

Grafting onto Polyester Fibers. II. Kinetics of Grafting of Acrylic Acid, Acrylonitrile, and Vinyl Acetate onto Polyester Fibers

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Synopsis

The kinetics of grafting of acrylonitrile, acrylic acid, and vinyl acetate onto polyester fiber by catalytic initiation and radiation were studied. The energy of activation determined for acrylic acid grafting by the catalytic method was 10.7 kcal/mole and that for vinyl acetate grafting by the radiation method, 11.7 kcal/mole. In the case of acrylonitrile grafting by the catalytic method, the rate of grafting decreased with increase in temperature of grafting, showing the differential behavior of the precipitating type of polymer from that of homogeneous polymerization.

INTRODUCTION

Vlagicu and Stannett¹ studied the kinetics of radiation-induced graft copolymerization of styrene onto poly(ethylene terephthalate) fibers and found the overall activation energy for grafting to be 13.7 kcal/mole. The reaction was carried out in the nonaqueous phase, and the presence of water in the reaction mixture was found to decrease the activation energy to a certain extent.

Sakurada and co-workers²⁻⁴ carried out radiation-induced graft copolymerization of poly(ethylene terephthalate) using methacrylic acid and acrylic acid as monomers and copper sulfate and Mohr salt as inhibitors. They found that in the presence of ethylene dichloride, the activation energy for acrylic acid was 8.0 kcal/mole in the temperature range of 18–40°C and 8.77 kcal/mole for methacrylic acid in the range of 15–20°C. In the absence of ethylene dichloride the activation energies were considerably higher.

Suzuki, Kido, and Katsuki⁵ reported 14.7 kcal/mole as activation energy for the graft copolymerization of poly(ethylene terephthalate) with glycidyl methacrylate using benzoyl peroxide as initiator.

In a previous communication,⁶ polyester-acrylic acid graft copolymer was described with respect to optimum conditions for grafting and the changes in the electrokinetic properties of the grafted polyester fiber.

The aim of the present paper is to report the kinetics of the grafting reaction onto polyester fiber using both radiation and chemical methods.

EXPERIMENTAL

Materials

The materials used and the method of grafting using benzoyl peroxide as catalyst for grafting of acrylonitrile and acrylic acid are the same as reported earlier.⁶

Grafting of Vinyl Acetate Onto Polyester by Radiation Method

For grafting of vinyl acetate onto polyester fibers, the fibers were preswollen in ethylene dichloride (100%) at 70°C for 1 to 2 hr. The swelling agent was removed by ether exchange and the fibers were dried at room temperature. About 1 to 1.5 g of this swollen polymer was soaked in 60 parts vinyl acetate and 40 parts methanol and *M*/50 scavenger to inhibit homopolymerization. This was placed in a tube, sealed, and kept for 18 hr at 75°C. The mixture was then irradiated as such with γ rays from a ⁶⁰Co source. After irradiation, the samples were tested for the presence of homopolymer by adding a small portion of it to water. The presence of homopolymer was indicated by the formation of a film. In case film was formed the grafted sample was washed with methanol several times, boiled in water, and then dried to constant weight. By varying time of irradiation, monomer concentration, total dose, etc., different amounts of poly(vinyl acetate) were grafted onto polyester.

Grafting by Chemical Method

The polyester fiber was swollen in a solvent-nonsolvent system consisting of 1,2-dichloroethane and water (20/80 v/v) at 90–95°C for 2 to 8 hr. Dichloroethane was then removed completely from the fiber by treatment with boiling water. This swollen fiber was then used for grafting, the method of grafting was similar to the procedure reported earlier.⁶

RESULTS AND DISCUSSION

Grafting of Acrylic Acid Onto Polyester Fibers

In Figure 1, the percentage of acrylic acid graft versus reaction time is shown; it is seen that saturation grafting is observed at all the three temperatures. Earlier, similar behavior had been noticed for the radiation method of grafting.⁶ This saturation phenomenon had been explained on the basis of the availability of the monomer in the swollen phase. However, in the chemical method, it is seen that the amount of saturation grafting decreases as the grafting temperature increases. In the chemical method of grafting using benzoyl peroxide as an initiator and in the absence of any scavenger to suppress the parasitic homopolymerization, there are two competitive processes taking place, i.e., homopolymerization and graft copolymerization. Though the initial rate of grafting increases with temperature, the saturation grafting decreases. This is presumably due to the decrease in the monomer concentration in the swollen phase, as the rate of consumption of the monomer due to homopolymerization is also higher at the higher temperature. In the chemical method of grafting the radical

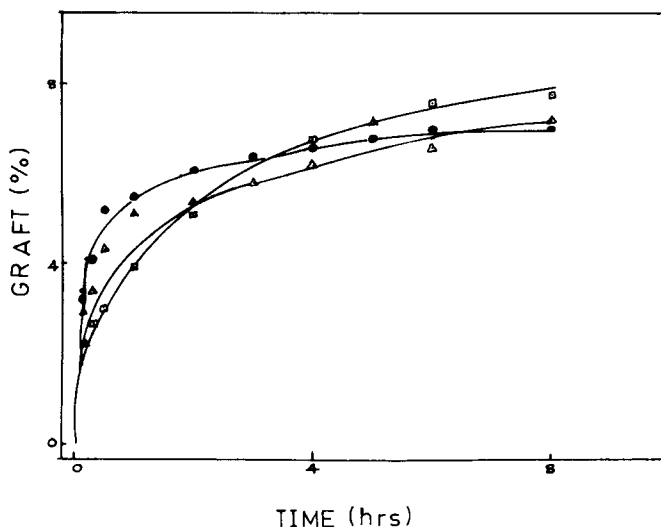


Fig. 1. Relation between graft % and time for grafting of acrylic acid on polyester at different temperatures: (●) 92°C; (▲) 81°C; (◻) 71°C.

responsible for graft copolymerization is generated either by the abstraction of a labile group or hydrogen from the backbone polymer or alternatively by chain transfer to the backbone polymer by the growing polymer from homopolymerization. The dose rate exponent determined in the case of grafting of acrylic acid onto polyester by the radiation method was ~ 0.5 , indicating that the termination is by reaction between two growing radicals.⁷

The energy of activation calculated from a plot of log rate of polymerization versus $1/T$ (Fig. 2) is ~ 10.7 kcal/mole. The energy of activation determined in the case of chemical grafting should take into account the following processes: (i) decomposition of the catalyst to give an initiating species; (ii) abstraction of a group or an atom from the backbone polymer to give an initiating species for graft copolymerization; (iii) propagation; and finally (iv) termination.

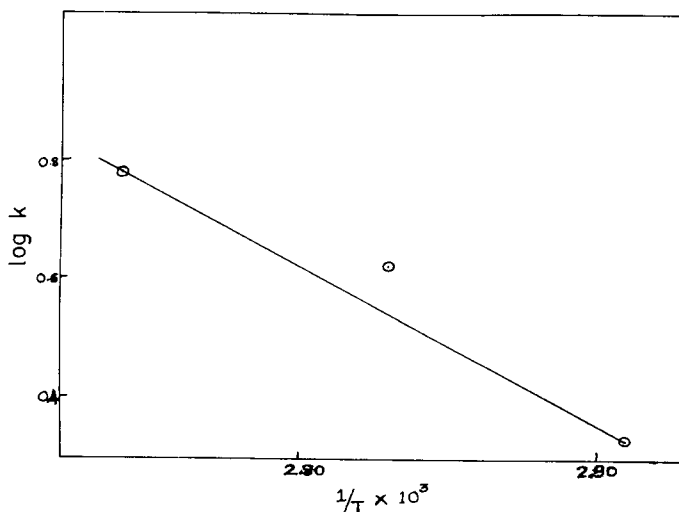


Fig. 2. Relation between $\log k$ vs $1/T$ for grafting of acrylic acid on polyester.

Assuming a normal kinetic scheme for grafting, the total energy of activation, E , for the process should be

$$E = E_d/2 + E_{tr}/2 + (E_p - E_t/2)$$

where E_d is the energy of activation for the decomposition of the catalyst; E_{tr} is the energy of activation for the abstraction reaction to generate an initiating species on the backbone polymer; E_p is the energy of activation for propagation; and E_t is the energy of activation for termination.

If all the energy parameters are taken into account, the energy of activation for the process could be computed as ~ 25 kcal/mole. However, the energy of activation determined appears to be less by $E_d/2$ (14.8 kcal/mole). This result clearly indicates that the initiating species obtained for grafting appears to be only the growing homopolymer, abstracting an hydrogen atom from the backbone polymer. It can be presumed that the radical produced from the decomposition of the catalyst would prefer to add onto the monomer rather than migrate to the backbone polymer and abstract an H atom from it. However, the energy of activation for overall grafting is comparable to the data obtained by Chapiro⁹ in the polyethylene system.

Grafting of Acrylonitrile Onto Polyester

In Figure 3, the percentage of acrylonitrile graft vs reaction time is shown and one could see that the initial rate of grafting of acrylonitrile decreases with the increase in temperature. In the polymerization of acrylonitrile the polymer precipitates out as the polymerization takes place, and as the temperature increases the amount of homopolymer formed also increases. The polymer swells in its own monomer, and hence the monomer available for grafting decreases as the temperature increases and hence the rate of grafting decreases.

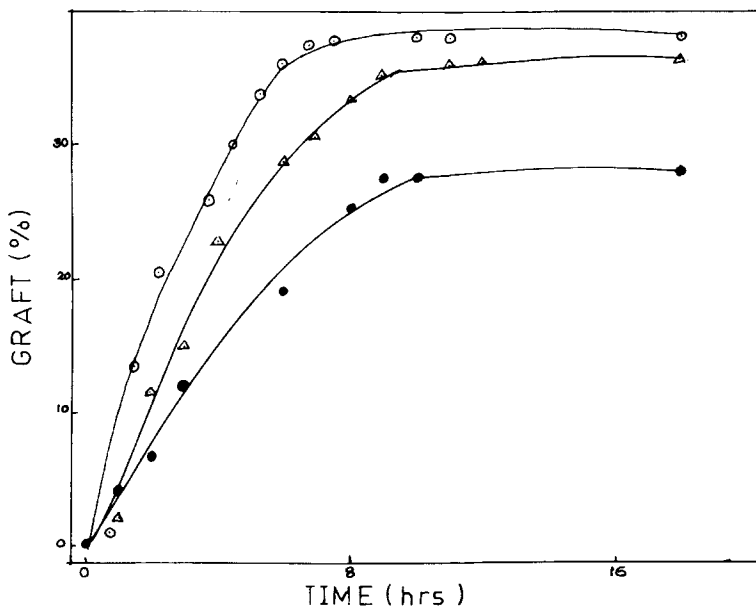


Fig. 3. Relation between graft % and time for grafting of acrylonitrile on polyester at different temperatures: (●) 96°C; (▲) 82°C; (○) 70°C.

Grafting of Vinyl Acetate Onto Polyester

Figure 4 shows the amount of grafting of vinyl acetate onto polyester at various temperatures. The results show that initially the rate is linear with time and thereafter it undergoes autoacceleration. From the initial rates of grafting the energy of activation calculated from the plot of log rate of polymerization versus $1/T$ (Fig. 5) is 11.7 kcal/mole. This is the same order of magnitude as is determined for conventional grafting. In the radiation method of grafting, the overall activation energy should be taken as equivalent to $E_{\text{diff}}/2 + (E_p - E_t/2)$, where the E_{diff} term is due to the diffusion of the monomer to the reactive site produced by radiation on the backbone polymer. In the homopolymerization of vinyl acetate, the energy of activation, $E_p - (E_t/2)$, is ~ 3.6 kcal/mole.⁸ The energy

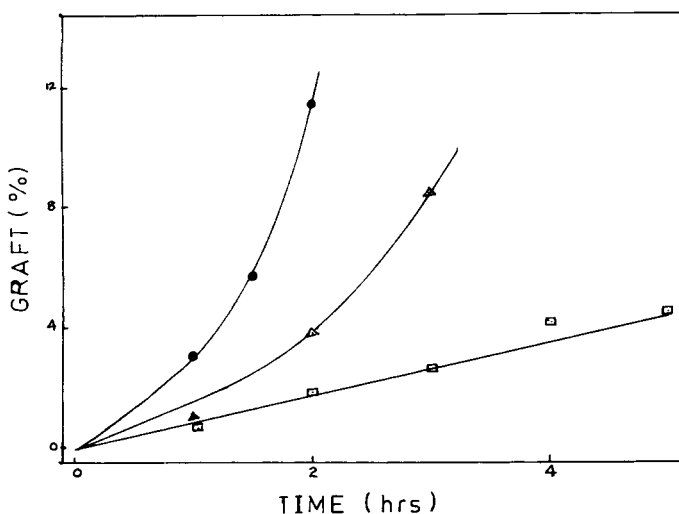


Fig. 4. Relation between graft % and time of irradiation of vinyl acetate on polyester at different temperatures: (●) 40°C; (▲) 30°C; (□) 20°C.

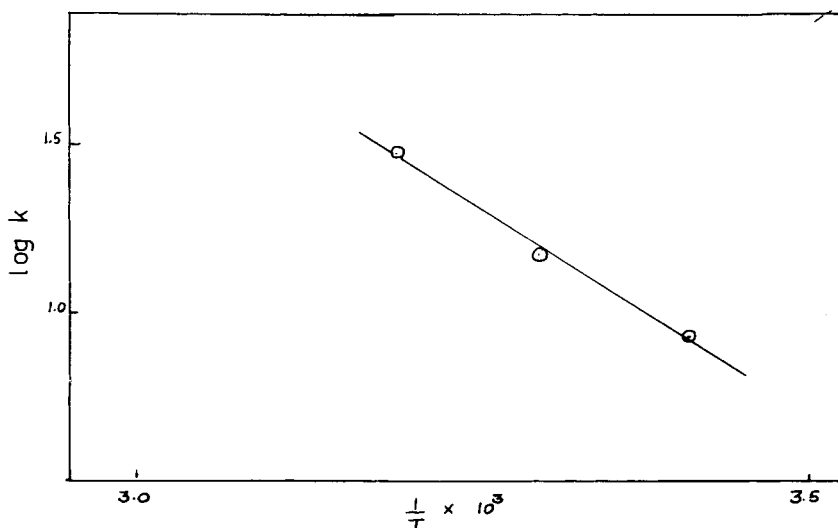


Fig. 5. Relation between $\log k$ vs $1/T$ for grafting of vinyl acetate on polyester.

of activation determined is ~ 8.1 kcal/mole more, and this is of the same order for the diffusion of the monomer into the crystalline regions of the backbone polymer.⁹

From Figure 4, one can see that there is an autoacceleration, and this can be explained only on the basis of chain transfer to the polymer, as is shown by Stannet et al.¹ on the grafting of styrene onto polyester. In conclusion, it can be said that the activation energy for grafting depends not only on the monomer used but also on the backbone polymer and its relation to the monomer.

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