Azobisisobutyronitrile-Initiated Graft Copolymerization of Methyl Methacrylate onto Poly(ethylene terephthalate) Fibers

MEHMET SAÇAK,[1,*] NERIMAN BAŞTUĞ,[2] and MUZAFFER TALU[2]

[1]Ankara University, Faculty of Sciences, Chemistry Department, 06100 Ankara, Turkey; and [2]Gazi University, Faculty of Science and Arts, Chemistry Department, 06500 Ankara, Turkey

SYNOPSIS

In this study, the grafting of methyl methacrylate onto poly(ethylene terephthalate) fibers using azobisisobutyronitrile is reported. An increase in temperature and monomer concentration were found to increase the graft yield. The graft yield increased up to an initiator concentration of 0.90×10^{-2} mol/L and decreased at higher initiator concentrations. The fiber densities decreased, and fiber diameters and intrinsic viscosities increased with increasing graft yield. Moisture regain values showed a slight increase with the grafting. Fiber orientation decreased the graft yield to an important extent. The overall activation energy for grafting was calculated to be 11.9 kcal/mol. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Vinyl monomers can be grafted onto poly(ethylene terephthalate) (PET) fibers by various ways. However, since PET is a hard substrate, containing no chemically reactive groups, its graft yield is much lower compared with other fibers.[1] Radiation grafting is easy to control; however, it gives a low radical yield and there is a problem of degradation of PET (above 5 Mrad).[2,3] Chemical methods are more advantageous as regards the degradation of the main polymer.[4]

ESR studies showed that the irridiation of PET with γ-rays gave the following radicals[5,6]:
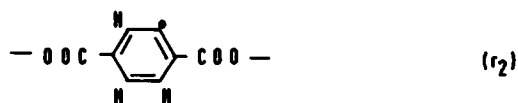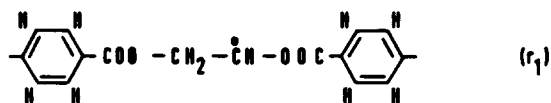
These radicalic sites (r_1 and r_2) that are necessary for the initiation of grafting can be generated by radiation[7-13] or chemical methods.[14-19] The main purposes of grafting various vinyl monomers onto PET fibers are to improve their inferior properties and to furnish them with new properties. These studies also concentrate upon the effects of various factors such as monomer and initiator concentrations, temperature, time, cations, and pH upon the graft copolymerization as well as investigating the properties of grafted fibers.[4,7,9,12,15,18]

Methyl methacrylate is one of the monomers that has been used by various workers for grafting onto PET fibers. Nayak et al. used potassium permanganette-oxalic acid,[20] pentavalent vanadium,[21] and tetravalent cerium[4] as initiators in the grafting of methyl methacrylate onto PET fibers. Hebeish et al.[19] investigated the grafting of methyl methacrylate onto PET fibers using hydrogen peroxide. There are also reports concerning grafting with potassium bromate–thiourea[17] and the acetyl acetonate complex of tetravalent vanadium.[22]

However, there are no studies in the literature concerning radicalic methyl methacrylate grafting onto PET fibers using asobisisobutyronitrile. This report is about the results of methyl methacrylate grafting onto PET fibers using a radicalic initiator.

EXPERIMENTAL

Materials

The PET fibers used in the experiments (28 flament, stretch ratio 2) were provided by SASA Co. (Adana, Turkey). The fiber samples prepared as small hanks (0.30 ± 0.01 g) were Soxhlet-extracted with acetone for 6 h and dried at ambient conditions. Methyl methacrylate (MMA) (Merck) was washed with 5% NaOH three times, kept over $CaCl_2$ overnight, and distilled in vacuum at 46°C. Azobisisobutyronitrile (AIBN) (BDH) was recrystallized twice from methanol and dried over P_2O_5 in a vacuum desiccator. AIBN was freshly prepared and kept in the dark throughout the experiments. Other chemicals were chemically pure grade.

Grafting Procedure

The graft copolymerization was carried out in 100 mL Pyrex tubes. The polymerization tube containing the PET fiber sample, monomer, and 45 mL deionized water was placed in a water bath (Lauda D 40 S, Germany, ±0.1°C) adjusted to the polymerization temperature and kept there for 5 min and then 5 mL acetone containing appropriate amount of AIBN was added. The fibers taken from the polymerization system following the grafting procedure were roughly washed with acetone and kept in 100 mL benzene overnight. They were then Soxhlet-extracted with benzene for 8 h and with acetone for 6 h. The samples were finally dried and weighed. The graft yield was gravimetrically determined from the difference between the original and grafted fiber weights.

Measurement of Density and Diameter

The densities of the fiber samples were determined using a density gradient tube (with a height of 40 cm and radius of 5 cm) prepared with xylene and carbon tetrachloride at 23°C. The calibration of the column was made with marker floats (made by Davenport Ltd.) whose densities were known at an accuracy of 1/10,000. The levels of the fiber samples and marker floats were determined using a cathetometer (within a sensitivity of ±0.01 mm).

The diameter measurements were carried out using a Nikkon Type 104 optical microscope at a magnification of ×600. The diameters were measured using at least five samples.

Determination of Moisture Regain and Intrinsic Viscosity

The fiber samples were conditioned at 20°C in a medium having a relative humidity of 65% to determine the moisture regain value. The moisture regain values were calculated from the weight difference between the dry and conditioned samples. The viscosities were determined using a Ubbelohde viscosimeter in m-cresol at 25°C.

RESULTS AND DISCUSSION

The common method for the removal of the homopolymer of the grafted monomer from the fiber is the extraction of the homopolymer with an appropriate solvent or solvents. This time- and solvent-consuming process is preferred due to its easy applicability. It has a minimal effect upon the structure of the main polymer. In the studies concerning with the grafting of MMA, the major solvents used for the extraction of the homopolymer are acetone[19,23,24] and benzene.[25,26] Here, both these solvents were used subsequently for the extraction of poly(MMA). It is not very clear whether the marked increase in the fiber weight was due to the grafting and/or to *in situ* polymerization even after prolonged solvent extraction. However, it is believed that the mechanism of these polymerization reactions is a grafting process. That was why the increase in the fiber weight after the grafting was taken here as the graft yield.

Effect of Temperature and Time

MMA is a monomer known to have a tendency toward thermal polymerization.[27] The fact that whether there was any thermal grafting present or not was controlled by preexperiments. For this purpose, the fiber samples were kept in a medium having only water and monomer (no initiator) at 90°C for 4 h; then, they were washed, dried, and weighed. No variation in the fiber weight was observed after these experiments were repeated several times. This completely eliminated any question of thermal grafting.

The graft copolymerization was carried out at five different temperatures between 60 and 90°C. The experimental data are given in Table I. Some experiments were carried out more than once in order to check the reproducibility of the data. One may think that the reproducibility in Table I was poor. This could have been caused by the entrapment of poly(MMA) within the fiber structure in spite of the long extraction times. This poor experimental reproducibility was also observed in the grafting studies carried out onto PET,[15,18] wool,[28] and nylon.[29]

Figure 1 was drawn by taking the averages of the values in Table I (given in parentheses). It shows

Table I Effect of Polymerization Temperature and Time upon Graft Yield[a]

Time (min)	Graft Yield (%)[b]				
	60°C	65°C	70°C	80°C	90°C
5	0.0	0.0	0.7	0.8	2.2
				1.3	2.6
				(1.1)	(2.4)
10	0.0	0.5	2.8	3.6	5.7
		0.7	1.4	3.6	4.9
		(0.6)	(2.1)	(3.6)	(5.3)
15	0.0	1.2	3.8	5.1	6.7
		1.7	3.9		7.7
		(1.5)	(3.9)		(7.2)
20	0.0	1.8	4.5	5.3	8.5
		2.6	4.6	5.7	8.5
		(2.2)	(4.6)	(5.5)	(8.5)
30	0.6	1.9	5.5	6.5	12.0
		2.7	5.6	6.7	
		(2.3)	(5.6)	(6.6)	
45	1.1	3.7	6.2	7.6	14.7
				8.5	
				(8.1)	
60		3.5	7.6	9.8	14.4
		3.5	7.8	8.2	15.0
		(3.5)	(7.7)	(9.0)	(14.7)
75	1.3	4.2	7.4	9.0	15.8
				8.6	13.9
				(8.8)	(15.4)
90	1.5	3.9	6.7	9.2	14.3
			7.8		14.7
			(7.3)		(14.5)

[a] [MMA] = 0.150 mol/L; [AIBN] = 0.90 × 10^{-2} mol/L.

[b] Values given in parentheses are the averages of the graft yields.

that increase in the temperature increases the rate of grafting and the saturation graft yield. It took about 45 min to reach the saturation graft yield at all the temperatures tried except 60°C. There was a 20 min induction period at 60°C.

In the polymerization system similar to ours, monomer is consumed in both the grafting and homopolymerization steps. The fact that graft yield remains constant after a certain time (saturation graft yield) is clearly due to a decrease in monomer concentration present in the solution and diffused into the fiber phase.
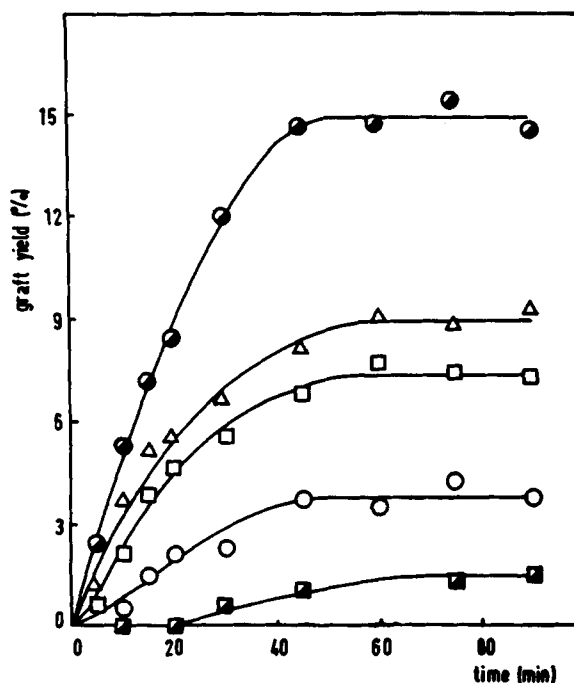
The increase in the temperature increases the rate of initiation and propagation reactions. It also increases the swellability of PET fibers and facilitates the diffusion into the fiber structure. The PET segments are more mobile particularly at temperatures above the glass transition temperature (80°C).[7] The reactivity of PET fibers is also increased above this

temperature. From Figure 1, it can be seen that the saturation graft yield shows a sharp increase for 90°C. The saturation graft yield increased from 7.5 to 9.0% when the temperature was increased from 70 to 80°C (20% increase in saturation graft yield). Increasing the temperature from 80 to 90°C, on the other hand, caused a 66% increase in the saturation graft yield to 15.0% (Fig. 1).

The overall activation energy for grafting was computed from the Arrhenius plot of log rate of grafting (Rg) vs. $1/T$ (Fig. 2); it amounts to 16.1 kcal/mol.

Effect of Monomer and Initiator Concentration

The graft yields obtained at various MMA concentrations, keeping other factors constant, are plotted in Figure 3. The increase in the monomer concentration caused the saturation graft yield and the grafting rate to increase. An induction period of 10 min for an MMA concentration of 0.038 mol/L was observed only among all the monomer concentrations employed. The increase in the monomer concentration increases the amount of MMA present in the external solution and diffused into the PET fiber phase. This enhances the chance of PET macroradicals and growing side poly(MMA) chains to react with MMA molecules. The number of active

Figure 1 Variation of graft yield with polymerization temperature: [MMA] = 0.150 mol/L; [AIBN] = 0.90 × 10^{-2} mol/L: (■) 60°C; (O) 65°C; (□) 70°C; (△) 80°C; (●) 90°C.
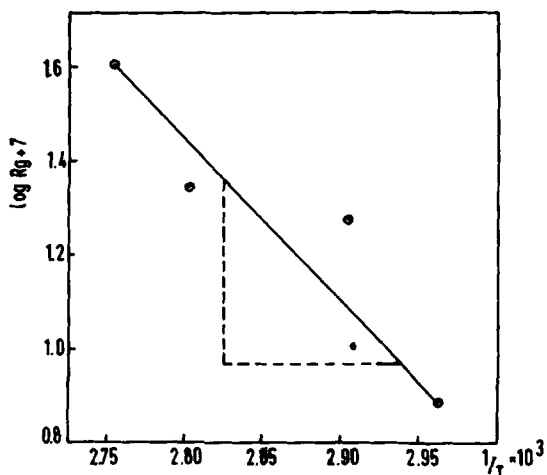
Figure 2   Arrhenius plot of log Rg vs. $1/T$.

poly(MMA) chains in the polymerization medium also increases depending upon the increase in the monomer concentration. This increases the probability of chain-transfer reactions between these active chains and PET macromolecules that form the active sites necessary for grafting. These factors increase both the graft yield and the rate of grafting.

The monomer consumption time will increase with increasing monomer concentration, provided that all other factors remain constant. In other words, the time to reach the saturation graft yield will be longer. When Figure 3 is examined, it is seen that the time to reach the saturation graft yield was
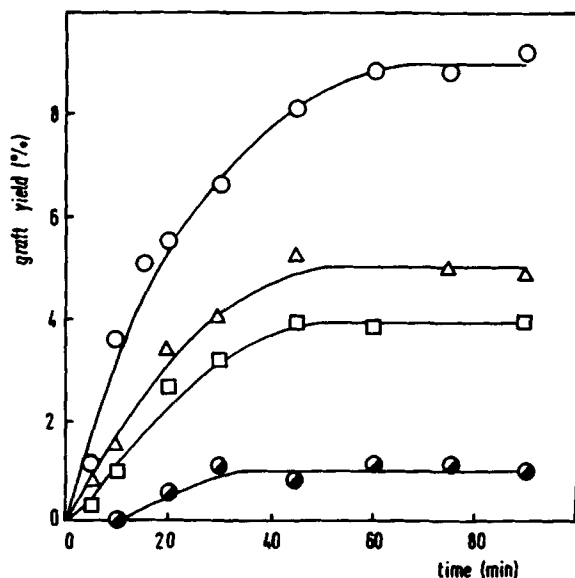
30 min for a monomer concentration of 0.038 mol/L and that it increased up to 60 min for a monomer concentration of 0.152 mol/L.

Figure 4 gives the relation between the graft yield and AIBN concentration. The graft yield rapidly increased up to an initiator concentration of 0.90×10^{-2} mol/L and decreased at concentrations higher than that. This is a typical behavior observed in many studies.[15,18,19] The increase in AIBN concentration increases the number of active poly(MMA) chains that give chain-transfer reactions with PET macromolecules. Also, the number of free radicals formed as a result of AIBN dissociation increases. These free radicals may create suitable active sites for grafting by hydrogen abstraction directly from the PET backbone. These chain-transfer and hydrogen abstraction reactions have an increasing effect upon the graft yield. However, the further increase in the initiator concentration (above 0.90×10^{-2} mol/L) causes the termination reactions to dominate and decreases the graft yield.

The experimental results showing the change of the rate of grafting (Rg) with concentration of AIBN and MMA are tabulated in Tables II and III. Kinetic investigation of the effect of AIBN (Fig. 5) on Rg revealed that Rg was proportional to the 0.92 power of AIBN concentration.

Figure 6 shows the plot of Rg vs. MMA concentration. As is evident, Rg is also proportional to the
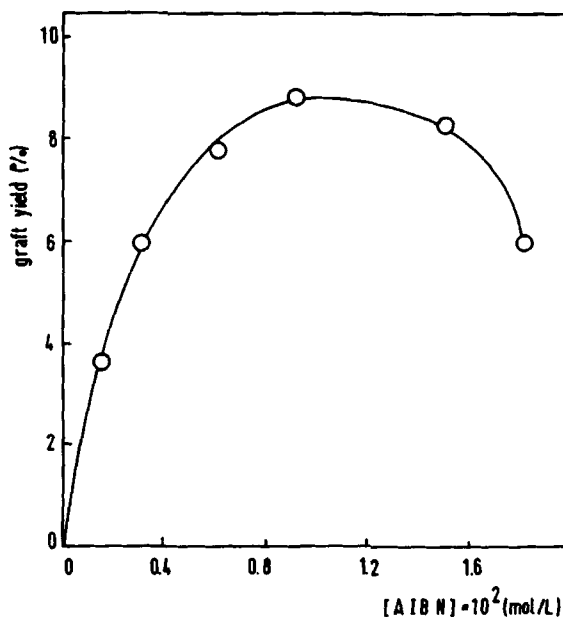

Figure 3   Variation of graft yield with MMA concentration: [AIBN] = 0.90×10^{-2} mol/L; temperature, 80°C; [MMA] (mol/L): (●) 0.038; (□) 0.075; (△) 0.113; (○) 0.1.50.

Figure 4   Variation of graft yield with AIBN concentration: [MMA] = 0.150 mol/L; temperature, 80°C; time, 1 h.

Table II Dependence of Rate of Grafting (Rg) on AIBN Concentration

Graft Yield[a] (%)	log[AIBN] + 4	log Rg + 8
0.2	0.288	1.000
0.8	1.288	1.597
2.3	1.589	2.068
5.5	1.855	2.439

[a] Values obtained, before reaching saturation, at 13th min.

1.30th power of [MMA]. Therefore, the grafting rate equation of MMA onto PET fibers can be written as

$$Rg = k[MMA]^{1.30}[AIBN]^{0.92}$$

Effect of Reaction Medium

Table IV lists the experimental data related to the effects of various solvents upon the graft yield. It is seen that all the solvents employed have a decreasing effect upon the graft yield. The increase in the amount of solvent in the water/solvent mixture further decreases the graft yield. The grafting is completely inhibited at 60/40 (v/v) water/methanol and 80/20 (v/v) water/DMSO ratios. The effects of solvents added to the graft copolymerization medium are highly complex. These solvents may take place in the chain-transfer, initiation, and termination reactions. They may have a serious effect upon the diffusion of monomer, initiator, and other reactivities into the fiber phase (by affecting the swellability of PET fibers). However, according to Table IV, we can conclude that the solvents used in the grafting of MMA onto PET fibers with AIBN have the following order as regards their effect upon the graft yield:

n-propanol > pyridine > ethanol–DMF

> DMSO–methanol

Table III Dependence of Rate of Grafting (Rg) on MMA Concentration

| Graft Yield[a] (%)	log[MMA] + 2	log Rg + 7
1.1	0.580	0.564
3.2	0.875	1.028
4.0	1.053	1.125
6.6	1.176	1.342

[a] Values obtained, before reaching saturation, at 13th min.
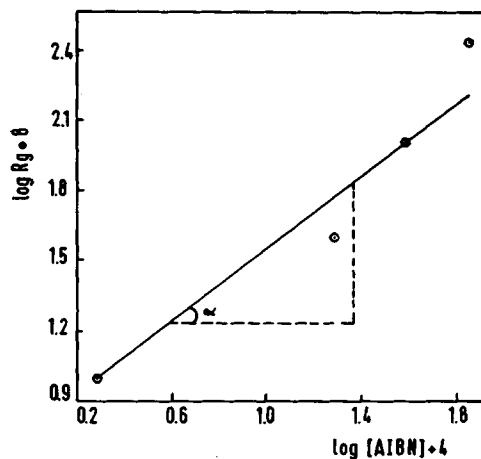
Figure 5 Rates of grafting (Rg) vs. [AIBN].

Effect of Orientation

In this part of study, the effect of orientation upon the graft yield was examined. The PET fibers (with a stretch ratio of 2) were mechanically stretched at room temperature.

These fiber samples were subjected to graft copolymerization at the same conditions employed with the unstretched PET fibers. Figure 7 shows that orientation decreased the graft yield significantly. The graft yield of 9.0% that was obtained with unstretched fibers after 1 h decreased to 3.0% with stretched fibers. An induction period of 10 min was observed in the stretched fibers. The easy diffusion of monomer molecules into the PET fibers is of great importance for effective grafting. Orientation causes randomly distributed long PET chains to lie parallel to the fiber axis. This type of orientation impedes the diffusion into the fiber phase. Also, the orientation of the PET chains makes them
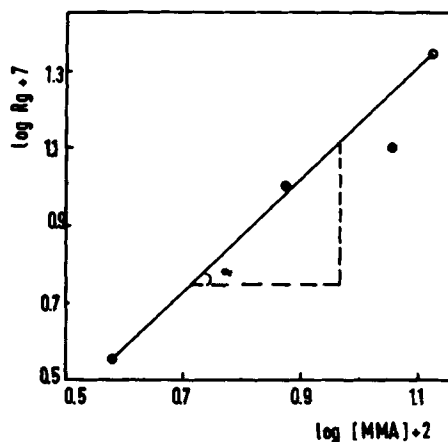
Figure 6 Rates of grafting (Rg) vs. [MMA].

Table IV Effect of Some Solvents on Graft Yield[a]

Water/Solvent Ratio (v/v)	Graft Yield (%)					
	n-Propanol	Pyridine	Ethanol	DMF[b]	DMSO[b]	Methanol
100/00	8.8	8.8	8.8	8.8	8.8	8.8
90/10	8.5	7.2	6.2	4.7	5.7	3.7
80/20	7.7	6.8	5.7	4.4	0.0	1.6
60/40	3.7	4.6	2.0	4.2	0.0	0.0
50/50	2.9	4.4	1.2	3.5	0.0	0.0
30/70	1.5	2.1	0.7	2.7	0.0	0.0

[a] [MMA] = 0.150 mol/L; [AIBN] = 0.90 × 10^{-2} mol/L; time 1 h; temp 80°C.
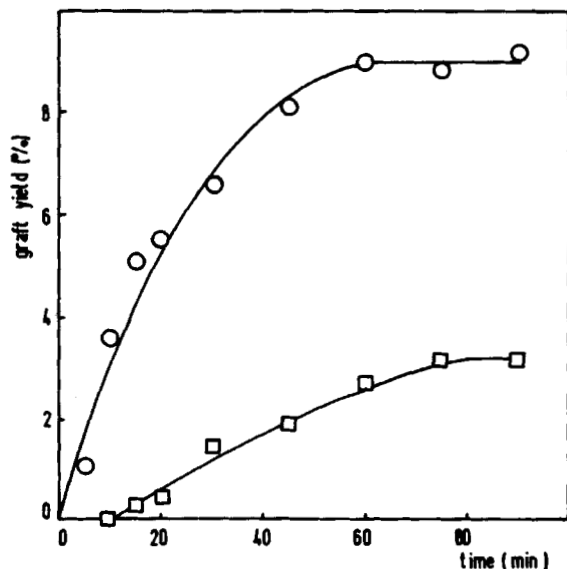[b] DMF = dimethylformamide; DMSO = dimethylsulfoxide.

approach each other and decreases the number of domains that can accept the grafted side polymer chains. The effect of these factors decreases the graft yield, as expected.

SOME PROPERTIES OF MMA-GRAFTED FIBERS

The diameter, density, and moisture regain values of PET fibers grafted with different amounts of MMA are given in Table V. According to this table, grafting increases the diameter but decreases the density of the fibers. For instance, the density of 1.3763 g/cm³ and diameter of 1.9528 × 10^{-2} mm of ungrafted PET fiber change to 1.3616 g/cm³ and

2.3393 × 10^{-2} mm of 14.6% MMA-grafted fiber, respectively. This shows that the contribution of grafting upon fiber volume is higher than upon fiber weight. Although poly(MMA) has a lower density than that of PET (1.1870 g/cm³ compared to 1.3763 g/cm³), one should also be aware of the contribution of the opening structure of the fiber due to grafting onto the decreasing density. Table V indicates that the moisture regain values do not show a significant increase with MMA grafting.

Figure 8 illustrates the η_{sp}/c–c relations of the grafted PET fibers. The intrinsic viscosity values (the points where the lines intersect the y-axis) increase with grafting. Similar behavior was observed in the grafting of acrylamide onto PET[15] and nylon 6.[30] The intrinsic viscosities of pure PET, 10.7% grafted PET, and 14.6% grafted PET were 0.60, 1.20, and 1.50 dL/g, respectively.

CONCLUSION

Our experimental results show that MMA can be grafted onto PET fibers using AIBN as an initiator. We have investigated the factors affecting grafting


Figure 7 The effect of orientation upon the graft yield: (O) unstretched PET; (□) stretched PET; temperature, 80°C; time, 1 h; [MMA] = 0.150 mol/L; [AIBN] = 0.90 × 10^{-2} mol/L.

Table V Diameter, Density, and Moisture Regain Values of MMA-Grafted PET Fibers

Graft Yield (%)	Diameter (mm × 10^{-2})	Density (g/cm³)	Moisture Regain (%)
Ungrafted	1.9528	1.3763	0.42
3.2		1.3745	0.45
5.7	2.0504	1.3695	0.53
7.4		1.3686	0.58
10.7	2.1969	1.3660	0.62
12.0		1.3639	0.70
14.6	2.3393	1.3616	0.74
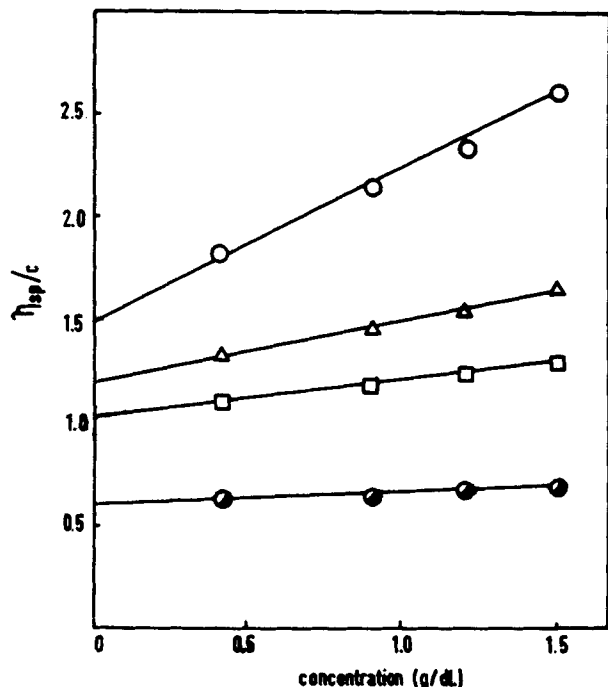
Figure 8 η_{sp}/c-c Relations of the MMA-grafted PET fibers. Grafting values: (⬤) ungrafted; (□) 5.7%; (△) 10.7%; (○) 14.6%.

and some properties of MMA-grafted PET fibers in detail. As can be seen from the experimental results, even at temperatures as low as 60°C, AIBN enables grafting of MMA onto PET fibers. This is due to a low decomposition temperature of AIBN compared to other radical initiators. To obtain high graft yields, it is necessary to increase temperature and monomer concentrations. On the other hand, the initiator concentration must be chosen at an optimum $(0.90 \times 10^{-2} \text{ mol/L})$ concentration. The research on oriented PET fibers showed that fiber orientation (diffusion) is an important parameter for an effective grafting. The solvent used in the graft copolymerization system is also an important factor affecting grafting. Experimental data have shown us that aqueous media is favorable for the grafting of MMA onto PET using AIBN. The grafting of MMA affects some properties of PET fibers. The intrinsic viscosity increases with the increase in grafting, but moisture regain shows very little increase with grafting. Also, grafting decreases the fiber density while increasing the fiber diameters.

REFERENCES

1. I. Sakurada, Y. Ikada, and T. Kawahara, *J. Polym. Sci. A*, **11**, 2329 (1973).
2. T. Memetea and V. Stannet, *Polymer*, **20**, 465 (1979).
3. S. P. Potnis, S. M. Shetty, K. N. Rao, and J. Prakash, *Angew. Makromol. Chem.*, **6**, 127 (1969).
4. A. K. Pradhan, N. C. Pati, and P. L. Nayak, *J. Appl. Polym. Sci.*, **27**, 1873 (1982).
5. D. Campbell, K. Araki, and T. Turner, *J. Polym. Sci. A-1*, **4**, 2597 (1966).
6. D. Campbell and T. Turner, *J. Polym. Sci. A-1*, **5**, 2199 (1967).
7. E. Schamberg and J. Hoige, *J. Polym. Sci. A-1*, **8**, 693 (1970).
8. S. A. Faterpeker and S. P. Potnis, *Angew. Makromol. Chem.*, **90**, 69 (1980).
9. M. H. Rao, K. N. Rao, H. T. Lokhande, and M. D. Teli, *J. Appl. Polym. Sci.*, **33**, 2707 (1987).
10. V. M. Rudoi, L. P. Sidorava, and V. YA. Kabanov, *Polym. Sci. U.S.S.R.*, **30**, 376 (1988).
11. Y.-L. Hsieh, M. Shinawatra, and M. D. Castillo, *J. Appl. Polym. Sci.*, **31**, 509 (1986).
12. P. D. Kale, H. T. Lokhande, K. N. Rao, and M. H. Rao, *J. Appl. Polym. Sci.*, **19**, 461 (1975).
13. A. Mey-Marom and L. A. Rajbenbach, *J. Appl. Polym. Sci.*, **28**, 2411 (1983).
14. A. Hebeish, S. Shalaby, A. Waly, and A. Bayazed, *J. Appl. Polym. Sci.*, **28**, 303 (1983).
15. M. Saçak and E. Pulat, *J. Appl. Polym. Sci.*, **38**, 539 (1989).
16. I. F. Osipenko and V. I. Martinovicz, *J. Appl. Polym. Sci.*, **39**, 935 (1990).
17. M. K. Mishra, B. L. Sar, and A. K. Tripathy, *J. Macromol. Sci.-Chem.*, **A18**(4), 565 (1982).
18. M. Saçak, F. Sertkaya, and M. Talu, *J. Appl. Polym. Sci.*, **44**, 1737 (1992).
19. A. Hebeish, S. E. Shalaby, and A. M. Bayazeed, *J. Appl. Polym. Sci.*, **26**, 3253 (1981).
20. A. K. Pradhan, N. C. Pati, and P. L. Nayak, *J. Appl. Polym. Sci.*, **27**, 2131 (1982).
21. P. L. Nayak, S. Lenka, M. K. Mishra, and A. K. Tripathy, *J. Appl. Polym. Sci.*, **26**, 2773 (1981).
22. S. Lenka, *J. Polym. Sci. Polym. Lett. Ed.*, **21**, 281 (1981).
23. Y. Huang, B. Zhao, G. Zheng, S. He, and J. Gao, *J. Appl. Polym. Sci.*, **45**, 71 (1992).
24. J. Mamauchi, A. Yamaoka, K. Ikemoto, and T. Matsui, *J. Appl. Polym. Sci.*, **43**, 1197 (1991).
25. D. S. Varma and N. D. Ray, *Angew. Makromol. Chem.*, **32**, 81 (1973).
26. M. H. El-Rafie, M. I. Khalil, and A. Hebeish, *J. Appl. Polym. Sci.*, **19**, 1677 (1975).
27. L. S. Luskin and R. J. Myers, in *Encyclopedia of Polymer Science and Technology*, Wiley, New York, 1964, Vol. 1, p. 268.
28. J. L. Garnet, R. S. Kenyon, and J. D. Leeder, *J. Polym. Sci. Polym. Lett. Ed.*, **15**, 93 (1977).
29. G. Odion, M. Sobel, A. Rossi, R. Klein, and T. Acker, *J. Polym. Sci. A*, **1**, 639 (1963).
30. A. K. Mukherjee, H. S. Sachder, and A. Gupta *J. Appl. Polym. Sci.*, **28**, 2217 (1983).