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Synthesis and Characterization of Graft Copolymerization of Methyl Methacrylate/2-Hydroxy Propyl Methacrylate onto Poly(ethylene terephthalate) Fibers with 4,4-Azobis(4-cyano valeric acid)

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In this research, the graft copolymerization of methyl methacrylate/2-hydroxypropyl methacrylate (MMA/2-HPMA) onto poly(ethylene terephthalate) fibers was studied using 4,4-azobis-4-cyanovaleric acid (ACV) as a radical initiator. The synergistic effect was found to be at its highest quantity when an MMA/2-HPMA mixture having 40 % methyl methacrylate (wt %) was used. The grafting was improved the moisture region of the fibers. The effect of different parameters, such as initiator, monomer mixture concentrations, reaction time and temperature were studied. Optimum condition were determined to be [ACV] = 4×10^{-3} M, t = 45 min, T = 85 °C and [MMA/2-HPMA] = 0.2 M. The rate of grafting was calculated to the 1.29 power of monomer mixture and 1.71 power of initiator. The overall activation energy for grafting was determined as 44.95 kJ/mol. The grafting fibers were characterized by Fourier transform infrared, scanning electron microscopy, thermo gravimetric analysis.

Keywords: Coplymerization, Grafting, 2-Hydroxy propyl methacrylate, Methyl methacrylate.

INTRODUCTION

The graft copolymerization of vinyl monomers onto natural or synthetic fibers have been improved their properties. Erstwhile, the grafting of acrylic acid [1], acrylamide [2], methyl methacrylate [3], 2-hydroxyethyl methacrylate [4], methacrylic acid [5], polystyrene [6], 4-vinyl pyridine [7], N-vinylimidazole [8], 2-hydroxypropyl methacrylate [9,10] onto poly(ethylene terephthalate) (PET) fibers were reported by researchers. Meanwhile, the grafting of binary mixtures of vinyl monomers has special importance in comparison to simple grafting of individual monomers and has been reported by many researches in two decade. The synergistic effect of the comonomer in grafting plays an important role in controlling the composition and grafting yield onto PET [11-19].

The aim of this work was to modification and determination of the best condition of the grafting of 2-hydroxy propyl methacrylate (2-HPMA)/methyl methacrylate (MMA) monomer mixture onto PET fibers using of 4,4'-azobis-(4-cyanovaleric acid) (ACV) as a radical initiator. On the other hand, the water absorption capacity, suggestion mechanism and some of the kinetic parameters were investigated.

EXPERIMENTAL

Methyl methacrylate and 2-hydroxypropyl methacrylate were bought from Merck Co. of Germany and after purification were used in grafting procedure. For this aim, MMA was washed three times with 5 % NaOH, dried over $CaCl_2$ and finally distilled in vacuum at 46 °C. 2-Hydroxypropyl methacrylate as monomer has been used after distilled under reduced pressure in inert atmosphere (23 mm Hg). Radicalic initiator (ACV) has been used after purification in all experiments. For this aim, firstly, it was suspended in doubly distilled water, then for dissolvation of it, the solid sodium bicarbonate was added and the solution was acidified by adding of 1 M HCl and precipitated. Finally, the solid was filtered and washed with ice cold water and dried at room temperature in vacuum. The PET fibers (stretch ratio 2, 44 filaments, 110 dTex) were purchased from Textile Department of Amir Kabir University and Technology, Tehran. They were cut as small hank (0.2 ± 0.01 g), Soxhlet extracted for 6 h with acetone and dried at ambient temperature. Reagents and solvents were all high purity and supplied by Merck and doubly distilled water used in all experiments.

Grafting procedure: Clear fiber samples (0.2 g) were placed in a 100 mL pyrex tube. The polymerization tube containing monomers and 18 mL doubly distilled water was placed in water bath and kept there for 2 min and then 2 mL acetone receptacle of ACV was added. After copolymerization the removing of homopolymers in media were done by Soxhlet with N,N-dimethylformamide (DMF) and mixture of (toluene and acetone) (50 % vol. acetone) for 6 and 8 h, respectively.

Finally, the samples were dried in vacuum at 50 °C. The percentage of grafting (G) was calculated from the equation [3,7]:

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

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

Before the saturation, the relation of the rate of grafting reaction to the change of monomers and initiator concentration at the 15th min of polymerization, were determined by these equations:

$$R_g = \frac{W_g - W_o}{V.t} \text{ and } R_g = k[I]^m[M]^n \text{ or}$$

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

where V is the volume of the solution (L), t is the polymerization time (S), [I] is the initiator concentration, [M] is the monomer mixture concentration and m, n are orders of reaction respect to initiator and monomers [14].

Determination of water absorption capacity: For this aim, the fiber samples with various per cent of grafting were achieved in 65 % sulphuric acid with density of 1.275 g/mL for 24 h. Then they were oven dried in 100 °C. Finally, they were kept in desiccator over P_2O_5 for 1 h and weighed. The per cent of the water absorption capacity was calculated according to the equation [9,17]:

$$\text{Water absorption capacity } (\%) = \left(\frac{M_n - M_o}{M_o}\right) \times 100$$

here M_n and M_o are the weights of fibers in wet environment and dry fibers, respectively.

Characterization methods: The FTIR spectra of the grafted and ungrafted fibers were recorded using a Bruker Equinox FTIR spectrophotometer with KBr discs. The SEM micrographs of PET fibers, coated with gold, were achieved using a Philips XL 30 scanning electron microscope. The therrmograms of the PET fibers carried out with TGA V5.1A Dupont in He atmosphere at the flow rate of 200 mL/min between (25-700 °C) at a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

Effect of initiator and monomer concentration: The effect of monomer mixture onto grafting yield was done at different wt % of monomers at the fixed condition of other variables ([M] = 0.2 M, [ACV] = 4.0×10^{-4} M, T = 85 °C, t = 60 min). As shown in Fig. 1 the best condition was observed at (2-HPMA/MMA) % = (60/40) %. With an increase in the monomer concentration from 0.2 to 1.5 M, the per cent of grafting was increased from 76 to 217 %. Higher quantity of grafting is undesirable for textile industry but it can be used for removal of pollutants in waste water (Table-1). The effect of ACV concentration was accomplished by the variation of ACV concentration from 2.0×10^{-3} M to 7.0×10^{-3} M at the fixed other variables. Fig. 2 showed that the maximum grafting was observed at 4.0×10^{-3} M. 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. However, the excess

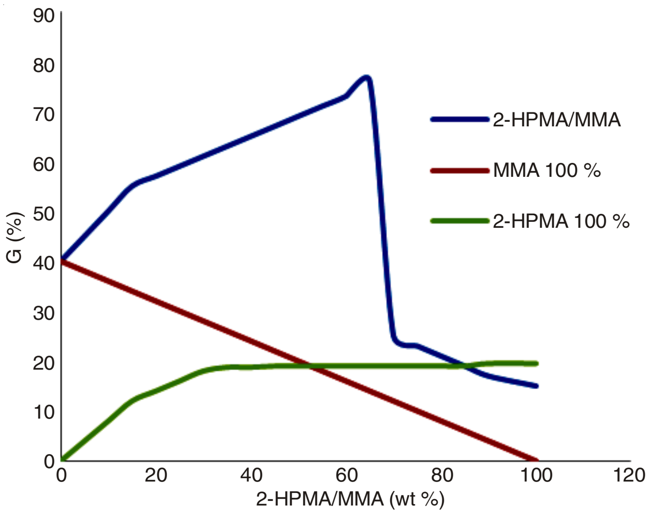


Fig. 1. Effect of monomer mixture ratio on the grafting yield: [ACV] = 4.0 × 10^{-3} M, temperature = 85 °C, [M] = 0.2, t = 60 min

TABLE-1
EFFECT OF MONOMER MIXTURE CONCENTRATION ON GRAFTING YIELD

Grafting (%)	(M)
76	0.2
122	0.5
165	1.0
217	1.5

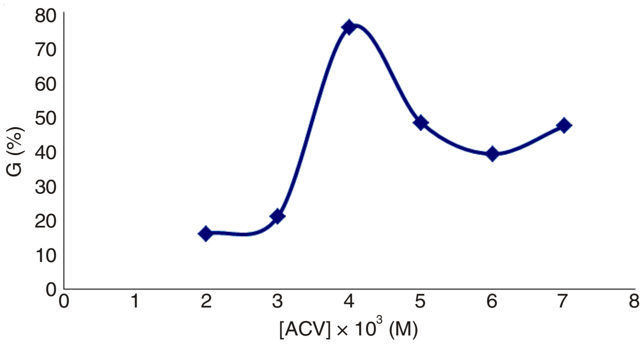


Fig. 2. Effect of ACV concentration on the grafting yield: [2-HPMA/MMA] = 0.2M (60 % 2-HPMA)/(40 % MMA) = temperature = 85 °C, t = 60 min

increasing of ACV concentration, causes an increasing of the rate of termination reactions with PET macroradicals, growing polymer chains or combination reactions. Therefore, the grafting yield decreases [9-19].

Effect of temperature and time: The effect of the temperature on the graft yield as a function of time at different temperatures (65 to 90 °C) were investigated. Usually, in a temperature, higher than T_g (≈ 70 °C), the flexibility, swellability and mobility of the PET chains increase. Subsequently, at higher temperature, the rate of ACV decomposition increases. As a result of this phenomenon, diffusion of the monomers onto PET chains and the yield of grafting become greater. Decreasing in the graft yield at higher temperature (above 85 °C) may be imputed to the increase in the rates of termination reactions [9]. The results were shown in Fig. 3.

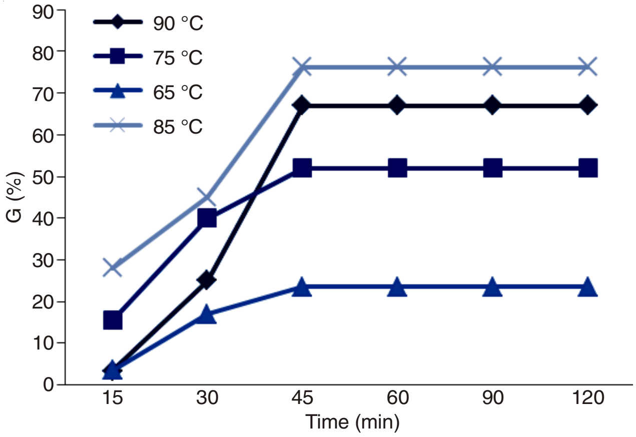


Fig. 3. Effect of temperature and time on the grafting yield: [2-HPMA/MMA] = 0.2 M, [ACV] = 4.0 × 10^{-3} M

The optimum time for grafting was determined at 45 min. After this time, due to the increasing in viscosity of solution and the parallel homopolymerization reaction causes an inhibition effect of diffusion to the PET chains [14-19].

Kinetics of grafting: Results of the variation of the monomers concentration (2-HPMA/MMA = 60/40) % from 0.05 to 0.5 M at the fixed condition (temperature = 85 °C, [ACV] = 4.0 × 10^{-3} M, time = 15 min) determined the order of reaction respect to monomer. Relation of the ln R_g + 4 *vs.* ln [M] + 3 distinguished that the rate of grafting was 1.29-order with respect to the monomer mixture (Fig. 4) and the variation of the initiator concentration from 1.0 × 10^{-3} to 6.0 × 10^{-3} M at the fixed condition (temperature = 85 °C, [M] = 0.5 M, time = 15 min), revealed the order of reaction respect to initiator. Relation of the ln R_g + 4 *vs.* ln [ACV] + 4 identified the rate of grafting was 1.71 order with respect to the ACV (Fig. 5).

Therefore, the grafting rate was determined as:

$$R_g = k[ACV]^{1.71}[M]^{1.29}$$

The overall activation energy for grafting was determined from Arrhenius plot of the log R_g + 3 *vs.* 1/T × 10^3 at the range of 65 to 85 °C in 60 min the overall activation energy was calculated 44.95 kJ/mol (Fig. 6).

Characterization of the fibers: The FTIR spectrums were recorded for grafted and ungrafted PET fibers (Fig. 7). The stretching bands at 3420 and 2967 cm^{-1} related to the ν(O-H) and ν(C=O) band observed at 1710 cm^{-1}. These absorption peaks as well as emphasized the grafting of monomers onto

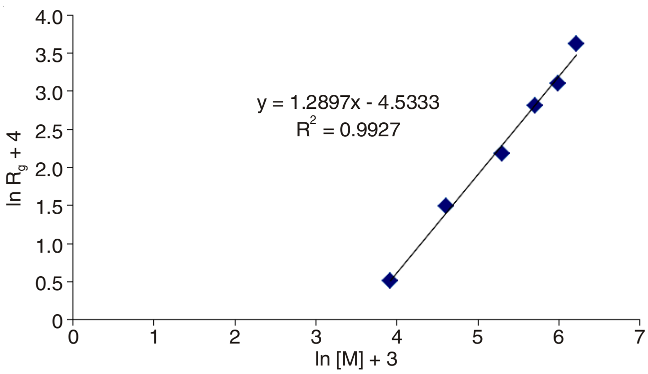


Fig. 4. Rate of grafting reaction *vs.* monomer concentration: [ACV] = 4.0 × 10^{-3} M, temperature = 85 °C, time = 15 min

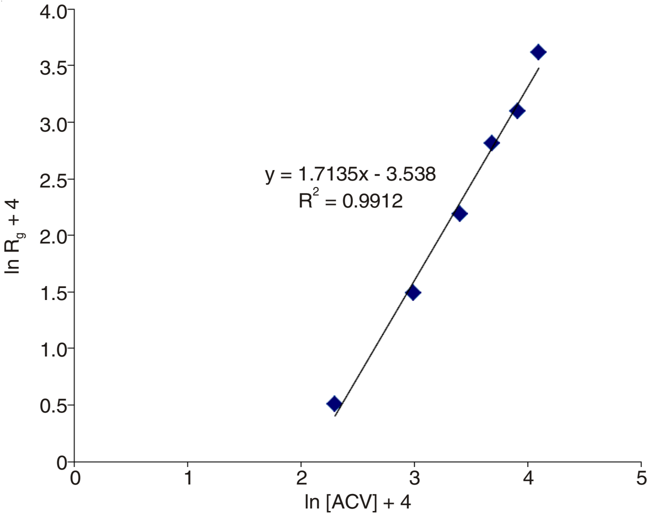


Fig. 5. Rate of grafting reaction *vs.* initiator concentration: [2-HPMA/MMA] = 0.2 M, temperature = 85 °C, time = 15 min

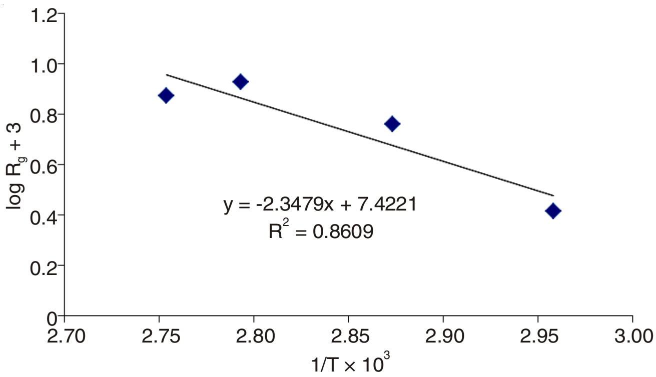


Fig. 6. Arhenius plot of log R_g *vs.* 1/T

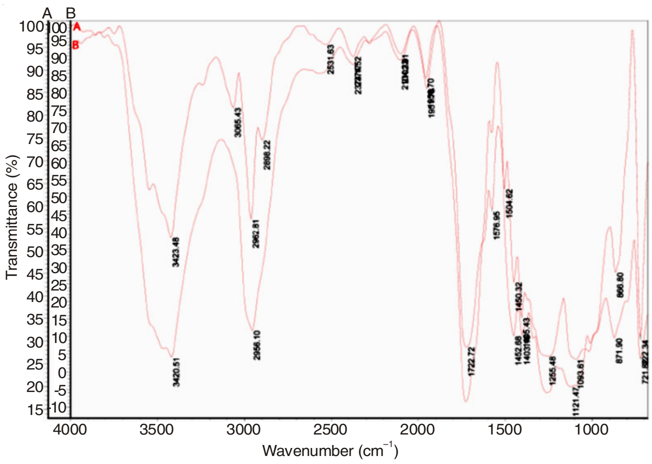


Fig. 7. FTIR spectrum of grafted and ungrafted PET fiber

PET fibers. The surface morphologies of fibers showed that with an increase of the grafting, the fibers showed a heterogeneous rough surface structure [10,11] (Fig. 8). The results of the thermograms displayed that the decomposition temperature of the fibers decreased with an increasing of the grafting [13]. Thermal decomposition temperature of 51 and 76 % of the grafted fibers decreased from 400 °C (in ungrafted PET) to 370 and 355 °C, respectively (Fig. 9). Due to the grafting, crystallinity of the fibers showed decreasing and decomposition temperature was decreased [17-19].

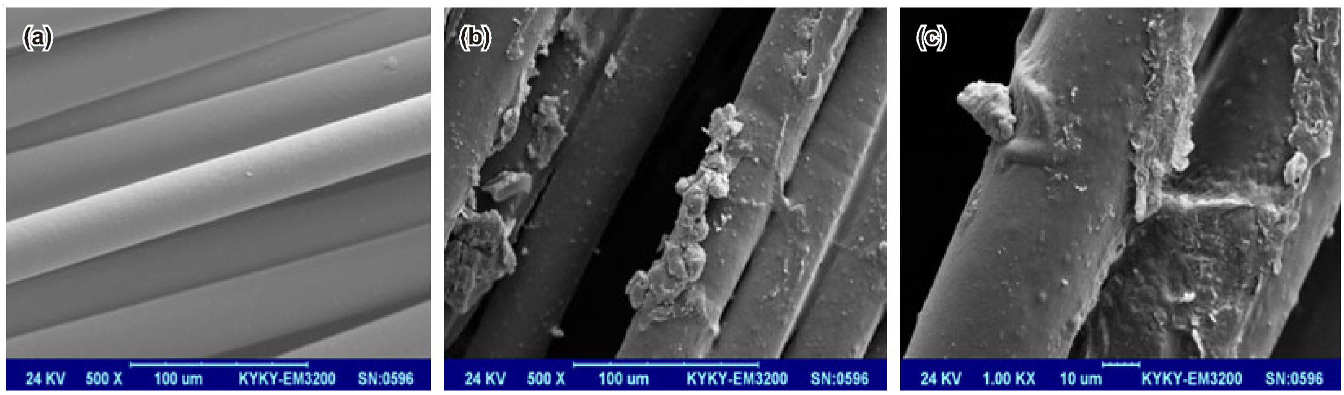


Fig. 8. SEM micrographs of (a) 0.0 % (500x), (b) 51.0 % grafted (500x) and (c) 76.0 % (1000x)

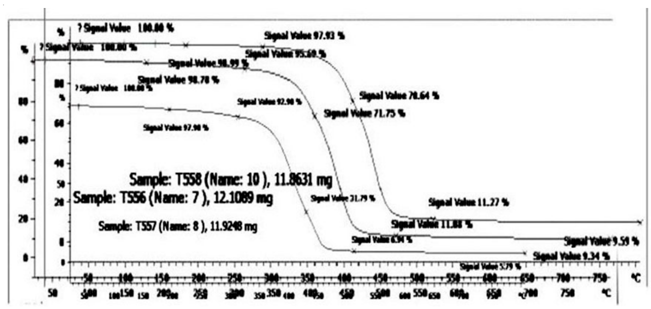


Fig. 9. Thermograms of PET fibers (a) 0.0 %, (b) 51.0 % and (C) 76.0 %

All of these results supported the grafting of monomer mixture onto PET chains. The water absorption capacity as a result of the grafting of secondary alcohol group in 2HPMA increased (Table-2).

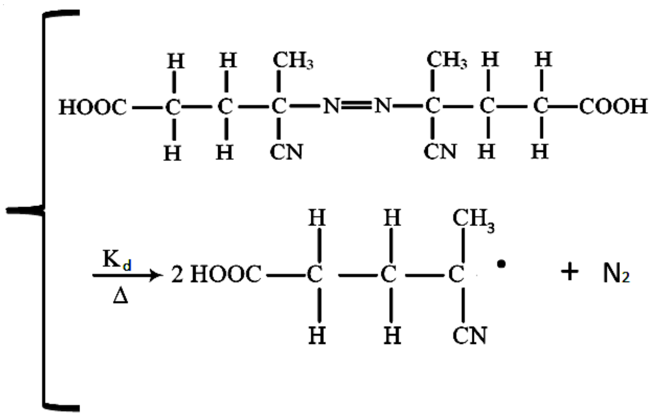
TABLE-2
EFFECT OF THE GRAFTING YIELD ON WATER ABSORPTION CAPACITY

Grafting (%)	Water absorption capacity (%)
0	0.4
19	1.2
51	2.6
76	3.1

Suggested mechanism of grafting

The suggested mechanism of grafting as this form:

Dissociation:



Initiation:

$$\text{PET} + \text{MMA} \xrightarrow{Ki(1)} \text{PET—MMA}^{\bullet}$$

$$\text{PET} + \text{2HPMA} \xrightarrow{Ki(2)} \text{PET—2HPMA}^{\bullet}$$

Propagation:

1) $\text{PET}\!-\!(\text{MMA})_{n-1}\!-\!\text{MMA}^{\bullet} + \text{MMA} \xrightarrow{K11} \text{PET}\!-\!(\text{MMA})_{n}\!-\!\text{MMA}^{\bullet}$

2) $\text{PET}\!-\!(\text{2HPMA})_{m-1}\!-\!\text{2HPMA}^{\bullet} + \text{2HPMA} \xrightarrow{K22} \text{PET}\!-\!(\text{2HPMA})_{m}\!-\!\text{2HPMA}^{\bullet}$

3) $\text{PET}\!-\!(\text{MMA})_{n-1}\!-\!\text{MMA}^{\bullet} + \text{2HPMA} \xrightarrow{K12} \text{PET}\!-\!(\text{MMA})_{n}\!-\!\text{2HPMA}^{\bullet}$

4) $\text{PET}\!-\!(\text{2HPMA})_{m-1}\!-\!\text{2HPMA}^{\bullet} + \text{MMA} \xrightarrow{K21} \text{PET}\!-\!(\text{2HPMA})_{m}\!-\!\text{MMA}^{\bullet}$

Termination:

1) $\text{PET}\!-\!(\text{MMA})_{n}\!-\!\text{2HPMA}^{\bullet} + \text{2HPMA}^{\bullet}\!-\!(\text{MMA})_{n}\!-\!\text{PET} \xrightarrow{K(t1)} \text{PET}\!-\!(\text{MMA})_{n}\!-\!\text{2HPMA—2HPMA}\!-\!(\text{MMA})_{n}\!-\!\text{PET}$

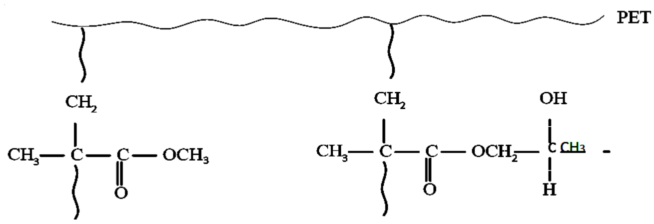
2) $\text{PET}\!-\!(\text{2HPMA})_{m}\!-\!\text{MMA}^{\bullet} + \text{MMA}^{\bullet}\!-\!(\text{2HPMA})_{m}\!-\!\text{PET} \xrightarrow{K(t1)} \text{PET}\!-\!(\text{2HPMA})_{m}\!-\!\text{MMA—MMA}\!-\!(\text{2HPMA})_{m}\!-\!\text{PET}$

3) $\text{PET}\!-\!(\text{MMA})_{n}\!-\!\text{2HPMA}^{\bullet} + \text{MMA}^{\bullet}\!-\!(\text{2HPMA})_{m}\!-\!\text{PET} \xrightarrow{K(t1)} \text{PET}\!-\!(\text{MMA})_{n}\!-\!\text{2HPMA—MMA}\!-\!(\text{2HPMA})_{m}\!-\!\text{PET}$

4) $\text{PET}\!-\!(\text{MMA})_{n}\!-\!\text{2HPMA}^{\bullet} + \text{PET}\!-\!(\text{2HPMA})_{m}\!-\!\text{MMA}^{\bullet} \xrightarrow{K(t2)} \text{PET}\!-\!(\text{MMA})_{n}\!-\!\text{2HPMA—PET}\!-\!(\text{2HPMA})_{m}\!-\!\text{MMA}$

5) $\text{PET}\!-\!(\text{MMA})_{n}\!-\!\text{2HPMA}^{\bullet} + \text{PET}\!-\!(\text{MMA})_{n}\!-\!\text{2HPMA}^{\bullet} \longrightarrow \text{PET}\!-\!(\text{MMA})_{n}\!-\!\text{2HPMA}$

6) $\text{PET}\!-\!(\text{2HPMA})_{m}\!-\!\text{MMA}^{\bullet} + \text{PET}\!-\!(\text{2HPMA})_{m}\!-\!\text{MMA}^{\bullet} \longrightarrow \text{PET}\!-\!(\text{2HPMA})_{m}\!-\!\text{MMA}$



Conclusion

In this study, grafting of the 2-HPMA/MMA mixture onto PET fibers by the using of ACV as an initiator was done, successfully. The optimum conditions of grafting were determined to be [ACV] = 4.0 × 10^{-3} M, [2-HPMA/MMA] = 0.2 M, (2-HPMA/MMA) = (60/40) wt %, temperature = 85 °C, time = 45 min. The rate of grafting was found to 1.29 power of monomer and 1.71 power of initiator. The overall activation energy for grafting was calculated as 44.95 kJ/mol. With an increase of the grafting yield the water absorption capacity increased.

REFERENCES

1. M. Okoniewski, J. Sojka-Ledakowicz and S. Ledakowicz, *J. Appl. Polym. Sci.*, **35**, 1241 (1988).
2. M. Sacak and E. Pulat, *J. Appl. Polym. Sci.*, **38**, 539 (1989).
3. M. Sacak, N. Bastug and M. Talu, *J. Appl. Polym. Sci.*, **50**, 1123 (1993).
4. E.M. Abdel-bary, A.A. Sarhan and H.H. Abdel-Razik, *J. Appl. Polym. Sci.*, **35**, 439 (1988).
5. M. Sacak, F. Sertkaya and M. Talu, *J. Appl. Polym. Sci.*, **44**, 1737 (1992).
6. M.M. Nasef, *J. Appl. Polym. Sci.*, **84**, 1949 (2002).
7. M. Arslan, M. Yigitoglu, O. Sanli and H.I. Unal, *Polym. Bull.*, **51**, 234 (2003).
8. H.I. Unal, C. Inegollu and O. Sanli, *Turk. J. Chem.*, **27**, 403 (2003).
9. F. Azizinezhad, *Asian J. Chem.*, **23**, 899 (2011).
10. F. Azizinezhad, *Asian J. Chem.*, **23**, 839 (2011).
11. M. Celik and M. Sacak, *J. Appl. Polym. Sci.*, **59**, 609 (1996).
12. A. Hebeish, S.E. Shalaby and A. Bayazeed, *J. Appl. Polym. Sci.*, **27**, 197 (1982).
13. R. Coskun, *Eur. Polym. J.*, **43**, 1428 (2007).
14. R. Coskun, M. Sacak and M. Karakisla, *J. Appl. Polym. Sci.*, **97**, 1795 (2005).
15. M. Arslan, *Korean J. Chem.*, **27**, 991 (2010).
16. M. Yigitoglu and M. Arslan, *Polym. Bull.*, **58**, 785 (2007).
17. F. Azizinejad, M. Talu, M. Abdouss and M. Shabani, *Iran. Polym. J.*, **14**, 33 (2005).
18. F. Azizinejad, *Bull. Environ. Pharmacol. Life Sci.*, **3**, 176 (2014).
19. F. Azizinejad, *Eur. J. Exp. Bio.*, **4**, 560 (2014).