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THE RATE OF GRAFTING AND SOME KINETIC PARAMETERS OF THE GRAFT COPOLYMERIZATION OF POLY(ETHYLENE TEREPHTHALATE) FIBERS WITH ACRYLAMIDE

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ABSTRACT

In this study the grafting rate relation of acrylamide onto the poly (ethylene terephthalate) fibers using benzoyl peroxide was deduced and the overall activation energy of grafting was calculated. The rate of grafting was found to be proportional of the 0.98 and 0.62 powers of acrylamide and benzoyl peroxide concentrations respectively. The overall activation energy was calculated to be 81.5 kJ/mole in the range of 75–92 °C and the overall rate constants were determined at different experimental temperatures.

INTRODUCTION

There are many studies concerning the grafting of various monomers onto poly (ethylene terephthalate) (PET) fibers. For example, the grafting of styrene (Sakurada et al. 1973, Schamberg and Hoigne 1970, Vlagiu and Stannett 1973), acrylic acid and methacrylic acid (Kale et al. 1975, Bonnefis and Puig 1971, Rao et al. 1972), vinyl acetate (Faterpeker and Potnis 1980) and bromostyrene (Mey-Marom et al. 1983) onto PET fibers have been reported. Many of the studies carried out on this subject are directed to investigate the properties of grafted fibers and to find out the factors affecting the grafting reaction. But there are some studies to obtain some kinetic data about these reactions as well.

Shalaby et al. (1978) gave the rate of grafting of 2–methyl–5–vinylpyridine onto PET fibers using benzoyl peroxide, in terms of monomer and initiator concentrations and determined the overall activation energy of the reaction.

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The activation energy of grafting of glycidyl methacrylate onto PET fibers was reported to be 61.4 kJ/mole (Suzuki et al. 1974).

Kaji et al. (1974) found the activation energies of radiation-induced grafting of methacrylic acid onto PET fibers in the ranges of 50–70 °C and 70–80 °C as 94.4 kJ/mole and 44.7 kJ/mole respectively, and stated that the activation energy showed a significant decrease in the presence of ethylene dichloride.

The studies concerning the grafting of acrylamide onto PET fibers are generally patented (Schamberg and Hoigne 1970, Okamura et al. 1970, Achmatowicz et al. 1970, Gaceva et al. 1985). For this reason, detailed information about the conditions of grafting reaction are not clear. There are also no kinetic data found about the grafting of acrylamide onto PET fibers in the literature. In a previous communication (Saçak and Pulat), the factors affecting the grafting of acrylamide onto PET fibers using benzoyl peroxide and some properties of the grafted fibers were investigated.

The aim of this study is to determine the relation of the rate of grafting with the acrylamide and benzoyl peroxide concentrations and find out some kinetic parameters related to the grafting reaction.

EXPERIMENTAL

MATERIALS: The PET fibers were provided by the SASA Co. (Adana-Turkey). The fiber samples were washed with luke-warm water, Soxhlet-extracted for 6 h with acetone and dried at ambient conditions before the graft copolymerization. Benzoyl peroxide (Bz_2O_2) was twice precipitated from chloroform solution in methanol and dried in a vacuum desiccator for two days. Benzene was crystalized cooling in the refrigerator. The crystalized part was used to prepare the Bz_2O_2 solutions. Acrylamide (Aam) was used before being subjected to any further purification.

GRAFT COPOLYMERIZATION PROCEDURE: The graft copolymerization reactions were carried out in a 100 mL polymerization tube. The PET fibers were placed in a 45 mL deionized water containing monomer. 5 mL of Bz_2O_2 solution prepared in benzene and desired concentrations were added. The mixture was then put in a water bath (Lauda D 40S W.Germany, $\pm$ 0.1 °C) adjusted to the polymerization temperature. The fibers taken from polymerization mixture after a specified period and were washed in boiling water for 4 h. The washing water was changed at least four times. They were Soxhlet-extracted with water for 6 h in order to remove the homopolymer which may remain as a film upon the surface of the fibers. The times for the fibers having various grafting ratioes to reach constant weight were determined by pre-experiments. The washing times were evaluated according to the results obtained in these experiments. The fibers were then dried and weighed. The graft yield value was based on the weight.

RESULTS AND DISCUSSIONS

In a study where a monomer is grafted onto fibers inevitably there obtained homopolymer of monomer together with the grafted fibers. Therefore the monomer in the medium is used in both grafting and homopolymer formation processes. In such a system, the relation the rate of grafting with the monomer and initiator concentrations can be written as:

$$R_g = k\ [\text{monomer}]^m\ [\text{initiator}]^n$$

Here m and n can be experimentally determined.

The experimental results showing the change of the rate of grafting with the concentration of benzoyl peroxide keeping the concentration of acrylamide constant are tabulated in Table I.

Table I. Dependence of Rate of Grafting on Bz_2O_2 Concentration.

$[Bz_2O_2] \times 10^4$ (mole/L)	log $[Bz_2O_2]$	$R_g \times 10^6$ (mole/L sec)	log R_g
2.560	-3.592	1.055	-5.977
5.037	-3.298	1.527	-5.816
9.990	-3.000	2.439	-5.613
39.960	-2.398	4.408	-5.360

[Aam], 0.563 mole/L; t, 85 °C.

The slope of the log R_g vs log $[Bz_2O_2]$ graph plotted from the data given in Table I showed that the rate of grafting was proportional to the 0.62 power of benzoyl peroxide concentration (Figure 1).

Likewise, the initial rates of grafting were determined by changing the concentration of acrylamide from 0.141 mole/L to 0.563 mole/L, keeping the benzoyl peroxide concentration constant (Table II).

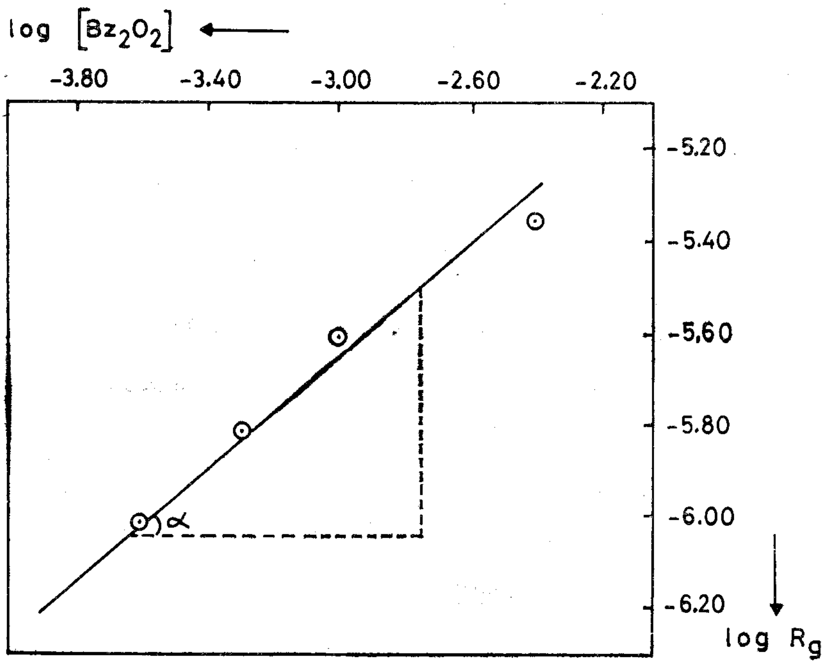

Fig. 1. Plot of log R_g vs log [Bz_2O_2].

Table II. Dependence of Rate of Grafting on Aam Concentration.

[Aam] (mole/L)	log [Aam]	R_g x10^6 (mole/L sec)	log R_g
0.141	-0.852	1.266	-5.898
0.281	-0.551	2.080	-5.682
0.422	-0.374	3.850	-5.415
0.563	-0.250	4.408	-5.360

[Bz_2O_2], 3.996 x10^{-3} mole/L; t, 85 °C.

The slope log R_g vs log [Aam] graph plotted using the data in Table II showed that the rate of grafting was proportional to the 0.98 power of the acrylamide concentration (Figure 2).

Therefore the grafting rate equation of acrylamide onto PET fibers can be written as:

$$R_g = k\ [Aam]^{0.98}\ [Bz_2O_2]^{0.62}$$

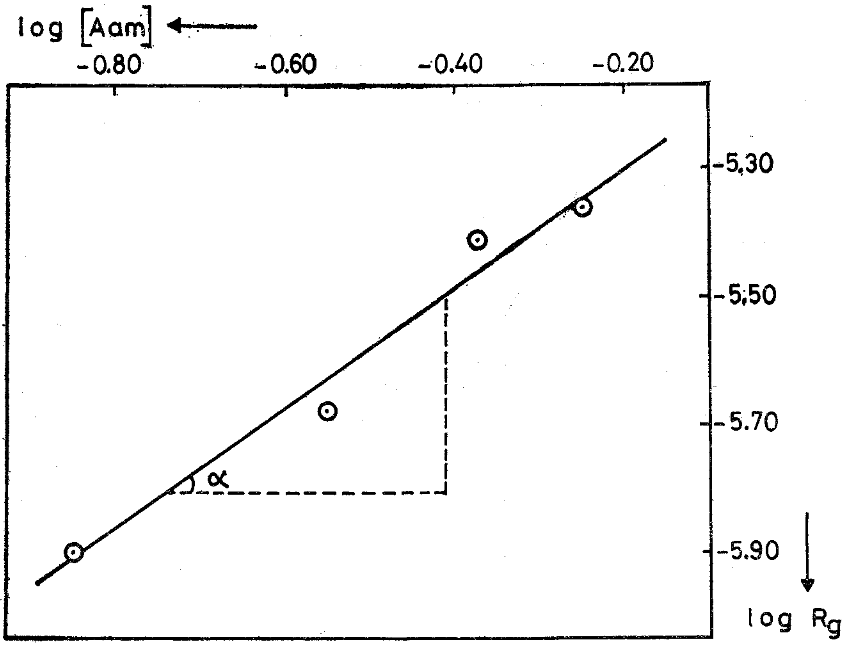

Fig. 2. Plot of log R_g vs log [Aam].

The overall activation energy for grafting was calculated to be 81.5 kJ/mole using the graph of initial rates of the polymerization carried ot at 75, 85 and 92 °C vs 1/T (Figure 3). The grafting of 2–methyl–5–vinylpyridine (Shalaby et al. 1978) and methyl methacrylate (Hebeish et al. 1981) onto PET fibers were stated to give similiar overall activation energies.

Table III shows the frequency factors and the overall rate constants calculated for the experimental temperatures. At is it seen from this table the frequency factors are not effected by the temperature while the overall rate constant increase with it.

The activation energy of the radicalic chain polymerization of vinyl monomers is known to be about 83.6 kJ/mole (Bilmeyer 1971). When one considers the overall activation energy and the rate equation for grafting given above it may be said that, the kinetics of grafting of acrylamide onto PET fibers follows almost a similiar kinetic path with radicalic vinyl chain polymerization.

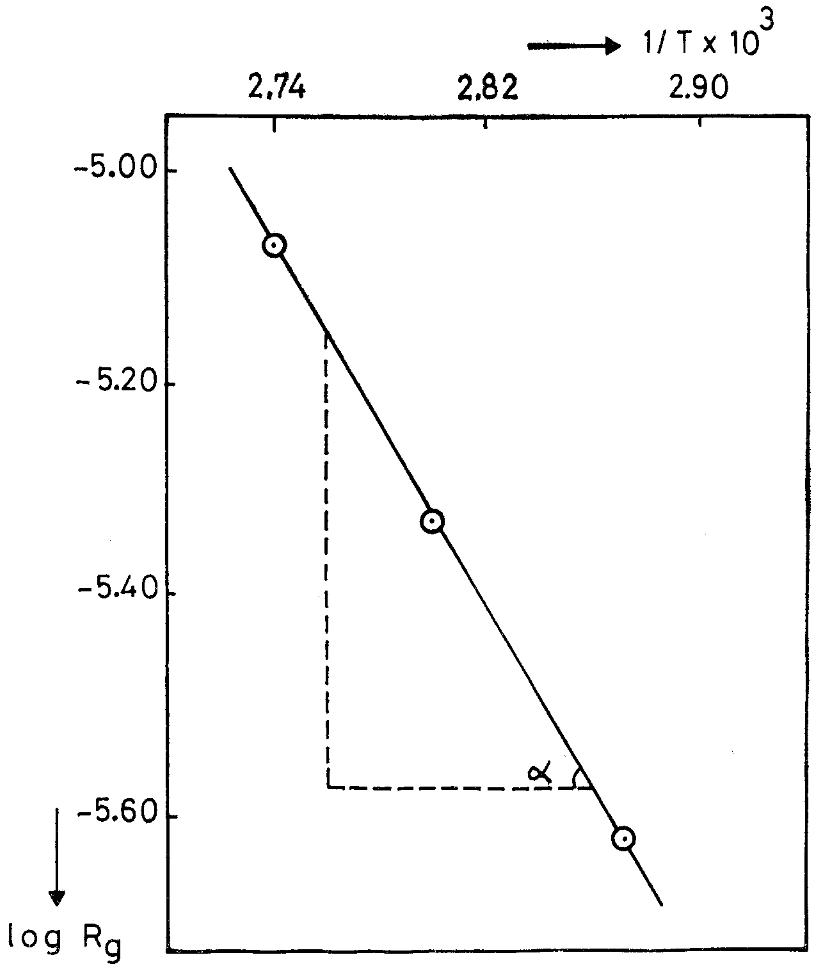

Fig. 3. Relation between log R_g vs 1/T for grafting of acrylamide onto PET fibers.

Table III. The Values of the Overall Rate Constants and Frequency Factors at Various Temperatures.

temperature (°C)	k x10^4 ($L^{0.6}$/$mole^{0.6}$sec)	frequency factor x10^{-8} ($L^{0.6}$/$mole^{0.6}$sec)
75	1.28	2.17
85	2.56	1.98
92	4.60	2.10

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