting proceeds in the temperature range directly adjoining the PE devitrification region. The graft copolymer yield amounts to ca. 1200%. The intensification of grafting is apparently caused by the following: (1) because of previous solution of TFE in the PE amorphous regions and filling of the micropores, the reaction in the initial stage is not limited by diffusion; (2) and the initiation efficiency is increased by slow passage through the PE devitrification region. The breaking strength of the graft copolymer is higher than that for the PE copolymer irradiated by the same dose.

INTRODUCTION

Polymerization of vinyl monomers proceeds at high rates and at low temperatures, provided it is initiated by γ-radiation of their glasslike solutions [1]. It has been shown in previous papers [2, 3] that on γ-irradiation of glasslike solutions of a number of vinyl monomers, active centers are formed in low molecular or polymer matrices. Then during slow warming of such a system, polymer chains arise in the region of its devitrification. After matrix transition from a glass to the supercooled liquid state one may observe intense polymerization which proceeds without termination of the polymer chains. Therefore, the low mobility of growing active centers in a viscous supercooled liquid prevents their termination. At the same time small monomer molecules move easily to the macroradical and the reaction is not limited. Such specific conditions provide the best polymerization.

When a polymer is used as the vitreous matrix in such systems, polymerization results in the formation of a graft copolymer in the process of devitrification [2]. In this case as well, grafting proceeds most effectively at the transition of the polymer matrix into a viscous-elastic state [2, 4].

Grafting of readily polymerizing monomers, such as tetrafluoroethylene (TFE), by the method of simultaneous irradiation has not yet been achieved, since the process of homopolymerization predominates. The grafting on the preirradiated polymers proceeds very poorly; for instance, it is possible to graft only ca. 3% of TFE on polyethylene [5]. It is possible to increase the yield of the TFE grafting on polyethylene (PE) only by employing a polymer with a rather developed surface (Takathene) and at lower temperatures [6].

In the present investigation we applied the method of postirradiation grafting after devitrification of the matrix to the PE-TFE system.

EXPERIMENTAL

A weighed amount of the PE powder was placed in a glass ampoule evacuated to ca. 10^{-3} Torr, and then a measured amount of dried, inhibitor-free TFE was added. The ampoule was sealed and maintained for about 24 hr at -60 to -40°C and irradiated at -196°C by γ-rays from a cobalt-60 source at a dose rate of 1-5 Mrad/hr. After irradiation the sample was slowly warmed (0.1-1°C/min) to room temperature. Graft polymerization occurred during the warming. After grafting, the unreacted monomer was purged by opening the ampoule, and the product was dried. The grafting yield was determined by weight gain. The homopolymer yield under such conditions does not exceed 2-3% [7].

Calorimetric measurements were obtained with a DSC calorimeter [8]. Calorimetric cells were prepared by the method described previously.

A low-pressure PE powder having a molecular weight of 1.4×10^5 was used. ESR measurements on the irradiated PE were carried out by means of the ESR-2 ICP spectrometer.

IR spectra were obtained for identification of the grafted polymer structure.

RESULTS AND DISCUSSION

A calorimetric analysis of the physical state of the system under investigation has been carried out. Pure TFE melts at -142° C, the specific heat of melting being 1.9 ± 0.1 kcal/mole.

After preparation, the ampoules were maintained for 24 hr at -60 to -40° C to ensure compatibility of PE with TFE. The pressure developed at these temperatures in sealed ampoules ($\geq$ 2 atm) favored the effective filling of PE pores with the monomer. Moreover, under these conditions TFE partially dissolves in PE, as one may judge by a decrease of the TFE melting heat. Since TFE dissolved in PE does not evolve into a separate phase at freezing, it is possible to determine the portion of the dissolved monomer to which the decrease of the melting heat pertains. Under these conditions, 1.5-2% of monomer is confined to PE.

According to calorimetric measurements, the glass transition of the amorphous regions of PE takes place in the range of -60 to -50° C.

Calorimetric experiments have been used to obtain the specific heat of the TFE graft polymerization in the temperature range -50 to -10° C; a value of 24 ± 2 kcal/mole was found.

Figure 1 presents the calorimetric curve of warming of the TFE-PE system after γ-irradiation at -196° C. Heat release caused by the post-irradiation grafting of TFE is recorded starting at ca. -47° C. The process of grafting is the most effective in the temperature range -40 to -30° C, i. e., after devitrification of PE is completed. Under the conditions of our experiment the grafting rate for a preirradiation dose of 10 Mrad at -35° C (see Fig. 2) is ca. 40%/hr, whereas, according to the data of Tabata et al. [6], for a preirradiation dose of 6 Mrad and subsequent grafting at -35° C on Takathene the reaction rate was

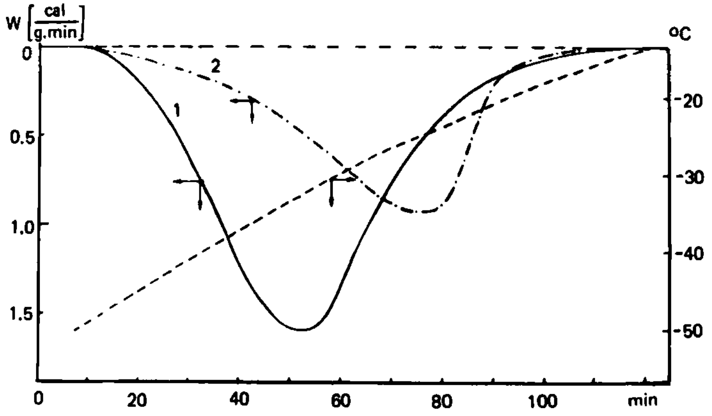

FIG. 1. Calorimetric measurements of TFE grafting rates (heat evolution) with warming of the γ-irradiated system. The preirradiation doses were (1) 10 Mrad and (2) 5 Mrad at -196° C.

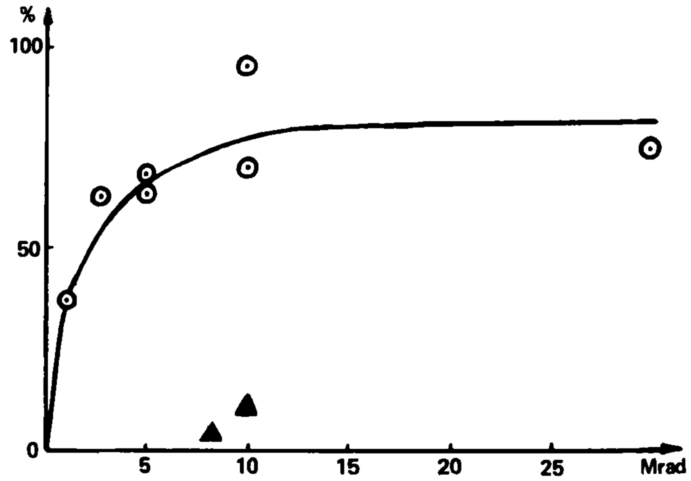

FIG. 2. Grafting as a function of the preirradiation dose during warming at a rate of 0.5° C/min with preirradiation at -196° C, dose rate 0.5 Mrad/hr: (▲) sample not conditioned in liquid TFE before irradiation; (○) preconditioned sample, initial ratio of PE/TFE = 1 (by weight).

small, reaching only 5.67%/hr. In our case high rates of grafting may be supposed to result from the fact that the monomer has been predissolved in the amorphous regions and the micropores filled with PE. Such close contact of the monomer with the substrate was not provided by Tabata [6].

This supposition was proved experimentally. The yield of the grafted polymer decreases sharply (see Fig. 2), if there is no increase in monomer pressure with increased temperature in the sealed ampoule, i. e., there is no close monomer-substrate contact.

With a decrease in the preirradiation dose the grafting rate decreases and reaches a maximum at higher temperatures (compare curves 1 and 2 in Fig. 1).

Figure 3 shows the dependence of the graft copolymer yield on the preirradiation dose at -196° C for an initial of PE/TFE ratio of 1 (by weight). The yield of the graft polymer increases with the preirradiation dose and reaches the limiting value (ca. 80%) at a dose of ca. 10 Mrad. Such termination of the reaction may be naturally explained by the consumption of the monomer (monomer conversion ca. 80%).

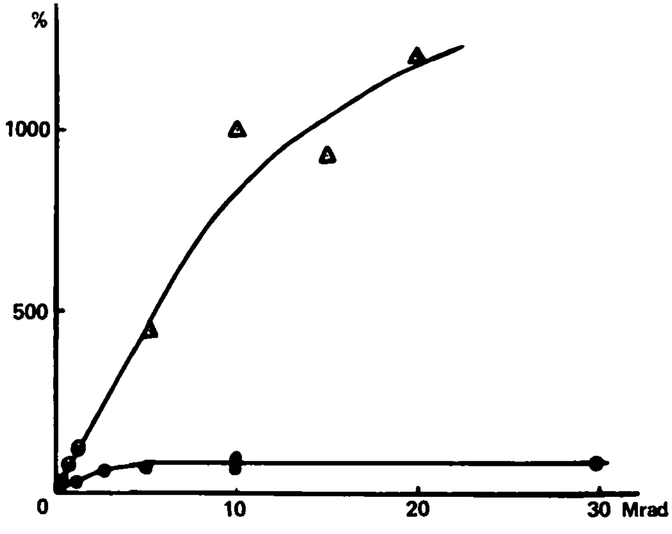

FIG. 3. Grafting with warming at a rate of 0.5°C/min as a function of the preirradiation dose: (●) PE/TFE = 1; (⊗) PE/TFE = 0.25; (▲) PE/TFE = 0.07. The preirradiation conditions were the same as in Fig. 2.

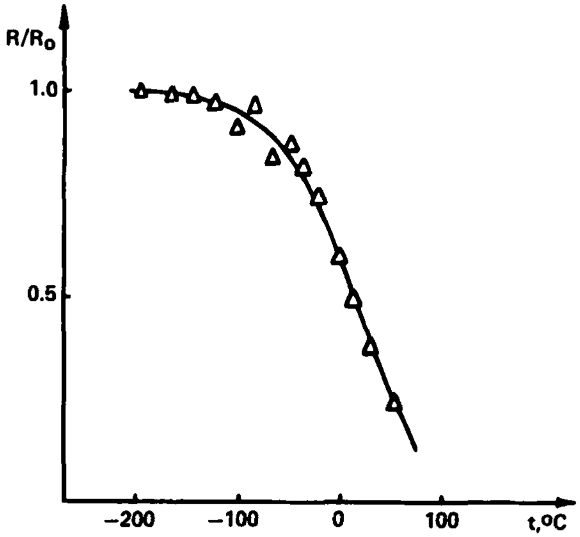

FIG. 4. Variation in relative concentrations of paramagnetic centers trapped in PE under irradiation. Irradiation dose, 10 Mrad at -196° C.

Figure 4 shows an analogous dependence of the graft copolymer yield on the dose, but for different initial PE/TFE ratios. It may be seen that at a PE/TFE ratio of 0.07 it becomes possible to achieve a graft copolymer yield of ca. 1200%.

It is essential to note that we may practically neglect the formation of a homopolymer under these conditions. In order to prove this, some experiments were carried out under similar conditions but without PE in the reaction mixture. The TFE homopolymer yield under these conditions did not exceed 2-5%. The formation of homopolymer by means of the chain transfer should be also excluded. It has been established experimentally that when even 350% of TFE is grafted on PE, we succeed in dissolving the sample in boiling xylene (content of the undissolved fraction in the sample = ca. 50%.

The ESR method has been used to determine the temperature region of the decay of radicals trapped in PE at -196° C. The decay of radicals was found to occur in the temperature range -80 to +20° C (see Fig. 4). It is in this region that the graft polymerization begins for our case. In the study of Tabata [6], just after introduction of the monomer the temperature of the reaction mixture increased to -35° C, at which temperature the grafting took place. In this case a greater number of radicals in PE disappear without initiating polymerization. The presence of the dissolved monomer in the PE amorphous regions and the slow rate of temperature rise over the whole temperature range allowed us to use the trapped active centers more efficiently and, consequently, to increase the graft copolymer yield. Moreover, the grafting rates increase with temperature, reaching a maximum at -30 to -25° C; thus, the reaction carried on with a regime of a slow warming appears to be more efficient than conditioning at -35°C [6].

We can estimate the average length of the graft chains of PTFE in our experiment. The radiation yield of the trapped active centers in PE is $G \simeq 4$ [9]. When it is assumed that most of these active centers concentrated in the PE amorphous regions participate in initiating polymerization, then for the system in which the graft yield is ca. 1200%, the initial ratio of PE/TFE is 0.07, and the preirradiation dose D is 20 Mrad, we obtain for the length of the grafted chain

$$\nu = QN/100MGD \simeq 1500$$

where N is Avogadro's number, M = 100 is the TFE molecular weight).

The IR spectra of the graft copolymer were obtained. In the copolymer spectrum, there arises an intense absorption band at 1120 cm^{-1}, as well as bands at 1160 and 1200 cm^{-1} which are absent in pure PE and are characteristic of PTFE and of the grafted copolymer [6].

As has been shown by physicomechanical tests, the graft copolymer possesses higher breaking strength than the initial PE irradiated to the same dose, less breaking extension, and higher density (see Table 1).

TABLE 1

No.	Sample	Preirradiation dose (Mrad)	Breaking strength (kg/mm^2)	Breaking extension (%)	Polymer density (g/cm^3)
1	Nongrafted PE	12	1.84	640	0.927
2	Grafted PE, 8% PTFE	12	2.39	460	0.977

CONCLUSIONS

The technique of postirradiation grafting on devitrification of the polymer matrix for grafting of TFE on PE allows one to carry out the reaction under most optimal conditions and to achieve the grafted copolymer yields of ca. 1200%. Such an intensification of the reaction is apparently due to the following: (1) preliminary solution of TFE in the amorphous regions of PE and filling of the micropores, and (2) an increase in the efficiency of initiation on slow heating of the system in the PE devitrification region.

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