

Chemically Induced Graft Copolymerization of Acrylic Acid onto Polyester Fabrics. I. Kinetic Investigation of Grafting

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Synopsis

The kinetics of grafting of acrylic acid onto poly(ethylene terephthalate) fabrics initiated by benzoyl peroxide has been studied. Extent of grafting depended upon time, concentration of the initiator and the monomer, as well as the presence of the activator used. From the temperature dependence of the initial rate of grafting the overall activation energy for grafting was found to be 90 kJ/mol. The results of the monomer and temperature dependence found in this study are consistent with the rate expression derived from a normal kinetic scheme for grafting.

INTRODUCTION

Certain desirable properties of poly(ethylene terephthalate) (PET) fibers such as dyeability, antistatic properties, and moisture regain can be improved by graft copolymerization with vinyl monomers¹⁻³ such as acrylic acid, acrylamide, etc. The reaction was mostly initiated by the irradiation methods.⁴⁻⁹ However, recently much more attention has been given to the chemical methods of initiation.⁹⁻¹⁵ Many of these studies have been devoted to the investigation of physicochemical properties of the grafted PET. Relatively little information, however, is available regarding the kinetics of grafting.

Suzuki et al.¹⁰ studied the kinetics of graft copolymerization of PET with glycidyl methacrylate using benzoyl peroxide as an initiator and reported 61.6 kJ/mol as activation energy for grafting. Some experimental results of the graft copolymerization of 2-methyl-5-vinylpyridine (MVP) onto PET with the use of benzoyl peroxide as an initiator were given by Shalaby et al.¹¹ The effect of initiator and monomer concentration and reaction time as well as the effect of temperature on the graft yield were investigated to discover the optimal conditions for grafting. Abdel-Fattah et al.¹² used the same monomer MVP and the initiator in aqueous medium for grafting onto polyester/wood-blended fabrics. However, the authors¹² conclusions concerning the kinetics of the process are of a qualitative nature.

Rao et al.¹³ studied the kinetics of acrylonitrile, acrylic acid, and vinyl acetate grafting onto polyester fiber by catalytic initiation and radiation. The energy of activation determined for acrylic acid grafting by the catalytic method was 44.8 kJ/mol and that for vinyl acetate grafting by the radiation method 49.0 kJ/mol. Sakurada and co-workers⁴⁻⁶ carried out radiation-induced graft copolymerization of PET using methacrylic acid and acrylic

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acid as monomers and copper sulfate in aqueous solutions as an inhibitor. The activation energy found for the process in the absence of ethylene dichloride was even as high as 94.7 kJ/mol.

This short literature survey on the kinetics of vinyl monomers grafting onto PET reveals that the knowledge of this subject is rather poor and new kinetic investigations of grafting should be undertaken in order to describe this very complex process in a more quantitative way.

EXPERIMENTAL

Materials

The fabric used in this study was woven from 100% polyester (PET) filaments (dtex 84, density 0.42 g/cm³, thickness 0.24 mm, silk type). The fabric was extracted with methanol to remove any material adhering to the surface. After washing for 20 min at 333 K the samples were rinsed with hot and cold water, followed by drying at 378 K for 2 h. Acrylic acid was freed from the inhibitors by vacuum distillation at 333 K. Benzoyl peroxide was laboratory grade.

Grafting Procedure

The graft copolymerization was carried out in the laboratory dyeing apparatus Linitest. The grafting procedure was patented¹⁶ and reported first at the 11th International Congress Intercolor 1977 in Budapest.¹⁷ The patent¹⁶ claimed the usage of an activator-swelling agent in the grafting bath. Out of many potential swelling agents, diphenyl was found to facilitate diffusion of both monomer and initiator into fabric. Its role has not been fully explained yet, however, without the use of diphenyl it was impossible to obtain an appropriate extent of grafting. Moreover, the addition of salts (e.g., NaCl) into the reaction mixture improves the extent of grafting. The details of the method of grafting are given elsewhere.¹⁸ The reaction was allowed to proceed for different periods of time. The reaction parameters were varied in the following ranges: the initial concentrations of monomer, initiator, and activator, 10–80 g/dm³, 0.5–4.0 g/dm³, and 0–10 g/dm³, respectively, and temperature 349–403 K.

Theoretical Background

Interest in studies of the kinetics of grafting has been low, perhaps because of the complexities of such systems. Hebeish and Guthrie¹⁹ have provided the basis for an understanding of the kinetics of the grafting reaction involving vinyl monomers. Assuming a normal kinetic scheme for grafting the rate of graft copolymerization is given by

$$r_p = k_p \left(\frac{r_i}{2k_t} \right)^{1/2} C_M \quad (1)$$

where r_p is the rate of grafting reaction, r_i is the initiation rate, k_p and k_t are the propagation and termination rate constants, respectively, and C_M is the

monomer concentration. Substituting the rate of initiation in Eq. (1) by

$$r_i = 2fk_iC_I \quad (2)$$

where f is the factor which represents the fraction of primary radicals which initiate chains (initiator efficiency), k_i is the reaction constant for this reaction, and C_I is the initiator concentration, gives

$$r_p = \frac{k_p k_i^{1/2} f^{1/2}}{k_t^{1/2}} C_I^{1/2} C_M \quad (3)$$

This equation reveals that the rate of build-up of copolymer is of the first order with respect to the monomer concentration but only of half order with the concentration of the initiator.

The changes in rate constants with temperature are given by the Arrhenius equation

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (4)$$

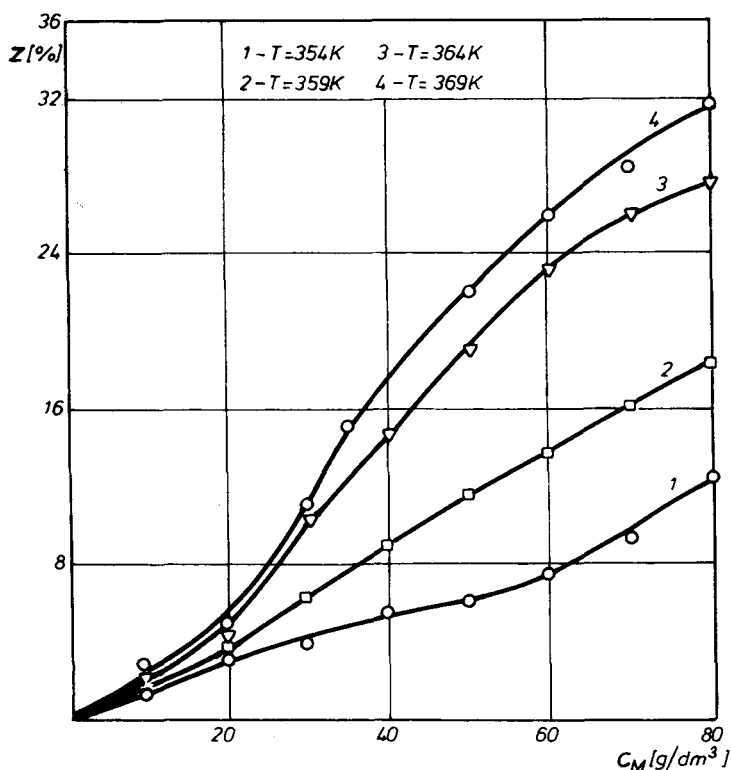


Fig. 1. Effect of monomer concentration on the graft yield. Reaction time 120 min, concentration of benzoyl peroxide 2 g/dm³, concentration of diphenyl 5 g/dm³, concentration of NaCl 36 g/dm³, material-to-liquor ratio 1:30.

where A is the collision frequency factor, E is the energy of activation, T is the absolute temperature, and R is the gas constant. All the rate constants from Eq. (3) obey Eq. (4), hence the overall activation energy may be written as

$$E = E_p + \frac{E_i - E_t}{2} \quad (5)$$

where E_p is the energy of activation for propagation, E_i is the activation energy of initiation, and E_t is the activation energy for termination.

Assuming that the initiation consists of two steps: decomposition of the initiator and generation of free radicals on the backbone polymer, the total energy of the activation for the process should be

$$E = E_p + \frac{E_d}{2} + \frac{E_g}{2} + \frac{E_t}{2} \quad (6)$$

where E_d is the energy of activation for the decomposition of the initiator and E_g is the activation energy for the abstraction reaction to generate an initiating species on the backbone polymer.

Discussion of the kinetics is confined here to homogeneous systems, but we have tried to extend this theoretical approach to heterogeneous conditions. It

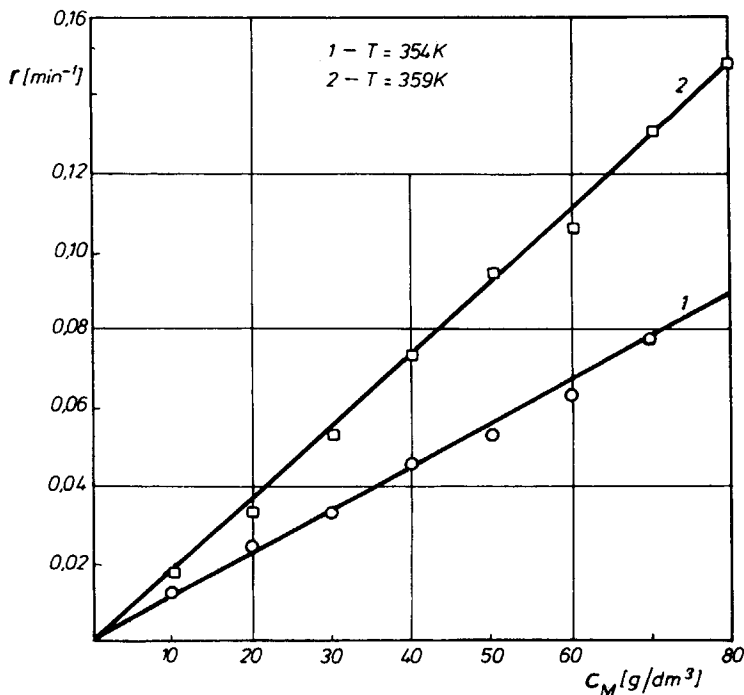


Fig. 2. Initial rate of grafting as a function of acrylic acid concentration. Material-to-liquor ratio 1 : 30, benzoyl peroxide concentration 2 g/dm³, diphenyl concentration 5 g/dm³, concentration of NaCl 36 g/dm³.

is sometimes the only way to describe the kinetics in such a complex system by a simplified kinetic model, regardless of the true mechanism of the reaction. Moreover, Hebeish and Guthrie¹⁹ claimed that grafting reaction is not usually diffusion controlled. This assumption is justified since equilibrium swelling is attained in all cases prior to the commencement of initiation.

It is important to note that the kinetic model represented by Eqs. (3)–(6) may be violated by real systems for reasons other than experimental problems associated with carrying out a copolymerization.

According to Rao et al.¹³ if all the energy parameters are taken into account, the energy of activation for the process could be computed as approximately 105 kJ/mol. However, the activation energy for grafting 44.8 kJ/mol determined by the authors¹³ appeared to be lower by 61.8 kJ/mol, which was identified with $E_d/2$. The authors explained this result by presumption that the radicals produced from the decomposition of the initiator initiate homopolymerization rather than copolymerization.

RESULTS AND DISCUSSION

The effect of initiator and monomer concentration and reaction time on the graft yield was investigated to discover the optimal conditions for grafting.¹⁸

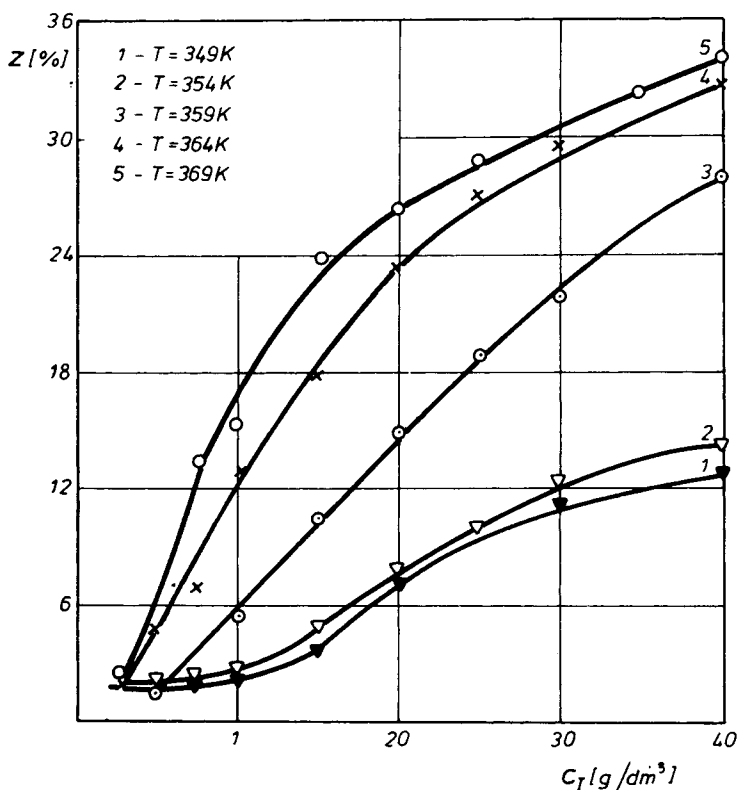


Fig. 3. Effect of the benzoyl peroxide concentration of percent graft yield. Initial concentration of acrylic acid 60 g/dm³, diphenyl concentration 5 g/dm³, NaCl concentration 36 g/dm³, reaction time 120 min, material-to-liquor ratio 1:30.

The graft yield was calculated on the basis of constant dry weight of the original PET sample m_1 and dry weight of grafted PET sample, from which homopolymer was washed out m_2 .

Percentage of the graft yield Z was calculated as follows:

$$Z\% = \frac{m_2 - m_1}{m_1} \times 100 \quad (7)$$

The effect of the monomer concentration on the graft yield at various temperatures is shown in Figure 1. It is clear that an increase in the acrylic acid concentration from 10 to 80 g/dm³ causes an enhancement in the graft yield up to 32% at the temperature of 369 K. It is well known^{8,12} that regardless of the monomer concentration, the grafting reaction proceeds initially at a fast rate and decreases with time to a slower rate. However, data used in the determination of reaction rates were restricted to the initial stages of grafting. As it is shown in Figure 2, the initial rate of acrylic acid grafting

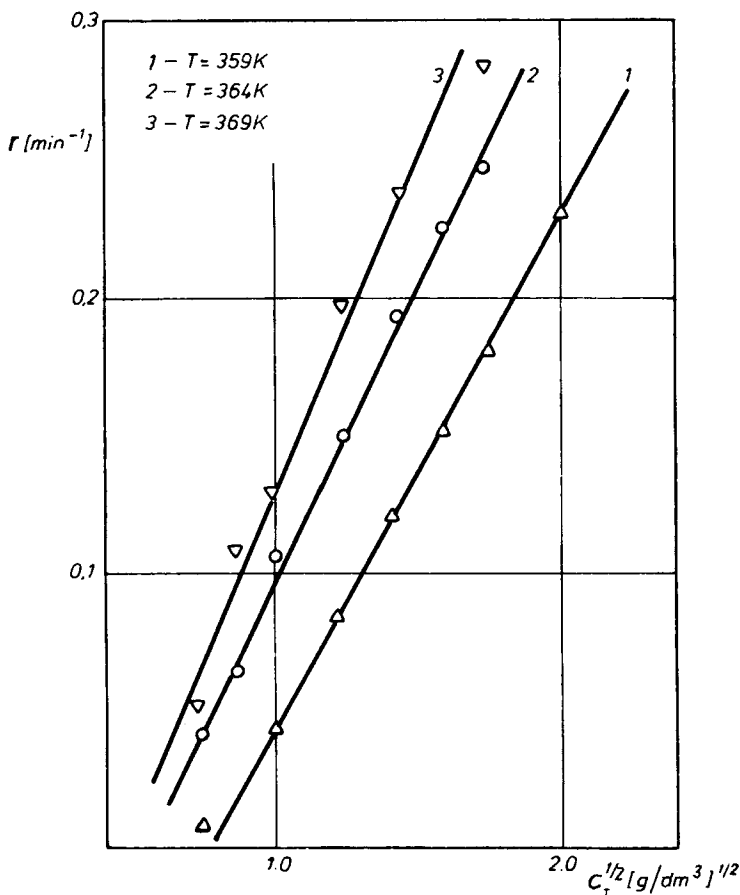


Fig. 4. Initial rate of grafting versus square root of benzoyl peroxide concentration. Acrylic acid concentration 60 g/dm³, diphenyl concentration 5 g/dm³, NaCl concentration 36 g/dm³, material-to-liquor ratio 1 : 30.

on PET is a linear function of the monomer concentration. This is in agreement with Eq. (3) indicating that the grafting reaction is of the first order with respect to the monomer concentration. The same relationship was observed by Sharma et al.²⁰ for graft copolymerization of vinyl acetate and acrylonitrile.

Figure 3 shows the effect of benzoyl peroxide concentration on the graft yield in the temperature range 349–369 K. As it is evident, the graft yield increases with the increasing concentration of the initiator and the temperature. It is interesting to note that at higher temperatures ~ 400 K (not shown in Fig. 3) a maximum graft yield has been observed at the concentration about 1.5 to 2.0 g/dm³. The leveling of grafting could be associated with depletion of benzoyl peroxide radicals in the termination reaction. It is also possible that when the concentration of benzoyl peroxide was increased beyond the maximum amount, homopolymerization rate increased. Indeed, a tremendous increase in viscosity of grafting bath was observed upon use of larger amounts of the initiator at a higher temperature which indicated a homopolymer formation. An attempt was made to correlate the initial rate of grafting with the concentration of benzoyl peroxide according to Eq. (3). As seen in Figure 4 the theoretical dependence of initial rate on square root of the initiator concentration can be experimentally confirmed only above some concentration

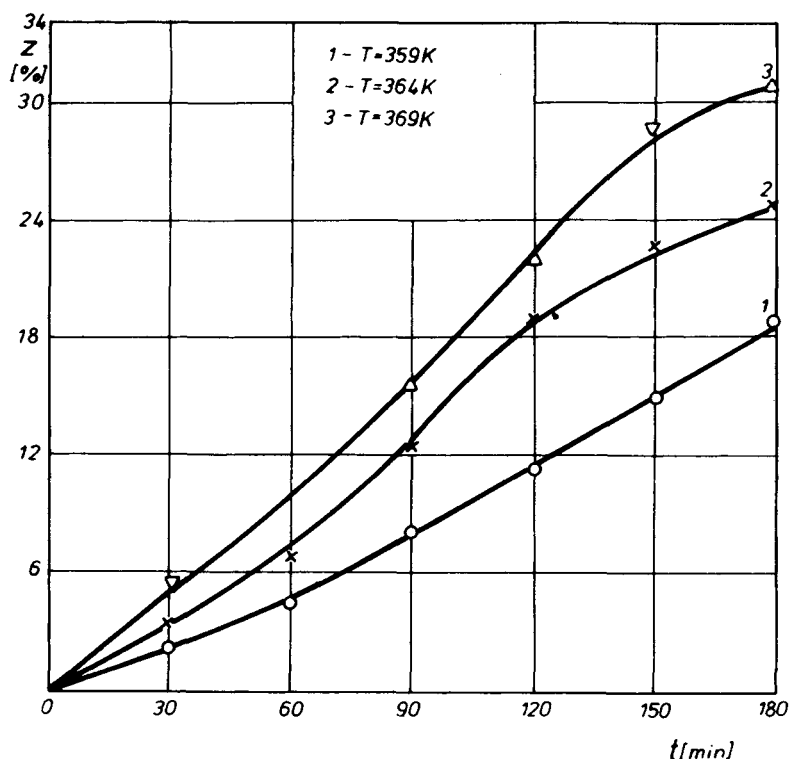


Fig. 5. Relation between graft yield and time for grafting of acrylic acid on polymer fabric at different temperatures. Acrylic acid concentration 50 g/dm³, benzoyl peroxide concentration 2 g/dm³, diphenyl concentration 5 g/dm³, NaCl concentration 36 g/dm³, material-to-liquor ratio 1 : 30.

of the initiator in the range of 0.6–0.7 g/dm³. This means that there is a minimum concentration of the initiator which is necessary for commencing the initiation step. As the straight lines in Figure 4 do not pass the origin, one can conclude that the theoretical approach to the kinetics of graft copolymerization of acrylic acid onto polyester fabrics represented by Eqs. (3)–(6) is not fully confirmed. The possible explanation of this discrepancy is the rather different mechanism of initiation than that assumed in derivation of Eq. (2), namely that the first step in the initiation is the decomposition of the initiator. Graft copolymerization of polar vinyl monomers onto PET by chemical activation has been presumed to be the result of propagation from radical sites generated on the polymer backbone. The importance of chain transfer of the polymer backbone with the primary radicals is demonstrated¹⁸ by the variation in grafting efficiency with the nature of the initiator.

The positive effects of temperature on grafting yield are shown in Figures 1, 3 and 5. An increase of the grafting temperature from 354 to 369 K enhances the rate of grafting. Further enhancement of the grafting rate was achieved by raising the temperature to 373 K. On the basis of the results of Figure 5, the apparent activation energy was determined from a plot of log of the initial grafting rate versus reciprocal of temperature (Fig. 6). The apparent energy of

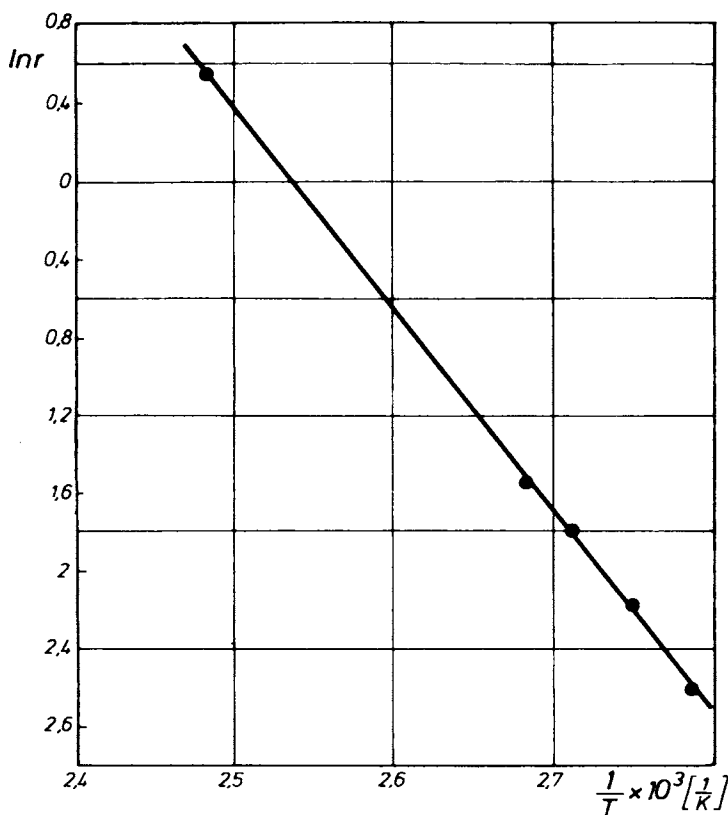


Fig. 6. Logarithm of initial rate of graft copolymerization of acrylic acid versus reciprocal of temperature. Reaction conditions the same as those in Fig. 5.

activation calculated from the slope of the straight line in Figure 6 is about 90 kJ/mol, which is of the same order (105 kJ/mol) as that computed for the process by Rao et al.¹³ However, this value of activation energy is higher than that found experimentally by other authors.^{12,13} Our results indicate that the energy of activation for the decomposition of the initiator ($E_d/2$) cannot be neglected in the total activation energy for the grafting copolymerization and that the initiation step plays an important role in the rate of the overall process. A kinetic study of the decomposition of benzoyl peroxide will be a subject of the second part of this paper.

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