Surface Modification by Continuous Graft Copolymerization. IV. Photoinitiated Graft Copolymerization onto Polypropylene Fiber Surface

ZHANG PEI YAO* and BENGT RÅNBY,† *Department of Polymer Technology, The Royal Institute of Technology, S-100 44 Stockholm, Sweden*

Synopsis

Photochemically induced graft copolymerization (with UV light) of acrylamide (AM) and acrylic acid (AA) on polypropylene (PP) fiber surface by the presoaking method under nitrogen atmosphere in a continuous process has been developed. The results are measured by means of ESCA spectra. In grafting AM and AA, the relative intensity N_{1s}/C_{1s} and O_{1s}/C_{1s} of the fiber increase from 3–5 and 20% (background) to 8–13 and 23–39% in 9–10 s irradiation time, respectively. Titration results show that 1.75–3.58 mg/m² poly(acrylic acid) has been grafted on the surface of PP fiber at various monomer concentrations of the presoaking solution. Commercial additives, such as antioxidant and UV stabilizer, affect the grafting yield of the fiber. As solvent in the presoaking solution, acetone is better than MEK and MPK. Various monomer and initiator concentrations in the presoaking solution have been studied. In the process developed 0.5–0.8 M acrylamide or 1.5–2.0 M acrylic acid and 0.2 M benzophenone (BP) in the presoaking solution are appropriate.

INTRODUCTION

Polypropylene (PP) is one of the largest and fastest growing polymers because of its useful properties, wide applicability, and low cost. It can be used as film, fiber, plate (sheet), and injection-molded as well as blow-molded articles. The surface properties of the polymer, such as dyeing, printing, paintability, and adhesion, are very important for polypropylene fiber, film, and sheet. The homopolymer polypropylene, however, contains no hydrophilic groups on the polymer chain. Both physical and chemical methods have been applied to modify the surface properties of polypropylene. Bellobono et al.[1] investigated the photografting of 4-(N-ethyl,N-2-acryloxyethyl) amino 4'-nitroazobenzene on polypropylene fiber surface, and studied kinetically the rate and extent of graft copolymerization without any added initiator. Needles and Alger[2] reported the sensitized photopolymerization of methyl acrylate on the surface of polypropylene fiber using aqueous dispersions of metal oxides. Seiber and Needles[3] studied photoinitiated vapor-phase grafting of methyl acrylate on polypropylene fiber in the presence of a wetting agent. Other studies deal with modification of polypropylene film.[4–7]

* Visiting scientist from Yan Shan Petrochemical Co., Beijing, People's Republic of China.
† To whom correspondence should be addressed.

In our previous articles[8,9] AM and AA were shown to be photografted successfully onto HDPE tape film, and PET fiber using the presoaking method developed with the purpose of practical use. This article deals with photografting of AM and AA on PP fiber surface using the same method as before. Our method has several advantages compared with the other methods already mentioned:

1. All chemicals used here are common and commercially available.
2. Our process of photografting on polymer fiber is continuous and simple.
3. The irradiation time of the fiber is short.

It seems possible to apply this process to industrial applications.

EXPERIMENTAL

Materials

Polypropylene fiber was obtained from Hercules Fibres Technical Center, USA. Type 7750-47-1 is an experimental finish-free yarn, 2200 total denier, 667 filaments. It contains less than 0.15% of total additives (antacid and phenolic antioxidant). Type 303 is a production yarn, 420 denier, 70 filaments, i.e., surface area is about 0.0067 m^2/m. It contains 1.7% finish (a proprietary combination of ethoxylated fatty acid derivatives) and 0.35% additives (antioxidant, UV stabilizer, antacid). The fiber samples are thoroughly washed in 80–90°C water containing an aqueous detergent for 30 min and then dried prior to use.

Acrylic acid (AA), $CH_2=CHCOOH$, MERCK, synthetic grade, 99% (GC), polymerization inhibitor removed on Al_2O_3 column before use. Acrylamide (AM), $CH_2=CHCONH_2$, MERCK, synthetic grade, 99% (GC), recrystallized from acetone before use. Benzophenone (BP), $C_6H_5COC_6H_5$, MERCK, synthetic grade, 98% (GC), is used without purification. Acetone, CH_3COCH_3, MERCK, analytical grade, min. 99.5% (GC). Methylethylketone (MEK = butanone), $CH_3COCH_2CH_3$, KEBO puriss, min. 99%. Methylpropylketone (MPK = pentanone-2), $CH_3COCH_2CH_2CH_3$, MERCK, synthetic grade, 98% (GC). The three ketones were used without purification. Sodium hydroxide, NaOH, MERCK, Titrisol, 0.01 M. Sodium chloride, NaCl, MERCK, Titrisol, 0.1 M. The UV light source was PHILIPS HPM-15, high-pressure metal halide lamp with lead and gallium iodide additives. It was made of ozone-free quartz with an active radiation between 320 and 440 nm.

Photografting Polymerization Procedure

The experimental arrangements used here are the same as those described before.[8,9] A bundle of PP fiber is passed through a presoaking solution, then fed into the reactor continuously by turning on the driving motor. The irradiation time of the fiber is varied from 3 to 300 s by changing the motor speed. The reactor is closed and filled with a flow of nitrogen during the reaction period. The exhaust gas, containing nitrogen, vapor of solvent, monomer, and initiator, escapes through an outlet. The reaction temperature measured by

thermocouple in the reactor (shielded from the lamp) is in the range 68–74°C. Vapor of AM is sublimated from solid AM in a vessel under the running roll. The vapor pressure of AM is 0.029 mmHg at 40°C and 2 mmHg at 87°C. The distance from the light source to the substrate surface is 20 cm. Different monomer and initiator concentrations in the presoaking solution of the three solvents have been tested.

After the photografting polymerization, in the case of AM as monomer, the fiber is immersed in acetone for 30 min and washed thoroughly to remove residual monomer and initiator from the fiber surface, then immersed in hot water (85–92°C) for 30 min and washed thoroughly to remove AM homopolymer. In the case of AA as monomer, the fiber is directly immersed in hot water (85–92°C) for 30 min to remove residual monomer and homopolymer of acrylic acid and finally rinsed with water and dried.

Analysis

ESCA spectroscopy is used here for the analysis of nitrogen, oxygen, and carbon on the fiber surface. The relative intensity (RI) of the ESCA lines indicates various grafting yields. In this study, the relative intensities of ESCA lines N_{1s}/C_{1s} and O_{1s}/C_{1s} are measured. The blank sample (without grafting) of PP fiber showed an N_{1s} ESCA line here. Probably the blank PP fiber sample immersed in the same hot water together with other grafted sample adsorbs some homopolymer of acrylamide from the hot water that had been dissolved from the grafted samples. The contamination was small. The ESCA relative intensity N_{1s}/C_{1s} of the blank sample is regarded as background. PP is easily oxidized in the air during spinning and processing. Therefore the blank sample of PP fiber also showed O_{1s} line; the relative intensity of ESCA lines O_{1s}/C_{1s} of the blank sample is regarded as background.

The ESCA analysis was performed by using a Leybold Heraeus ESCA/Auger Spectrometer LH 2000 unit with computer on line. A titration analysis method is used here to measure the amount of poly(acrylic acid) grafted on the PP fiber surface. The length of the PP yarn titrated is 20 m. The total surface area of this amount of Type 303 PP yarn is about 0.134 m^2 (the density of PP fiber is assumed 0.91 g/cm^3). The fiber cut into 1–2 cm staple length, immersed in 0.1 M sodium chloride solution, and stirred for 30 min. pH of the solution is measured by E632 Digital-pH-Meter (from METROHM Ltd., Switzerland). As the amount of poly(acrylic acid) grafted on the surface of PP fiber is very small, 0.01 M sodium hydroxide as neutralization agent was used.

RESULTS AND DISCUSSION

Effect of Various Monomer Concentrations in the Presoaking Solution

The mechanism of photografting of AM or AA onto PP fiber surface is assumed to be the same as that on PE tape film. The graft copolymerization is initiated by abstraction of hydrogen from the PP chains, caused by the triplet excited state of BP. The yield of grafted copolymer is so small (the order of magnitude is around 0.5 mg) that the weight increase of grafted fiber cannot
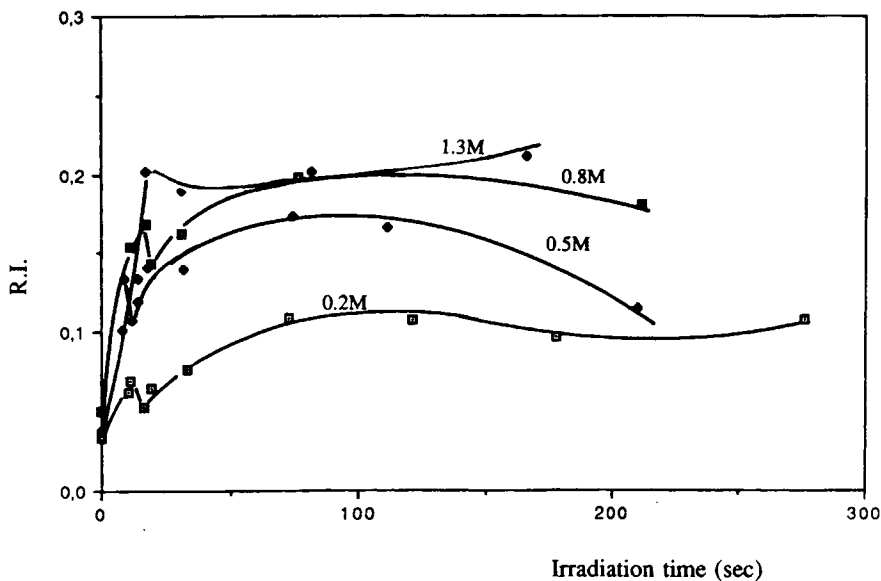
Fig. 1.   Effect of AM concentration in photografting PP fiber, 7750-47-1, presoaking solution: [BP] = 0.2 M, acetone as solvent.

be measured gravimetrically. However, the N_{1s} peak in ESCA spectrum clearly indicates the formation of a measurable grafted layer. The relative intensities of ESCA lines N_{1s}/C_{1s} at different irradiation times and in various [AM] in
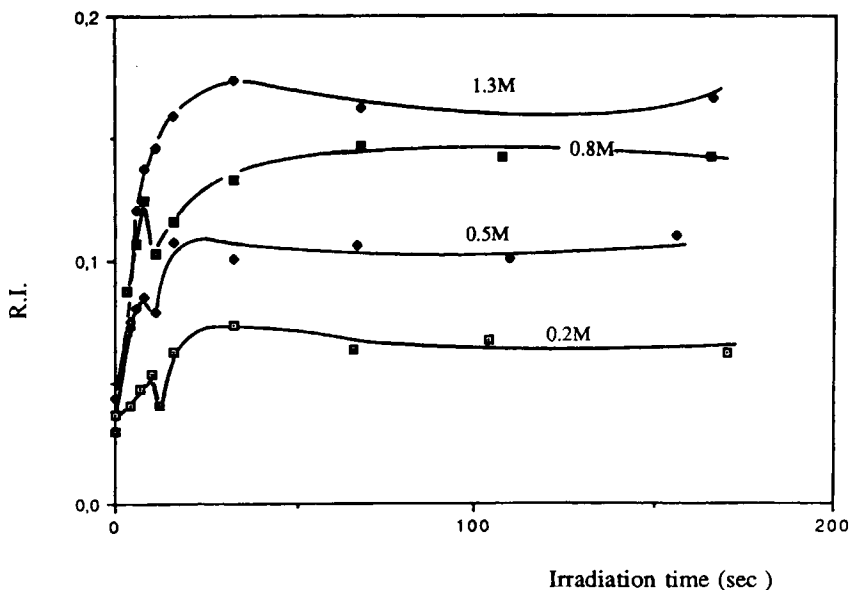

Fig. 2.   Effect of AM concentration in photografting PP fiber, type 303, measured as RI of N_{1s}/C_{1s} in ESCA spectra, presoaking solution: [BP] = 0.2 M, acetone as solvent.

the presoaking solution are shown in Figures 1 and 2. The relative intensities of ESCA lines O_{1s}/C_{1s} at 10-s irradiation time in various [AA] in the presoaking solution are shown in Figure 3.

The monomer concentration in the presoaking solution affects the photografting yield strongly. The higher the monomer concentration in the presoaking solution, the higher is the photografting yield. No obvious difference in the results could be found for [AM] = 1.3 M and 0.8 M at 8-s irradiation time. For prolonged irradiation time, however, the effect of high concentration of AM is clearly found. It showed that the controlling step of the graft copolymerization reaction is irradiation time, but monomer concentration in the presoaking solution also affects the yield of grafted polymer. All the curves in Figure 1 and three curves in Figure 2 have a "shoulder" at 10–20 s irradiation time. The shape of these curves is similar to those previously obtained for HDPE tape film[8] and PET fiber.[9] The curve shape is assumed to be due to evaporation of the solvent (acetone) from the presoaking solution on the fiber surface. Higher AM concentration in the presoaking solution gives larger amounts of monomer on the fiber surface with higher grafting yield as a result (Figs. 3 and 4). After the first rapid reaction, further grafting does not occur (Figs. 1 and 2). This would mean that initiator and monomer in the vapor phase in the reactor hardly graft to the PP fiber in short irradiation time. Similar observations were made for PET fiber[9] and in some cases also for PE tape film.[8]

The amount of grafted poly(acrylic acid) on the surface of PP fiber is affected by the AA concentration in the presoaking solution. Figure 4 shows the relationship between the amount of grafted poly(acrylic acid) per unit surface area of PP fiber and AA concentration in the presoaking solution at the same irradiation time. The higher the AA concentration used, the higher is the amount of grafted poly(acrylic acid) on the surface of PP fiber. This is in accordance with the measured relative intensity of ESCA lines O_{1s}/C_{1s} shown in Figure 3.

Assuming the density of grafted poly(acrylic acid) to be 0.95 g/cm^3, and the grafted layer to be even on the surface of PP fiber, we can calculate the average thickness of the grafted poly(acrylic acid) to be 18.4, 30.6, 35.3, and 37.6 Å at 0.5, 1.0, 1.5, and 2.0 M of [AA] in the presoaking solution, respectively.
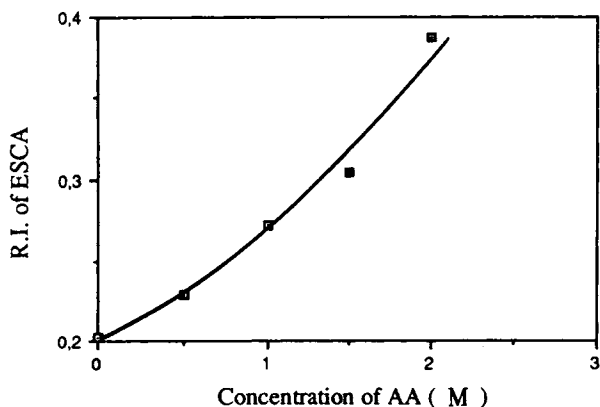

Fig. 3.   Effect of AA concentration in photografting PP fiber, type 303, measured as RI of N_{1s}/C_{1s} in ESCA spectra, presoaking solution: [BP] = 0.2 M, acetone as solvent.

Fig. 4. Amount of photografted poly(acrylic acid) on PP type 303 fiber surface at various AA concentrations in the presoaking solution: [BP] = 0.2 M, acetone as solvent, irradiation time 10 s.

It is known that ESCA measurements have a penetration depth of 50–100 Å. We assume that grafted poly(acrylic acid) layer on the PP fiber surface is not even. There are sites where the grafted poly(acrylic acid) chains are quite long and give a thick layer and other sites where the grafted poly(acrylic acid) chains are short and form a thin grafted layer. In the case of thick layers, it may be more difficult for the titration method to neutralize acidity of the surface layer completely. Perhaps, this is due to entanglement effects of longer poly(acrylic acid) chains or to the network structure of the thick grafted layer. Also, higher grafting yield may increase the effects of hydrogen bonding among the grafted poly(acrylic acid) chains on the fiber surface. The hydrogen bonds may partly prevent neutralization of the surface acidity of the grafted fiber surface. Probably, this is the reason that curves in Figures 3 and 4 have different shapes.

The grafting yield is also related to the type of PP fiber used. The RI of the ESCA lines N_{1s}/C_{1s} for grafting on PP 7750-47-1 fiber is higher than that of type 303, as shown by comparing Figures 1 and 2. PP 7750-47-1 fiber is also grafted at a higher rate than PP type 303. This is most probably due to the higher amounts of additives in PP type 303, mainly UV absorbers and radical scavengers. Both stabilizers would tend to prevent radical formation on the fiber surface and/or terminate free radical chains.

The main initiation reaction in this system is abstraction of hydrogen atoms from polymer chains by the triplet excited state of the initiator. Another radical-forming reaction is polymer photodegradation. The primary events following irradiation of PP with UV light at vacuum are chain bond scission and hydrogen abstraction at the tertiary carbon:

These radicals may lead to other reactions such as disproportionation and crosslinking. They may also react with AM or AA to produce graft copolymer like the radicals formed by the initiator. The additives, such as antioxidant and UV stabilizer in the polymer fiber, prevent the polymer chain from thermal and photodegradation. The higher amounts of stabilizing additives in type 303 PP fiber resulted in a lower degree of grafting, measured by ESCA. However, the fact that type 303 fiber containing 0.35% additive could be photografted with AM or AA in this reaction system is of great importance since most of commercial polymers contain such additives. Our process can be used to modify the surface property of such polymers.

PP fibers give higher yields of grafted polymer than PET fiber.[9] This may be due to more reactive tertiary bonded hydrogen on the PP chains compared with the hydrogen atoms on PET chains.

Effect of Various Ketones as Solvents

The solvent effects in photografting are shown in Figures 5 and 6, which give ESCA spectra of N_{1s} and relative intensity of the N_{1s}/C_{1s} ESCA lines. The shape of the curves in Figures 5 and 6 is similar to those in the case of PET.[9] There is no doubt that acetone is a more efficient solvent in this grafting process than MEK and MPK. The presence of antioxidant and UV stabilizer in the PP fibers decreased the grafting yield in the three ketone solvents, as shown in Figures 5 and 6.

Effects of Various Photoinitiator Concentrations in the Presoaking Solution

The different RI of the ESCA lines N_{1s}/C_{1s} for PP fiber grafted at various BP concentrations in the presoaking solution are shown in Figures 7 and 8.
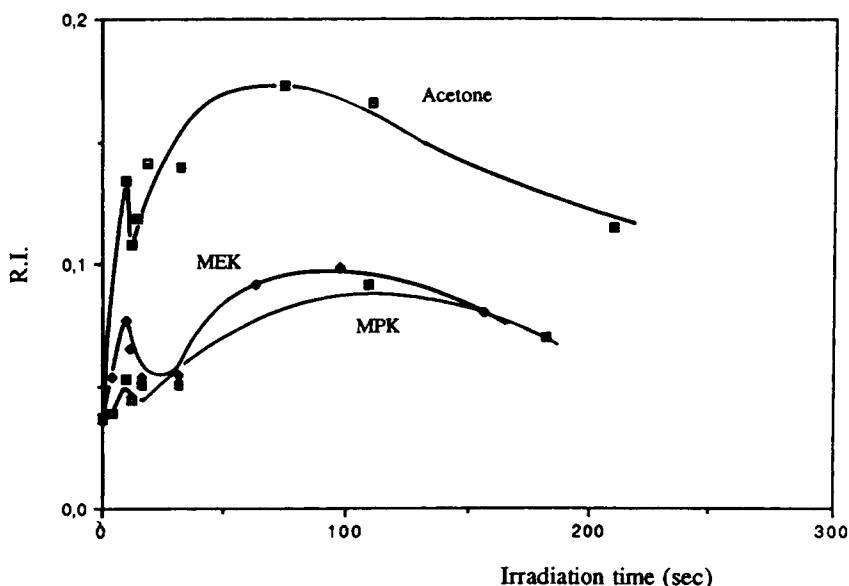
Fig. 5. Effect of solvents on photografting, PP 7750-47-1 fiber, presoaking solution: [BP] = 0.2 M, [AM] = 0.5 M, measured as relative intensity of ESCA lines N_{1s}/C_{1s}.
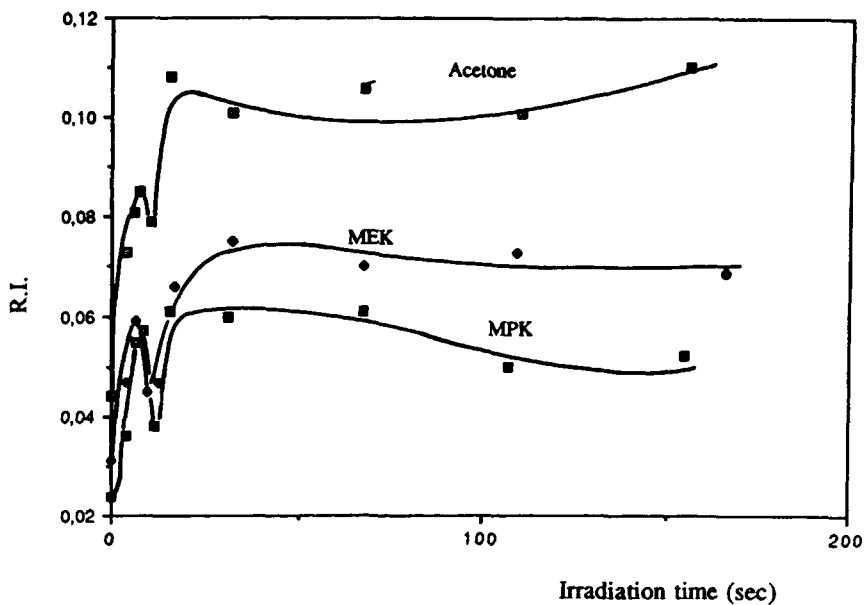
Fig. 6.   Effect of solvents on photografting, PP type 303 fiber, presoaking solution: [BP] = 0.2 M, [AM] = 0.5 M, measured as relative intensity of ESCA lines N_{1s}/C_{1s}.
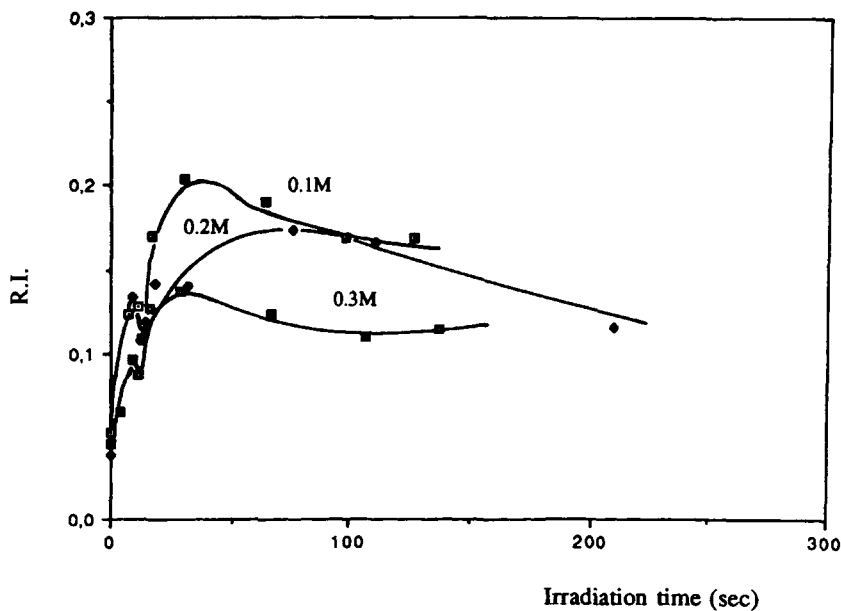

Fig. 7.   Effect of BP concentration on photografting, PP 7750-47-1 fiber, presoaking solution: [AM] = 0.5 M, acetone as solvent, measured as relative intensity of ESCA lines N_{1s}/C_{1s}.
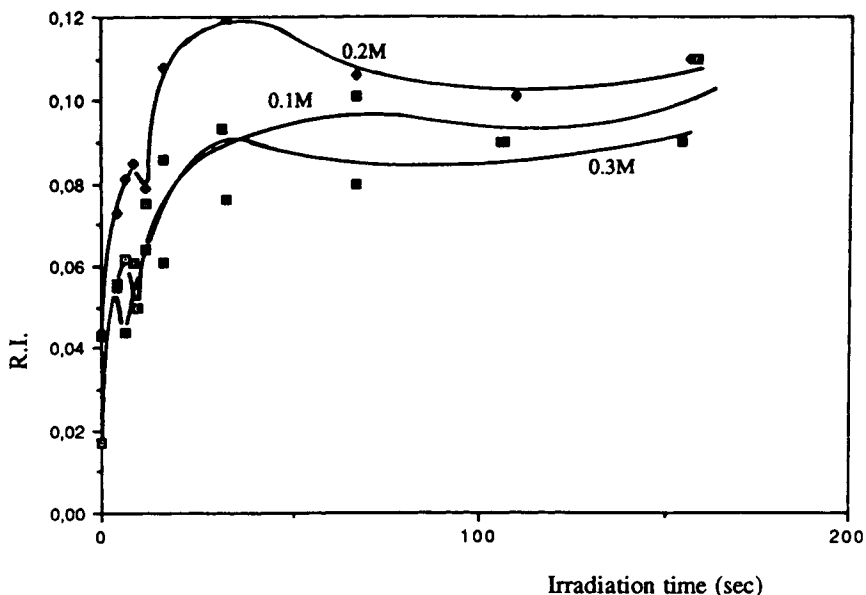
Fig. 8.   Effect of BP concentration on photografting, PP type 303 fiber, presoaking solution: [AM] = 0.5 M, acetone as solvent, measured as relative intensity of ESCA lines N_{1s}/C_{1s}.

The shape of the curves is similar to those for PET fiber. The interpretation of the shoulder, which appears in every curve, is the same as before. The effects of the BP concentration are rather small and irregular. For PP fiber 7750-47-1, increased BP concentration decreases the grafting yield, as shown in Figure 7. For PP fiber type 303, the effects of BP concentration are rather small and may not be insignificant, as shown in Figure 8, and the results are difficult to interpret.

CONCLUSION

In the continuous presoaking process developed, PP fiber can be grafted efficiently with AM and AA using UV light in the presence of photoinitiator and monomer in ketone solvents. The RI of ESCA lines (O_{1s}/C_{1s} and N_{1s}/C_{1s}) of the photografted fiber surface increased from 20% (background) to 22–38% and 3–5% (background) to 8–13% after 10 s and 9-s irradiation, respectively. The amount of grafted poly(acrylic acid) on the surface of PP fiber, type 303, is from 1.75 to 3.58 mg/m^2 with 0.5–2.0 M of [AA] in the presoaking solution at 10-s irradiation time. Antioxidant and UV stabilizer in the commercial PP polymer fiber used cause some decrease of the photografting yield. It was found, however, that even type 303 PP fiber, which contains 0.35% additives (antioxidant, UV stabilizer, and antacid), can be photografted efficiently with AM and AA using our method. This indicates that the continuous presoaking process for photografting has great possibilities for practical applications. The kind of ketone solvent used has effects on the grafting yield. Acetone is a better solvent than MEK and MPK. The effect of initiator concentration in the presoaking

solution is small and low concentration can be used ($0.1\ M$). Increasing monomer concentration in the presoaking solution increases the grafting yield considerably. Favorable results are obtained with $[AA] = 1.5–2.0\ M$, $[AM] = 0.5–0.8\ M$, and $[BP] = 0.2\ M$ in the presoaking solution.

References

1. I. R. Bellobono, F. Tolusso, and E. Selli, *J. Appl. Polym. Sci.*, **26**, 619–628 (1981).

2. H. L. Needles and K. W. Alger, *J. Appl. Polym. Sci.*, **19**, 2207–2223 (1975).

3. R. P. Seiber and H. L. Needles, *J. Appl. Polym. Sci.*, **19**, 2187–2206 (1975).

4. C. H. Ang, J. L. Garnett, R. Levot, and M. A. Long, *J. Macromol. Sci. Chem.*, **A17**(1), 87–98 (1982).

5. S. Tazuke and H. Kimura, *Die Makromol. Chem.*, **179**, 2603 (1978).

6. Y. Ogiwara, M. Kanda, M. Takumi, and H. Kubota, *J. Polym. Sci. Polym. Lett. Ed.*, **19**, 457–462 (1981).

7. K. Nito, S. I. Suzuki, K. Miyasaka, and K. Ishikawa, *J. Appl. Polym. Sci.*, **27**, 637–643 (1982).

8. P. Y. Zhang and B. Rånby, *J. Appl. Polym. Sci.*, to appear.

9. P. Y. Zhang and B. Rånby, *J. Appl. Polym. Sci.*, to appear.