

The Rate of Grafting and Some Kinetic Parameters of the Graft Copolymerization of Methacrylic Acid on Poly (Ethylene Terephthalate) Fibers with Azobisisobutyronitrile

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In this study the rate of grafting and some kinetic parameters of the graft copolymerization of methacrylic acid on poly(ethylene terephthalate) fibers with azobisisobutyronitrile was investigated. The rate of grafting was found to be proportional to the 0.94 and 1.22 powers of initiator and monomer concentrations, respectively. By carrying out the graft copolymerization reaction at four different temperatures ranging from 70 °C to 90 °C, the overall rate activation energy of the reaction was found to be 130.4 kJ/mol. The overall rate constants were also calculated.

Introduction

There are many studies concerning the grafting of various monomers onto poly(ethylene terephthalate) (PET) fibers. For example, the grafting of 2- methyl-5-vinyl pyridine¹, acrylamide² and acrylic acid-styrene mixture³ onto PET fibers has been reported. Many of the studies carried out on this subject are directed to investigate the properties of grafted fibers and to determine the factors affecting the grafting reaction. But there are some studies to obtain some kinetic data about these reactions as well. For example, in the grafting of 2-methyl-5-vinyl pyridine onto PET fibers using benzoyl peroxide, Shalaby et al.⁴ have reported that the grafting rate is proportional to the 1.10 and 1.02 powers of the monomer and initiator concentrations, respectively. In the grafting of the same monomer with hydrogen peroxide, the above orders become 0.59 and 0.97¹.

It has also been stated that the grafting rate is 2.33 order with respect to monomer concentration and 0.92 order with respect to initiator concentration in the grafting of acrylic acid onto PET fibers using benzoyl peroxide⁵.

Activation energies of various grafting systems are also given in the literature. It was reported that the activation energy of grafting of methacrylic acid onto PET fibers in the ranges of 80-90°C was 139.9 kJ/mol⁶. The activation energy of grafting of methyl methacrylate⁷, glycidyl methacrylate⁸, and acrylamide⁹ onto PET fibers was reported to be 66.9 kJ/mol, 61.4 kJ/mol and 81.5 kJ/mol, respectively.

The aim of this study was to determine the relation between the rate of grafting and the methacrylic acid and azobisisobutyronitrile concentrations, and determine some kinetic parameters related to the grafting reaction.

Experimental

Materials

The multifilament PET fibers (110 dTex, 30 filaments, opaque, Mv =26000) manufactured and supplied by SASA (Adana, Turkey) were used after purification by treating with acetone for 8h in a Soxhlet apparatus. Methacrylic acid (MAA)(Merck) was vacuum distilled over a column filled with copper wires at 40°C. Azobisisobutyronitrile (AIBN)(BDH) was recrystallized twice from methanol and dried over P₂O₅ in a vacuum desiccator. All other chemicals were chemically pure grade.

Graft Copolymerization Procedure

The graft copolymerization procedure was detailed previously¹⁰. Fiber samples and monomer dissolved in 19 mL water at a suitable concentration were put in a 50 mL Pyrex polymerization tube placed in a water bath (Lauda D 40S). One milliliter of toluene containing a suitable concentration of initiator was added to this mixture after it had reached the polymerization temperature. The time at which the initiator was first added was considered the starting point of copolymerization. The sample taken at the end of graft copolymerization was washed with water at room temperature for 24 hours since the solubility of poly MAA is quite high at low temperatures¹¹. The sample was then Soxhlet-extracted for 8 hours with acetone, dried, and weighed. The amount of graft added onto the fiber was determined gravimetrically. The percent increase in fiber weight was taken as % graft yield (%G).

Rate Measurement

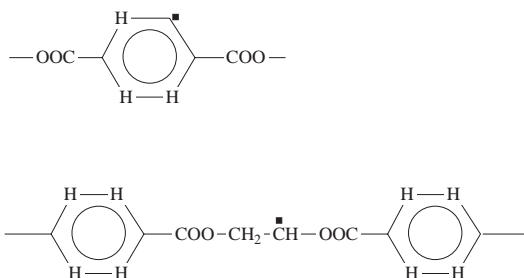
The rate of grafting (Rg) was calculated as follows;

$$\text{Rate of grafting (Rg)} = (\%G \cdot W_1 \cdot 1000) / (100 \cdot V \cdot t \cdot M)$$

where %G is percent graft yield, W₁ is weight of original fiber, V is total volume of the reaction mixture, t is reaction time, and M is molecular weight of MAA.

Results and Discussion

ESR studies showed that the irradiation of PET with γ -rays gave the following radicals¹²:



These radicals, which act as grafting sites, can be chemically created by the use of such radical initiators as hydrogen peroxide¹³, azobisisobutyronitrile (AIBN)¹⁴, and benzoyl peroxide^{15,16,17} under suitable conditions.

The number of studies concerning the grafting of vinyl monomers onto PET fibers using AIBN is quite limited. The grafting of methacrylic acid onto PET fibers using this initiator was recently reported by us.^{10,18}

In a study where a monomer is grafted onto fibers inevitably homopolymer of the monomer is obtained together with the grafted fibers. Therefore the monomer in the medium is used in both the grafting and homopolymer formation processes. In such a system, the relation between the rate of grafting and the monomer and initiator concentrations can be written as^{5,18}

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

Here m and n can be experimentally determined by the logarithmic form of the equation given above:

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

The experimental results showing the change in the rate of grafting with the concentration of AIBN keeping the concentration of methacrylic acid constant are shown in Table 1.

Table 1. Dependence of the rate of grafting (Rg) on azobisisobutyronitrile concentration

[AIBN]x10 ³ (mol/L)	%G	Rgx10 ⁶ (mol/L s)	log[AIBN] + 4	log Rg + 6
0.54	3.60	9.46	0.73	0.98
1.07	6.20	17.17	1.03	1.24
2.20	13.90	37.75	1.34	1.58
3.30	17.00	56.11	1.52	1.75
4.30	18.10	59.93	1.63	1.78

$$[\text{MAA}] = 0.37 \text{ mol/L; time} = 10 \text{ min; temp} = 85^\circ\text{C}$$

The slope of the log Rg vs. log [AIBN] graph plotted using the data given in Table 1 showed that the rate of grafting was proportional to the 0.94 power of the AIBN concentration (Figure 1).

Likewise, the initial rates of grafting were determined by changing the concentration of methacrylic acid from 0.05 to 0.53 mol/L, keeping the AIBN concentration constant (Table 2).

Table 2. Dependence of the rate of grafting (Rg) on methacrylic acid concentration

[MAA] (mol/L)	%G	Rgx10 ⁶ (mol/L s)	log[MAA] + 2	log Rg + 6
0.05	1.63	4.10	0.72	0.61
0.11	3.99	11.27	1.03	1.05
0.21	7.08	16.90	1.32	1.23
0.37	17.00	56.11	1.57	1.75
0.53	20.40	66.11	1.72	1.82

$$[\text{AIBN}] = 3.30 \times 10^{-3} \text{ mol/L; time} = 10 \text{ min; temp} = 85^\circ\text{C}$$

The slope of the log Rg vs. log [MAA] graph plotted using the data in Table 2 showed that the rate of grafting was proportional to the 1.22 power of the methacrylic acid concentration (Figure 2).

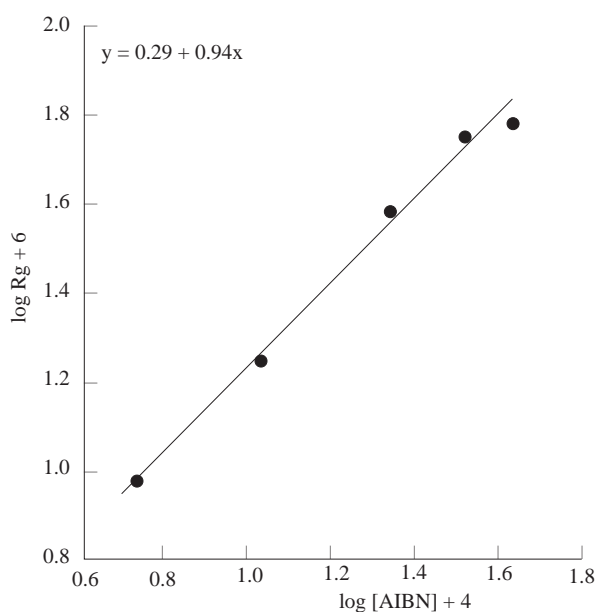


Figure 1. Rates of grafting reactions vs. initiator concentration.

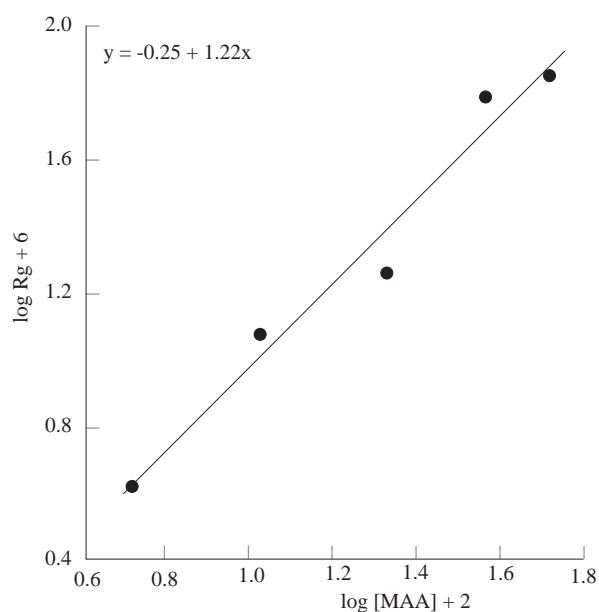


Figure 2. Rates of grafting reactions vs. monomer concentration.

Table 3 shows the overall activation energy for grafting calculated from the graft yields obtained at various temperatures.

Table 3. The values of the rate of grafting (Rg) and the overall rate constants (k) at various temperatures

temperature (°C)	%G	Rgx10 ⁶ (mol/L s)	log Rg + 6	kx10 ² (L ^{1.16} /mol ^{1.16} s)
70	2.20	2.22	0.35	0.16
80	15.90	14.49	1.16	1.05
85	19.50	16.15	1.21	1.17
90	31.30	28.97	1.46	2.10

$$[\text{AIBN}] = 3.30 \times 10^{-3} \text{ mol/L}; [\text{MMA}] = 0.37 \text{ mol/L}; \text{time} = 30 \text{ min}$$

The overall activation energy for grafting was calculated to be 130.4 kJ/mol from the Arrhenius plot of log Rg vs. 1/T (Figure 3).

The total grafting rate constants were also calculated for different temperatures and are shown in Table 3.

The calculated activation energy of grafting is for 70-90°C. In the first 30 minutes, at the temperatures under 70°C, no grafting was observed; so grafting yields obtained for the temperatures of 70, 80, 85 and 90°C were used to calculate the overall activation energy.

Conclusion

From the experimental results, the grafting rate equation of methacrylic acid onto PET fibers can be written as follows:

$$R_g = k [\text{AIBN}]^{0.94} [\text{MAA}]^{1.22}$$

As seen from the rate equation, the total degree of grafting is 2.16.

The overall activation energy for grafting of MAA onto PET fibers by AIBN was found to be 130.4 kJ/mol. In radiation-grafting of MAA onto PET fibers¹⁹, 94.4 kJ/mol and 44.7 kJ/mol activation energy values were reported for 50-70°C and 70-80°C, respectively. This study shows that the grafting of MAA onto PET fibers by chemical methods needs higher energy when compared with the radiation grafting.

As seen in Table 3, the overall rate constant increased with temperature similar to in conventional chemical reactions.

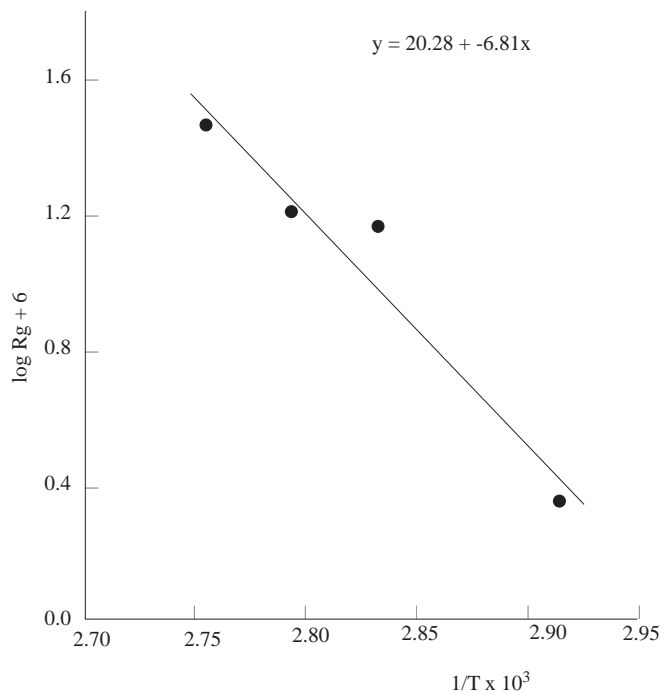


Figure 3. Arrhenius plot of log R_g vs.1/T for grafting MAA onto PET

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