

Grafting of Poly(ethylene Terephthalate) Fibers with Methacrylic Acid Using Benzoyl Peroxide

MEHMET SAÇAK,¹ FILIZ SERTKAYA,² and MUZAFFER TALU²

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

SYNOPSIS

The graft copolymerization of methacrylic acid onto poly(ethylene terephthalate) fibers, by the aid of benzoyl peroxide, have been investigated. The graft yield increased up to 85°C, and then decreased with the further increase in temperature. The maximum graft yield was obtained at benzoyl peroxide concentration of 4.0×10^{-3} mol/L. The increase in the concentration of monomer was found to increase the graft yield. The change in the graft yield was followed by the experiments carried out using different water/solvent mixtures. Also, the change in the properties of poly(ethylene terephthalate) fibers grafted with methacrylic acid such as moisture regain, density, and diameter were investigated.

INTRODUCTION

There is a widespread use of fibers of synthetic origin in the textile industry today. Poly(ethylene terephthalate) (PET) fibers have a prominent place among these synthetic fibers. However, in spite of many superior properties of PET fibers, some of their poor features such as low moisture regain, difficulty of dyeing, and poor antistatic properties limit their fields of usage.

One of the most common ways resorted to, to give new properties or improve poor features of PET fibers, is grafting various monomers onto them by graft copolymerization. It is generally thought that, as a result of graft copolymerization, the properties of PET backbone are not affected and the fibers acquire new properties, depending upon the monomer grafted.

The graft copolymerization can be chemically initiated using initiators such as benzoyl peroxide,¹⁻³ hydrogen peroxide,^{4,5} azobisisobutyronitrile,⁶ and ceric ion.^{7,8} The grafting studies carried out using irradiation techniques also have a prominent place in the literature.⁹⁻¹³

Many monomers such as acrylic acid,^{1,2,12,14,15} acrylamide,^{3,16} vinyl acetate,¹⁷ styrene,^{6,9,11} and bromostyrene¹⁸ have been employed in grafting studies.

There are also studies concerned with the grafting of methacrylic acid onto PET fibers in the literature. Schamberg¹⁹ investigated the behavior of PET fibers grafted with methacrylic acid in alkaline media. Rao et al.²⁰ examined the effect of addition of H and OH scavengers to the medium, upon the polymerization reactions (homopolymerization and grafting) during grafting of acrylic and methacrylic acid onto PET fibers with irradiation. Matsuzaki et al.²¹ investigated the stereoregularity of the PET fibers grafted with methacrylic acid and methyl methacrylate using irradiation technique. The other related literatures are generally patented.²²⁻²⁶

In graft copolymerization the investigation of the factors affecting the grafting (such as temperature, monomer, and initiator concentration) is as important as the investigation of the properties of grafted PET fibers. In this study, the effect of the changes of the graft copolymerization conditions upon the graft yield of methacrylic acid onto PET fibers using benzoyl peroxide initiator has been examined. Also the changes observed in the physical properties of PET fibers grafted with methacrylic acid such as moisture regain, diameter, and density are reported here.

EXPERIMENTAL

Materials

The PET fibers (126 denier, 28 filaments) used in these experiments were provided by Sasa Co. (Adana, Turkey). The fiber samples were first washed with luke-warm water. They were then Soxhlet-extracted for 6 h with acetone and dried at ambient temperature. Methacrylic acid (MAA) was saturated with NaCl, kept overnight, filtered, dried over CaCl₂, and vacuum-distilled over column filled with copper wires at 40°C. The MAA freshly distilled throughout the study and stored in dark. Benzoyl peroxide (Bz₂O₂) were recrystallized twice from methanol-chloroform mixture and dried in vacuum. All other chemicals were chemically pregrade.

Polymerization Procedure

The grafting procedures were carried out in 100 mL polymerization vessels. The mixture containing PET fiber sample (0.30 ± 0.01 g), monomer, and Bz₂O₂ at required concentration in 5 mL acetone was made up to 50 mL with deionized water. The mixture was immediately placed into the water bath (Lauda D 40 S, Germany) adjusted to the polymerization temperature. The fiber samples taken from the mixture at the end of the graft copolymerization was roughly washed with water. They were then subjected to a thorough washing procedure in boiling water for 4 h by changing the washing water at least three times during this period. It was finally Soxhlet-extracted with methanol for 8 h. The percentage increase in the fiber weight was taken as the graft yield percentage.

Measurement of Density

The densities of the fiber samples were measured by density gradient column at 23°C. Glass floats were used in the calibration of this column prepared from carbontetrachloride and xylene, the densities were known with an accuracy of 1/10,000. The levels of glass floats and fiber samples were determined by a cathetometer within a sensitivity of ± 0.1 mm.

Measurement of Diameter

The diameters of the fiber samples were measured by a Vanox (Olympus) microscope at a magnification of $\times 1000$. These measures were carried out using at least five samples taken from different regions of the fiber.

Determination of Moisture Regain

The fiber samples were conditioned at 20°C in a medium having a relative humidity of 65% in order to evaluate the moisture regain value. This value was calculated from the difference in the weight of the conditioned fiber and the dry weight of the original fiber.

Dyeing Procedure

Original and grafted PET fiber samples were dyed with methylene blue (6.0 g/L) at boiling for 2 h, keeping the material/liquor ratio 0.6/100. The dye uptake values of the fiber samples were calculated from the amount of the dye remaining in the dye-bath and the predetermined calibration curve. The amount of the dye remaining in the dye-bath was determined by the help of Bausch and Lomb Spectronic 2000 spectrophotometry at a wavelength of 663 nm.

FTIR Spectrum

The FTIR spectrum of MAA-grafted PET fiber was recorded using a Perkin-Elmer Model 1710 spectrophotometer with a KBr disc.

RESULTS AND DISCUSSIONS

During the graft copolymerization of a monomer onto the fibers, generally there occurs a certain amount of homopolymer of the grafted monomer in the polymerization medium, depending upon the graft copolymerization method used. The most commonly employed method for the removal of this homopolymer from the grafted fibers is the extraction of it, using appropriate solvent or solvents. Although this is a highly time- and material-consuming method, it is generally preferred due to its simplicity. Also the main polymer is relatively unaffected in this method. Various workers used water²⁰ or methanol^{21,27} as a solvent in the removal of poly(methacrylic acid) from the grafted fiber. In our study both of these solvents were sequentially employed for the extraction of homopolymer. The extraction periods were determined by preexperiments and the periods at which fiber weight remained constant were chosen.

Effect of Temperature on Grafting

Table I shows the change of graft yield of methacrylic acid onto PET fibers with temperature and

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

| Time (h) | Graft Yield (%) | | | | |
|----------|-----------------|------|------|------|------|
| | 70°C | 75°C | 80°C | 85°C | 90°C |
| 1/4 | 0.0 | 0.0 | 1.6 | 4.5 | 7.5 |
| | | | 1.8 | 4.5 | 4.8 |
| 1/2 | 0.0 | 0.0 | 2.6 | 10.6 | 20.6 |
| | | | 1.3 | 14.0 | |
| 1 | 0.0 | 2.0 | 7.8 | 24.6 | 20.3 |
| | | 1.2 | 9.8 | 30.0 | 21.9 |
| 3/2 | 1.0 | 3.7 | 14.0 | 32.6 | 22.8 |
| | | 2.8 | 17.4 | 29.6 | |
| 2 | 1.5 | 8.0 | 19.0 | 30.0 | 21.8 |
| | 1.0 | 5.0 | | 30.5 | |
| 5/2 | 1.4 | 9.4 | 21.5 | 30.4 | 22.8 |
| | | 6.5 | | 30.4 | |
| 3 | 3.1 | 10.8 | 20.2 | 31.2 | 22.0 |
| | 2.0 | | 21.8 | | 22.4 |

^a [MAA] = 1.88×10^{-3} mol/L; [Bz₂O₂] = 4.0×10^{-3} mol/L.

time. Some experiments were repeated more than once. As seen from Table I, the reproducibility of the experimental data is relatively poor. This could have been caused by the entrapment of homopolymer within the fibers, in spite of the long extraction times used. This poor experimental reproducibility was also observed in various grafting systems.^{3,28,29}

Figure 1 is plotted by taking the average values of the data tabulated in Table I. The graft yield was found to reach to maximum at 85°C, using the various experimental temperatures. The graft yield was

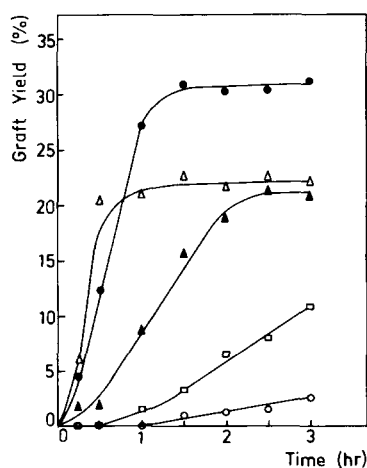


Figure 1 Variation of graft yield with polymerization temperature: [MAA] = 1.88×10^{-3} mol/L; [Bz₂O₂] = 4.0×10^{-3} mol/L; (○) 70°C; (□) 75°C; (▲) 80°C; (●) 85°C; (△) 90°C.

seen to decrease when the temperature was increased to 90°C.

The regions around the glass-transition temperature (T_g) of PET are the region in which maximum graft yield is obtained.¹⁰ The increase in temperature above T_g of PET increases the swellability of PET fibers and eases the diffusion into them. This facilitates the radical reactions as a result of the increased mobility of the polymer chains. Also the decomposition rate of Bz₂O₂ increases in parallel with the temperature. As a conclusion, the increase in temperature from 70 to 85°C increases graft yield. However, above this temperature (i.e., 90°C) the chain termination reactions and the combination of more and more radicals predominate and cause the graft yield to decrease. Nevertheless, although the increase in temperature lowers the graft yield, the rate of grafting continues to increase (Fig. 1).

Effect of Monomer and Initiator Concentration

The relation between the graft yield and the monomer concentration was investigated by the experiments carried out at four different MAA concentrations. The results are shown in Figure 2. The graft yields and saturation graft yields were found to increase with the increasing monomer concentration. The increase in the concentration of MAA will increase the MAA content diffused into the PET fibers and present in the outer solution, which increase the chance for the PET macroradicals and growing grafted side chains to find monomer units to add and increase the graft yield. The saturation graft yield is 5% for 0.47×10^{-3} mol/L MAA, which in-

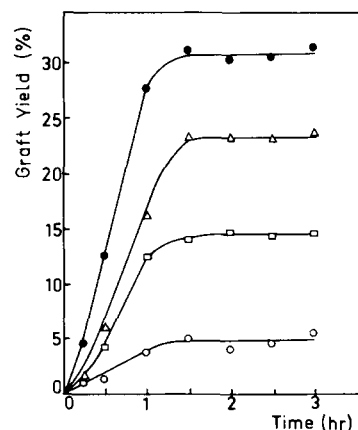


Figure 2 Variation of graft yield MAA concentration: [Bz₂O₂] = 4.0×10^{-3} mol/L; temperature, 85°C; time 2 h; [MAA] (mol/L): (○) 0.47×10^{-3} ; (□) 0.94×10^{-3} ; (△) 1.40×10^{-3} ; (●) 1.88×10^{-3} .

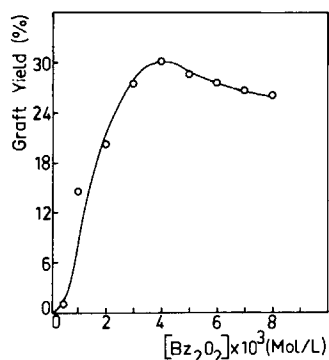


Figure 3 Variation of graft yield with initiator concentration: [MAA] = 1.88×10^{-3} mol/L; temperature, 85°C; time 2 h.

creases to about 30% for 1.88×10^{-3} mol/L MAA. The reason why the graft yield reached a constant value after 1–1.5 h with all the concentrations employed may be attributed to the significant decrease in the amount of MAA in the system.

Figure 3 shows the results of the experiments carried out to investigate the relation between the graft yield and initiator concentration. The graft yield increases up to Bz_2O_2 concentration of 4.0×10^{-3} mol/L, which passes through a maximum at this concentration. It is observed to show a slight decrease above this concentration.

The free radicals occur as a result of the decomposition of Bz_2O_2 may take place in various reactions in the polymerization media. The increase in the concentration of Bz_2O_2 increases the chance of hydrogen abstraction from the PET backbone and the chain transfer reactions of poly(methacrylic acid) homopolymer chains with PET. In both cases the graft yield increases. However, the excess increase in the concentration of Bz_2O_2 causes the free radical species formed from decomposition of Bz_2O_2

Table III Density and Diameter Values of MAA-Grafted PET Fibers

| Graft Yield (%) | Density (g/cc) | Diameter (mm × 10 ⁻²) |
|-----------------|----------------|-----------------------------------|
| 0.0 | 1.3749 | 2.0995 |
| 3.7 | 1.3726 | 2.1400 |
| 10.8 | 1.3718 | 2.2230 |
| 14.0 | 1.3706 | 2.3380 |
| 22.8 | 1.3696 | 2.3712 |
| 24.6 | 1.3657 | 2.4700 |
| 30.4 | 1.3651 | 2.5194 |

($C_6H_5COO\cdot$ and/or $C_6H_5\cdot$) to give termination reactions with PET macroradicals or growing polymer chains or combination reactions between them, and consequently the graft yield decreases. This effect is observed when Bz_2O_2 concentration is taken above 4.0×10^{-3} mol/L (Fig. 3).

Effect of Reaction Medium

The composition of graft copolymerization media plays an important role in the grafting of vinyl monomers onto PET fibers. The data obtained from the grafting studies carried out using various water/solvent ratios are tabulated in Table II. All the solvents used had an adverse effect upon grafting. Also, if one examines the experiments carried out for individual solvents, one can see that increase in the amount of solvent in the mixture decreases the grafting. The grafting was observed to be totally hindered at a water/ethanol, water/methanol, water/*n*-propanol, and water/DMSO ratio of 40/60 (v/v), water/*n*-butanol ratio of 60/40 (v/v), and water/pyridine ratio of 80/20 (v/v). The role of solvents added to polymerization system is very complicated indeed. The solvents may show varying

Table II Effect of Some Solvents on Graft Yield^a

| Water/Solvent Ratio (v/v) | Graft Yield (%) | | | | | | |
|---------------------------|-----------------|---------|--------------------|-------------------|------------------|-------------------|----------|
| | Methanol | Ethanol | <i>n</i> -Propanol | <i>n</i> -Butanol | DMF ^b | DMSO ^b | Pyridine |
| 100/00 | 30.3 | 30.3 | 30.3 | 30.3 | 30.3 | 30.0 | 30.0 |
| 90/10 | 16.0 | 15.0 | 22.4 | 4.3 | 12.0 | 7.5 | 4.3 |
| 80/20 | 5.7 | 5.0 | 7.3 | 2.0 | 5.0 | 6.0 | 0.0 |
| 60/40 | 2.0 | 0.5 | 1.0 | 0.0 | 2.0 | 1.0 | 0.0 |
| 40/60 | 0.0 | 0.0 | 0.0 | 0.0 | 0.9 | 0.0 | 0.0 |
| 20/80 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

^a [MAA] = 1.88×10^{-3} mol/L; [Bz_2O_2] = 4.0×10^{-3} mol/L; time 2 h; temperature 85°C.

^b DMF = dimethyl formamide; DMSO = dimethyl sulfoxide.

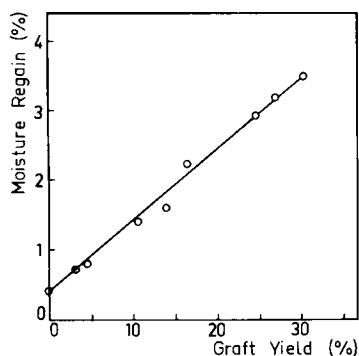


Figure 4 Moisture regain value of MAA grafted PET fibers.

effects upon their properties such as swellability of PET fibers and miscibility with monomer. They may also take place in reactions such as initiation, chain transfer, and termination. The effect of solvents used in grafting of MAA onto PET fibers upon the graft yield follows the following order:

n -propanol > methanol > ethanol > DMF
> DMSO > n -butanol > pyridine

SOME PROPERTIES OF MAA GRAFTED PET FIBERS

Density and Diameter

The density and diameter values of PET fibers grafted with various amount of MAA are given in Table III. As is clearly seen, the fiber densities decreased with the increasing graft yield. A possible explanation is that the grafted polymer chains are accommodated between the linear main polymer chains, which results in an increase in diameter. The decrease observed in density with the increase in diameter was most probably due to fact that the contribution of grafted side chains to the weight of fiber is less than their contribution to the volume of it. In other words, the increase in weight of fiber as a result of grafting is less than the increase in the volume of fiber.

Moisture Regain

The moisture regain value of hydrophobic PET fibers is very low. As seen from Figure 4, the moisture regain value of ungrafted PET fibers is 0.44%. The moisture regain value increases to 2.3% at the graft

yield of 16.5%, and 3.8% at the graft yield 30.0%. This can be explained by the insertion of polar groups ($-\text{COOH}$) to PET fiber and increase in the hydrophilic character of the fiber. It can also be claimed that the opening of PET structure (Table III) may have an influence in the increase in the moisture regain value of the fibers.

Dye Uptake

The dyeability of a textile fiber can be increased by introducing suitable functional groups in the fiber structure, so that they become the centers of adsorption or reaction with the appropriate class of dye molecules. As seen from the results of dyeing experiments of grafted PET fibers, using methylene blue, the dye uptake increases with graft yield (Table IV). This must be due to the increase in the number of $-\text{COOH}$ groups, which provides the higher dyeability. The dye uptake of ungrafted PET fiber is 0.011 g dye/g fiber while the dye uptake of PET fiber grafted with 30.4% MAA increases up to 0.154 g dye/g fiber. The opening of fiber structure as a result of grafting will undoubtedly contribute to improving the dye uptake of the fiber.

FTIR Spectrum

IR spectra are not sufficient to evaluate the points of the side chains binding to the main polymer backbone. However, IR spectra are given as supporting data in some grafting studies.^{3,17,30} The FTIR spectrum of the PET fiber grafted with 10.6% MAA is given in Figure 5. This was compared with the FTIR spectrum of the ungrafted PET fiber taken under the same conditions. There is seen a strong stretching band of OH groups coming from MAA, at 3440 cm^{-1} . There were no other differences observed between these two spectra.

Table IV Dye Uptake Values of MAA Grafted PET Fibers^a

| Graft Yield (%) | Dye Uptake (g dye/g fiber) |
|-----------------|----------------------------|
| 0.0 | 0.011 |
| 4.5 | 0.027 |
| 9.8 | 0.037 |
| 16.0 | 0.062 |
| 26.0 | 0.114 |
| 30.4 | 0.154 |

^a Dyed with methylene blue.

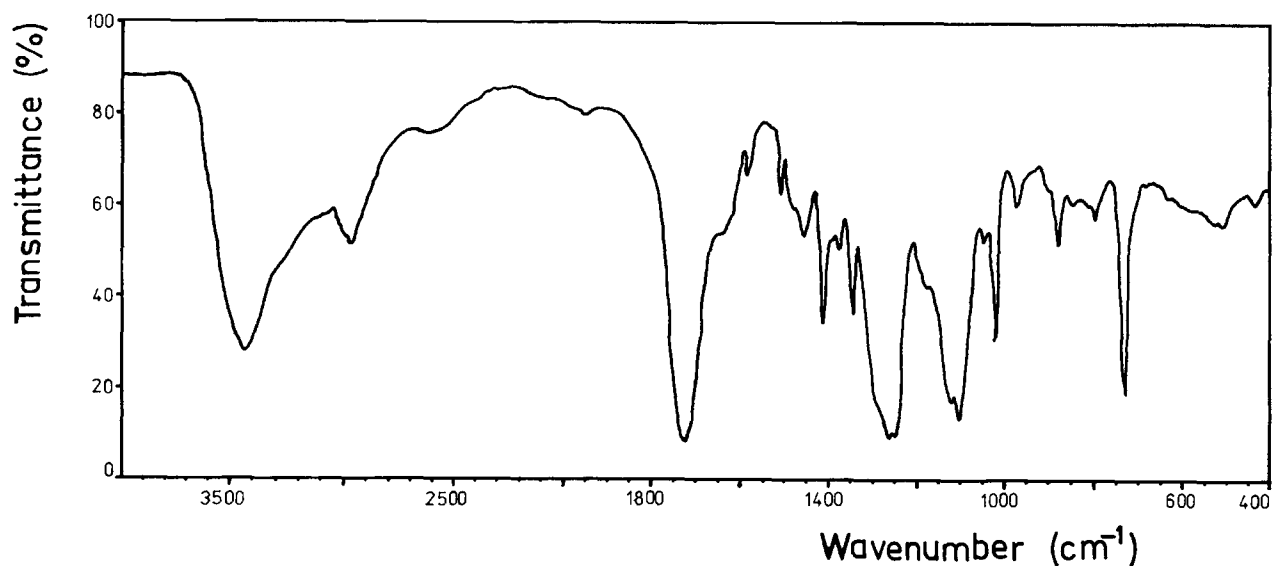


Figure 5 FTIR spectrum of PET fiber grafted with 10.6% methacrylic acid.

REFERENCES

- M. Okoniewski and J. Sojka-Ledakowicz, *Pr. Inst. Wlok.*, **29**, 153 (1981); *Chem. Abstr.*, **97**, 111231y (1982).
- P. D. Kale, H. T. Lokhande, K. N. Rao, and M. H. Rao, *J. Appl. Polym. Sci.*, **19**, 461 (1975).
- M. Saçak and E. Pulat, *J. Appl. Polym. Sci.*, **38**, 539 (1989).
- A. Hebeish, S. E. Shalaby, and A. M. Bayazeed, *J. Appl. Polym. Sci.*, **26**, 32523 (1981).
- E. Kuzumto and T. Uejima, *Jpn. Pat.* 76, 17, 659 (1974); *Chem. Abstr.*, **82**, 44972r (1975).
- R. Tsuzuki and S. Maeta, *Jpn. Pat.* 71, 29 918 (1971); *Chem. Abstr.*, **77**, 50069g (1972).
- A. K. Pradhan, N. C. Pati, and P. L. Nayak, *J. Appl. Polym. Sci.*, **27**, 1973 (1982).
- K. Suzuki, I. Kido, and N. Tanabe, *Sen'i Gakkaishi*, **28**(9), 343 (1972); *Chem. Abstr.*, **77**, 165878v (1972).
- T. Memetea and V. Stannett, *Polymer*, **20**, 465 (1979).
- E. Schamberg and J. Hoigne, *J. Polym. Sci., Part A-1*, **8**, 693 (1970).
- I. Vlagiu and V. Stannett, *J. Macromol. Sci. Chem. A*, **7**(8), 1677 (1973).
- T. Kada, K. Kaji, and I. Sakurada, *JAERI-5027*, 50 (1971); *Chem. Abstr.*, **76**, 114582r (1972).
- M. F. Blin, R. Candan, G. Gaussens, F. Lemaire, and D. Paoli, *Fr. Pat.* 2,045,261 (1969); *Chem. Abstr.*, **76**, 15692v (1972).
- H. D. Kim, D. L. Kim, and T. I. Chun, *Han'guk Somyu Konghakhoechi*, **21**(4), 233 (1984); *Chem. Abstr.*, **102**, 3128t (1985).
- J. C. Bonnefis and J. R. Puig, *J. Appl. Polym. Sci.*, **15**, 553 (1971).
- G. Gaceva, Z. Stojanoski, and D. Petov, *Polimeri*, **4**(9-10), 257 (1983); *Chem. Abstr.*, **100**, 193410y (1984).
- S. A. Faterpeker and S. P. Potnis, *Angew. Makromol. Chem.*, **90**, 69 (1980).
- A. Mey-Marom, L. A. Rajbenbach, and M. Levy, *J. Appl. Polym. Sci.*, **28**, 2411 (1983).
- E. Schamberg, *J. Polym. Sci. Polym. Lett. Ed.*, **10**, 119 (1972).
- K. N. Rao, M. H. Rao, P. N. Moorthy, and A. Charlesby, *J. Polym. Sci. Polym. Lett. Ed.*, **10**, 893 (1972).
- K. Matsuzaki, T. Kanai, and N. Morita, *J. Appl. Polym. Sci.*, **16**, 15 (1972).
- K. Kaji, T. Okada, and I. Sakurada, *JAERI-5028*, 52-60 (1970); *Chem. Abstr.*, **80**, 84518n (1974).
- T. Okamoto, K. Saito, and S. Toyama, *Jpn. Pat.* 62, 199, 875 (1987); *Chem. Abstr.*, **108**, 23297q (1988).
- S. Maeda, *Jpn. Pat.* 73, 27, 744 (1973); *Chem. Abstr.*, **80**, 134753h (1974).
- E. Schamberg and J. Hoigne, *Ger. Offen.* 2,027,178 (1970); *Chem. Abstr.*, **74**, 43470y (1971).
- Y. Maeed, *Jpn. Pat.* 79, 06, 263 (197); *Chem. Abstr.*, **91**, 22339y (1979).
- A. K. Mukherjee and D. Gupta, *J. Appl. Polym. Sci.*, **30**, 4455 (1985).
- J. L. Garnett, R. S. Kenyon, and J. D. Leeder, *J. Polym. Sci. Polym. Lett. Ed.*, **15**, 93 (1977).
- G. Odion, M. Sobel, A. Rossi, R. Klein, and T. Acker, *J. Polym. Sci. Part A*, **1**, 639 (1963).
- W. Gabara and S. Porejko, *J. Polym. Sci., Part A-1*, **5**, 1547 (1967).

Received February 27, 1991

Accepted June 14, 1991