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Kinetic Investigation of Grafting of Poly(ethylene terephthalate) Fibers with 2-Hydroxypropyl Methacrylate using 4,4'-Azo*bis*(4-cyanovaleric acid)

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The graft copolymerization of 2-hydroxypropyl methacrylate (2-HPMA) onto poly(ethylene terephthalate) fibers has been studied using 4,4'-azo*bis* (4-cyanovaleric acid) (ACV) as an initiator. The grafting increased the diameter and moisture regain. Effect of different parameters, such as initiator and monomer concentration, reaction time and temperature were studied. Optimum condition for grafting were determined to be [ACV] = 4.0×10^{-3} M, [2-HPMA] = 0.5 M, T = 75 ºC, t = 1 h. The rate of grafting was calculated to 1.25 power of monomer and 0.90 power of initiator. The overall activation energy for grafting was ascertained as 87.25 kJ/mol. The use of various emulsifiers such as DTAB, CTAB and SLS were shown an inhibition effect in grafting.

Key Words: Graft copolymerization, Poly(ethylene terephthalate), 2-Hydroxypropyl methacrylate, 4-4'-Azo*bis*(4-cyanovaleric acid)

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers have a salient place among synthetic fibers. Although, in spite of many excellent properties of PET fibers, some of their poor features such as difficulty of dyeing, low water wettability and poor antistatic properties limit their usage. The structure of PET fibers are high crystalline and hydrophobic and they have not got chemically reactive functional groups. Therefore, they can be improved by different methods. Graft copolymerization of vinyl monomers onto natural or synthetic fibers improve their properties. Many researchers have been reported the grafting of vinyl monomers onto PET fibers by chemical or radiation initiation[1-19]. Results emphasize chemical initiation are more advantageous as regards degradation of the main polymer. Vinyl monomers can be grafted onto PET fibers under the influence of free-radical initiators[10-19]. This paper reports graft copolymerization of 2-hydroxypropyl methacrylate (2-HPMA) onto PET fibers by the use of 4,4'-azo*bis*(4-cyanovaleric acid) as initiator. On the other hand the effect of anionic and cationic emulsifiers, moisture regain, diameter and some of the kinetic parameters were investigated.

EXPERIMENTAL

In this study 2-hydroxypropyl methacrylate (2-HPMA) was supplied by Merck (Germany). Poly(ethylene terephthalate) (PET) fibers (44 filaments and 167 dTex) were used in all experiments. 4,4'-Azo*bis*(4-cyanovaleric acid) (ACV) obtained from Aldrich (England). The emulsifiers (dodecyltrimethylammonium bromide (DTAB), cetyltrimethylammuniumbromide (CTAB), sodiumlaurylsulphate (SLS) and solvents such as dimethyl formamide (DMF), toluene, acetone and other chemicals were all of analytical grade and supplied by Merck and doubly distilled water has been used in all experiments. 2-Hydroxypropyl methacrylate as monomer has been used after distilled under reduced pressure in inert atmosphere (23 mmHg, T_{BP} = 99 ºC). 4,4'-Azo*bis*(4-cyanovaleric acid) (ACV) after purification has been used in experiments. For purification, at first it was suspended in doubly distilled water, then for dissolution of it, the solid sodium bicarbonate was added and the solution was acidified with the use of 1 M HCl and precipitated. Finally, the solid was filtered and washed with ice cold water and dried at room temperature in vaccum. The PET samples were prepared as small hank (0.3 ± 0.001 g) Soxhlet-extracted for 6 h with acetone and dried at ambient temperature. All emulsifiers and solvents without further purification have been used in experiments.

Grafting procedure: The PET fiber specimen were placed in a 100 mL pyrex tube possessing the required concentrations of monomer and initiator in 5 mL acetone. The volume of the mixture was immediately placed into a water bath at the fixed polymerization temperature. After desirable time, the fiber sample was taken out of the tube and for washing of undesirable homopolymers, Soxhlet-extracted with N,N-dimethylformamide (DMF) and mixture of (toluene and acetone) (50 % vol. acetone) for 6 and 8 h, respectively. Finally,

the sample was dried in vaccum at 50 ºC. Per cent graft yield was calculated from the increase in the weight of the original PET after grafting[16]:

$$G\ (\%) = \frac{W_g - W_o}{W_o} \times 100$$

In this equation, W_g and W_o denote the weights of the grafted and original PET, respectively.

Determination of moisture regain and diameter: Determination of the moisture of the fiber samples with various per cents of graft yield were accomplished in 65 % sulphuric acid with density of 1.275 g/mL for 24 h. Then they were oven dried in 100 ºC and finally were kept in desiccator over P_2O_5 for 1 h and weighted. The per cent of moisture regain was calculated by this equation[16]:

$$\text{Moisture region}\ (\%) = \left[\frac{M_n - M_0}{M_0}\right] \times 100$$

here M_n and M_0 are the weights of fibers in wet environment and dry fibers, respectively. The fiber diameters were measured with a Kyowa Microlux-11 microscope at a magnification of 1000×.

RESULTS AND DISCUSSION

Moisture regain and diameter: By increasing of the grafting yield, the ability of the water absorption increased and in 52.7 % of grafted sample, it attained 2.75 %. This property of ungrafted PET fiber was determined to be 0.4 %. This can be related to the hydrophilic group of -OH in 2-HPMA structure grafted to PET chain[12-16]. The diameter of fibers showed a changing from 1.432 mm × 10^{-2} (uncopolymerized fiber) to 3.052 mm × 10^{-2} [grafted production with 52.70 (%)]. Results tabulated in Table-1.

TABLE-1
VARIATION OF DIAMETER AND MOISTURE REGAIN WITH PER CENT OF GRAFTING YIELD

Grafting yield (%)	Diameter (mm × 10^{-2})	Moisture regain (%)
0.00	1.432	0.40
3.68	1.521	0.52
12.53	1.595	0.88
39.94	2.383	1.78
49.00	2.758	2.38
52.70	3.052	2.75

Effect of initiator and monomer concentration: The study of the effect of initiator concentration was fulfilled by increasing the concentration of ACV from 1.0 × 10^{-3} – 6.0 × 10^{-3} M at fixed other variables ([2-HPMA] = 0.5 M, temperature = 85 ºC, time = 1 h). Fig. 1 shows that grafting yield increases by increasing the ACV concentration up to 4.0 × 10^{-3} M and then decreased. As a result of the decomposition of ACV, the number of free radicals and the number of active sites in PET chain increase. Therefore the rate of homopolymerization and copolymerization increase as well. Although, the excess increase in the concentration of ACV causes the rate of terminal reactions with PET macroradicals, growing polymer chains or combination reactions increase and as a result of these reactions, the grafting yield decreases. Similar behaviours were reported by another researchers[10,13,16,18]. The effect of monomer concentration onto grafting yield was studied in the range of 0.1-0.75 M. Fig. 2 shows that by increasing of the monomer concentration, the percentage of grafting increase. The increase in the 2-HPMA concentration cause more diffusion into the PET fibers, but after the saturation of grafting (46.80 %), due to exceeding of homopolymer at high monomer concentration and as a result of this phenomena increase the viscosity of the solution and inhibit the monomer diffusion into the PET chains[13-19].

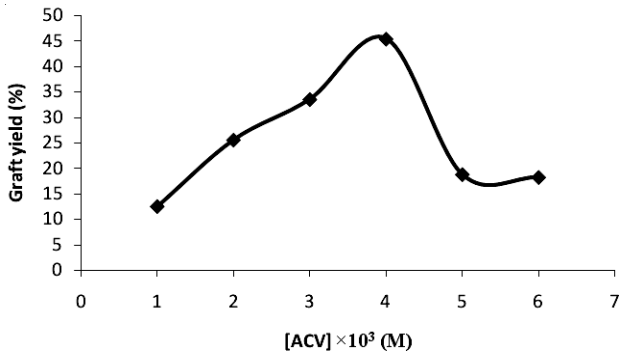

Fig. 1. Effect of ACV concentration on the grafting yield: [2-HPMA] = 0.5 M, temperature = 85 ºC, time = 1 h

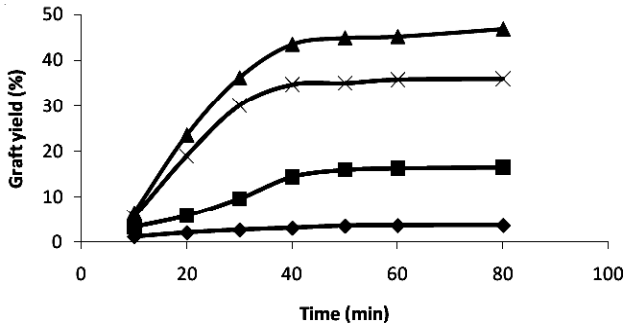

Fig. 2. Effect of 2-HPMA concentration on the grafting yield: [ACV] = 4.0 × 10^{-3} M, temperature = 85 ºC, [2-HPMA]: (♦) 0.10M, (■) 0.25M, (▲) 0.50M, (×) 0.75 M

Effect of temperature and time: Fig. 3 shows the effect of the temperature on the graft yield as a function of time at four different temperature from 65-85 ºC. When the temperature was increases, the grafting yields and rates of reaction increase. Generally, in a temperature higher than glass transition of PET (≈ 70 ºC), the flexibility, swellability and mobility of the PET

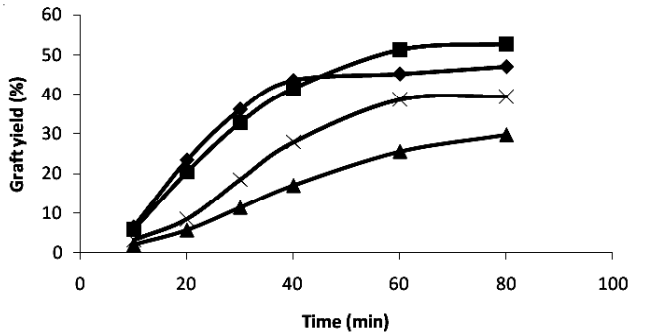

Fig. 3. Effect of temperature and time on the grafting yield: [2-HPMA] = 0.5 M, [ACV] = 4.0 × 10^{-3} M (▲) 65 ºC, (×) 70 ºC, (■) 75 ºC, (♦) 85 ºC

chains increase. On the other hand, increasing in temperature causes to higher rate of ACV decomposition. Consequently, the diffusion to PET and the yield of grafting becoming greater. Decreasing in the graft yield at higher temperature (more than 75 ºC) may be imputed to the increase in the rates of termination reactions. Other researchers were reported the same results[13,19].

The most suitable time is 1 h for copolymerization. After this time, the viscosity of solution increased due to homopolymerization reactions in the polymerization medium and this was established an inhibition effect of diffusion to PET chains[12-19].

Effect of different emulsifiers: The effect of anionic and cationic emulsifiers on the graft per cent was studied at various quantity of emulsifier in the fixation condition ([2-HPMA] = 0.5 M, [ACV] = 4.0×10^{-3} M, time = 1 h, temperature = 75 ºC).

Results showed that a decreasing in the graft yield in the presence of dodecyltrimethylammonium bromide (DTAB), cetyltrimethylammoniumbromide (CTAB) and sodiumlaurylsulphate (SLS). It seems that emulsifiers have terminating effect upon the PET macroradical and graft chain radicals and reaction of the initiator radical with emulsifier molecule cause decrease the number of active free radical sites on the PET. On the other hand, homopolymerization and emulsifier-monomer reactions occur much more than grafting reactions. Results tabulated in Table-2.

TABLE-2
EFFECT OF DIFFERENT EMULSIFIERS ONTO GRAFT YIELD

E (%)	0.5 (%)	1.0 (%)	2.0 (%)
G (SLS)	3.80	2.75	1.00
G (CTAB)	3.24	2.32	0.45
G (DTAB)	2.03	1.25	0.00

Kinetics of grafting: Some of the kinetic parameters of the graft copolymerization of 2-HPMA onto PET fibers with ACV, such as the relation of the rate of grafting reaction to the change of monomer and initiator concentration at the 15 min of polymerization (before reaching saturation), were determined by these equations:

$$R_g = \frac{W_g - W_0}{V.t.M}$$

and

$$R_g = k[I]^m[M]^n$$

or logarithmic form: $\log R_g = \log k + m \log [I] + n \log [M]$

where V = volume of the solution (L), t is the polymerization time (S) and M is the molecular weight of the 2-HPMA, [I] is the initiator concentration, [M] is the monomer concentration and m, n are orders of reaction respect to intiator and monomer and can be determined experimentally[3,8,9,17,18].

Results of the variation of the monomer concentration from 0.1-0.5 M at fixed condition (temperature = 75 ºC, [ACV] = 4.0×10^{-3} M, time = 15 min) determined the order of reaction respect to monomer. Relation of the log R_g + 8 *versus* log [2-HPMA] + 3 are tabulated in Table-3. The slope of the gragh distinguished that the rate of grafting was 1.25-order with respect to the 2-HPMA (Fig. 4).

Results of the variation of the initiator concentration from 1.0×10^{-3}-4.0×10^{-3} M at fixed condition (temperature = 75 ºC, [2-HPMA] = 0.5 M, time = 15 min), ascertained the order of reaction respect to initiator. Relation of the log R_g + 8 *versus* log [ACV] + 5 in the above range are tabulated in Table-4. The slope of the graph specified that the rate of grafting was 0.90-order with respect to the ACV (Fig. 5).

TABLE-3
DEPENDENCE OF THE RATE OF GRAFTING ON MONOMER CONCENTRATION
[ACV] = 4.0×10^{-3} M, temperature = 75 ºC, time = 15 min

[2-HPMA] (mol/L)	G (%)	$R_g \times 10^8$ (mol/L S)	log [2-HPMA] + 3	log R_g + 8
0.10	1.65	76.91	2.000	1.886
0.25	4.75	215.28	2.398	2.333
0.35	6.80	307.61	2.544	2.488
0.50	13.50	615.17	2.699	2.789

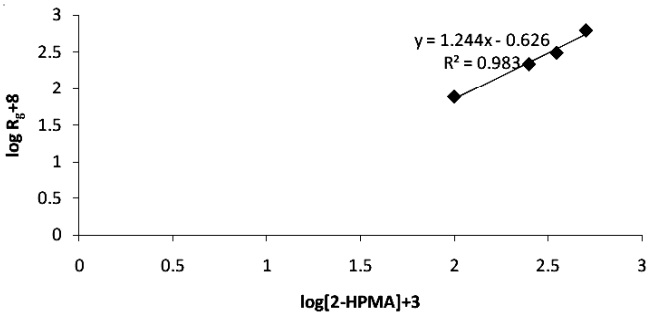

Fig. 4. Rate of grafting reaction *versus* monomer concentration: [ACV] = 4.0×10^{-3} M, temperature = 75 ºC, time = 15 min

TABLE-4
DEPENDENCE OF THE RATE OF GRAFTING ON INITIATOR CONCENTRATION
[2-HPMA] = 0.5 M, temperature = 75 ºC, time = 15 min

[ACV] × 10^3 (mol/L)	G (%)	$R_g \times 10^8$ (mol/L S)	log [ACV] + 5	log R_g + 8
1	3.83	184.50	2.000	2.266
2	7.95	354.00	2.301	2.549
3	10.60	492.04	2.477	2.692
4	13.75	645.65	2.602	2.810

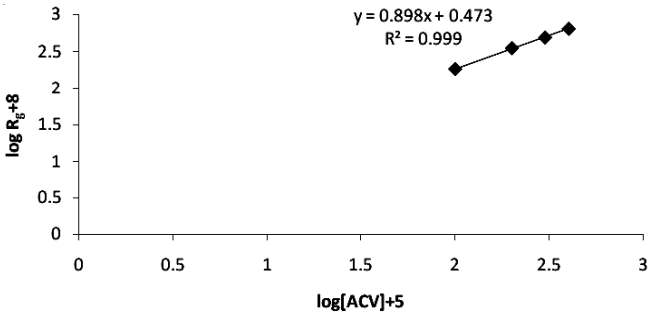

Fig. 5. Rate of grafting reaction *versus* initiator concentration: [2-HPMA] = 0.5 M, temperature = 75 ºC, time = 15 min

Thus, the grafting rate can be written as:

$$R_g = k[ACV]^{0.90} [2\text{-HPMA}]^{1.25}$$

The overall activation energy for grafting was calculated from Arhenius plot of the log R_g *versus* 1/T at four different temperatures from 60-75 ºC in 1 h. Table-5 and Fig. 6 showed that the overall activation energy was 87.25 kJ/mol.

TABLE-5
VALUES OF THE RATE OF GRAFTING
AT DIFFERENT TEMPERATURES
[2-HPMA] = 0.5 M, [ACV] = 4.0×10^{-3} M, time = 1 h

T (K)	$1/T \times 10^3$	G (%)	$R_g \times 10^8$ (mol/L S)	$\log R_g + 8$
333	3.003	13.33	153.81	2.187
338	2.958	28.50	327.34	2.215
343	2.915	39.00	461.31	2.664
348	2.873	53.00	615.17	2.789

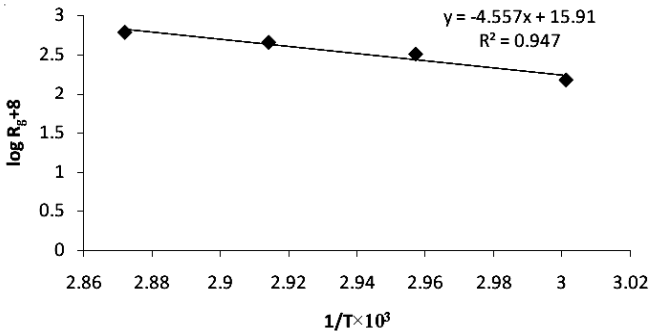

Fig. 6. Arhenius plot of log R_g *versus* 1/T

Conclusion

• Optimum conditions for grafting were found to be [ACV] = 4.0×10^{-3} M, [2-HPMA] = 0.5 M, temperature = 75 ºC, time = 1 h.

• The rate of grafting was found to 1.25 power of monomer and 0.9 power of initiator. The overall activation energy for grafting was calculated as 87.25 kJ/mol.

• The effect of anionic (SLS) and cationic (DTAB, CTAB) emulsifiers showed a decreasing in the graft yield as follows: SLS < CTAB < DTAB.

• The diameter and moisture regain of the grafted fibers increased.

REFERENCES

1. V.M. Rudoi, L.P. Sidorova and V. Ya Kabaniv, *Polym. Sci. USSR*, **30**, 376 (1988).
2. F. Osipenko and V.I. Martinovicz, *J. Appl. Polym. Sci.*, **39**, 935 (1990).
3. S.E. Shalaby, A.M. Bayazeed and A. Hebeish, *J. Appl. Polym. Sci*., **22**, 1359 (1978).
4. I.M. Trivedi and P.C. Mehta, *J. Appl. Polym. Sci.*, **19**, 1 (1975).
5. A. Hebeish, S.E. Shalaby and M.F. E1-Shaid, *Die Angew. Makromol. Chem.*, **66**, 139 (1978).
6. P.D. Kale, H.T. Lokhande, K.N. Rao and M.H. Rao, *J. Appl. Polym., Sci*., **19**, 461 (1975).
7. S. Lenka and P.L. Nayak, *J. Polym. Sci. Polym. Chem. Ed*., **21**, 1871 (1983).
8. A. Gopalan and A. Ramasubramanian, *J. Appl. Polym. Sci*., **56**, 1299 (1995).
9. R. Anbarasan, T. Vasudevan and A. Gopalan, *Eur. Polym. J*., **36**, 1725 (2000).
10. M. Sacak and E. Pulat, *J. Appl. Polym. Sci.*, **38**, 539 (1989).
11. M. Okoniewski, J. Sojka and S. Ledakowicz, *J. Appl. Polym. Sci*., **35**, 1241 (1988).
12. M. Sacak and F. Oflaz, *J. Appl. Polym. Sci*., **50**, 1909 (1993).
13. M. Sacak, F. Sertkaya and M. Talu, *J. Appl. Polym. Sci.*, **44**, 1737 (1992).
14. M. Sacak, N. Bastug and M. Talu, *J. Appl. Polym. Sci.*, **50**, 1123 (1993).
15. M. Sacak, N. Eski and M. Talu, *J. Macromol. Sci.*, *Pure. Appl. Chem*., **A32**, 1735 (1995).
16. F. Azizinejad, M. Talu, M. Abdouss and M. Shabani, *Iran. Polym. J*., **14**, 33 (2005).
17. M. Arslan, M. Yigitoglu, O. Sanli and H.I. Unal, *Polym. Bull*., **51**, 234 (2003).
18. R. Coskun, M. Sacak and M. Karakisla, *J. Appl. Polym. Sci*., **97**, 1795 (2005).
19. R. Coskun, *Eur. Polym. J*., **43**, 1428 (2007).