Graft Polymerization of Acrylic Acid onto Polyphenylene Sulfide Nonwoven Initiated by Low Temperature Plasma

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ABSTRACT: Graft copolymerization of acrylic acid (AA) onto polyphenylene sulfide (PPS) nonwoven initiated by low temperature plasma was studied. The effects of various conditions on graft reaction and the grafting rate were investigated. SEM images showed that PPS nonwoven was grafted, and the graft copolymerization only occurred on the surface of PPS. It may be due to the chain transference going with the graft copolymerization. It was found that with the increasing of plasma power, treatment time, space between electrodes, monomer concentration, and temperature of graft polymerization, the grafting rate increased at first, went to the top, and then decreased. The PPS non-woven surface graft reaction could be optimized by the following processing conditions: 120 s of plasma treatment time, 50 W of plasma power, 1.5 cm of space between electrodes, 30% (w/w) of monomer concentration, and 50°C of temperature of graft polymerization. Measurement of XPS showed that the peak of C1s of graft polyacrylic acid was existed, and the peak area increased with the increase of the grafting rate. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5884–5889, 2006

Key words: polyphenylene sulfide; acrylic acid; low temperature plasma treatment; graft copolymerization

INTRODUCTION

In recent years, graft copolymerization by low temperature plasma has generated considerable interest in polymer science.[1] It is demonstrated that modification of polymer surface could be obtained through graft polymerization under relatively mild conditions for a number of conventional polymers, such as polyolefins,[2–4] polyesters,[5,6] fluoropolymers,[7] and conjugated polymers,[8] after the surface were pretreated with glow discharge and corona discharge. Surface graft polymerization is one of the most versatile means for the molecular design of polymer surface to enhance their physical and chemical properties for specific applications. It is the most important advantage of this technique that different properties of modified surface can be obtained through applying different monomers.[9] It is noteworthy that there is no report about graft copolymerization onto PPS. It may be because PPS is radiation-resistant. The main objective of the present study is to determine the suitability of processing conditions in plasma-induced surface graft copolymerization with AA. And the morphology of grafted PPS nonwoven was investigated with SEM.

EXPERIMENTAL

Materials

Polyphenylene sulfide (PPS) nonwoven was purchased from Fushun Industry Cloth Company (Funshun, China), and was cleaned with water and anhydrous alcohol. Acrylic acid (AA), chemically pure, supplied by Tianjin Chemistry Reagent Company (Tianjin, China), was purified by distillation under reduced pressure before use.

Plasma-induced graft copolymerization

The PPS nonwoven was cut into strips of about 1.5 cm × 10 cm, and they were pretreated with N_2 plasma before graft copolymerization. RF low temperature plasma surface treater manufactured by Nanjing Suman Company (Nanjing, China) was used for plasma treatment. The plasma power applied was ranging from 40 to 70 W, and the space between electrodes was from 1 to 2 cm. The PPS nonwoven was placed between the two electrodes and subjected to the glow discharge for a predetermined period of time ranging from 0 to 180 s at a N_2 pressure of 0.9 Mpa. For the N_2 plasma-pretreated PPS nonwoven graft copolymerization with AA, each PPS nonwoven was immersed in the aqueous monomer solution in a Pyrex1 tube. The concentration of the AA solution injected with N_2 was varied from 10 to 35 wt %. In this case, the dissolved oxygen, which
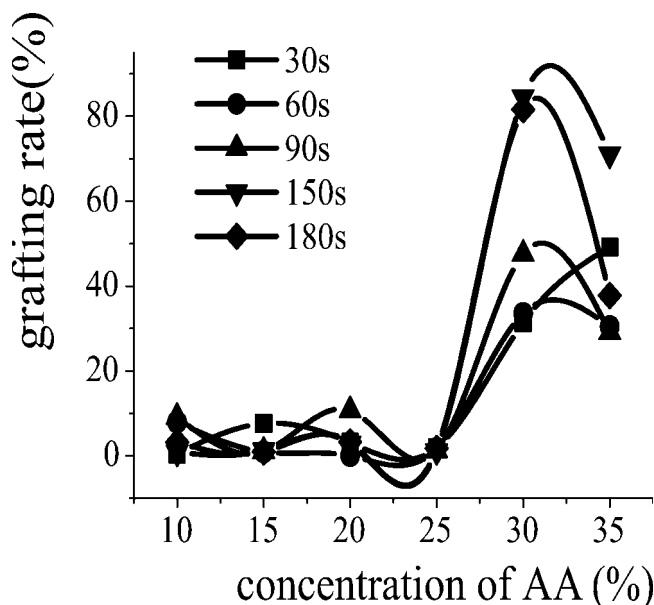
Figure 1 Effect of the concentration of AA on grafting rate under different plasma treatment time plasma power (70 W), temperature (80°C), and space between electrodes (1.5 cm).

could inhibit the radical-initiated copolymerization, was get ridden of by injecting the N_2. All plasma-induced graft copolymerization were carried out at constant temperature from 50 to 80°C. After each graft copolymerization, the PPS nonwoven was removed from the viscous homopolymer solution and washed with distilled water. It was then immersed in distilled water for 7 days, and washed with distilled water.

Characterization and testing of the graft polymer

The grafting rate was measured by gravimetric method: G (%) = $(M_g - M_0)/M_0$, where G is grafting rate, M_0 the quality of PPS nonwoven, and M_g the quality of grafted PPS nonwoven.

SEM was performed on a KYLY-2800 type electron microscope after coating the sample with gold vapor under vacuum.

The grafted substances was tested on the PerkinElmer5600 photoelectron spectrometer using XPS, stimulated by Mg Kα.

RESULTS AND DISCUSSION

Effect of the concentration of AA on the grafting rate

The effect of the AA monomer concentration on the grafting rate of the PPS nonwoven is recorded in Figure 1. AA is graft polymerized onto the N_2 plasma pretreated PPS nonwoven of different monomer concentration, ranging from 10 to 35%. It is

revealed that the effect of the AA monomer concentration is notable. The grafting rate of the PPS nonwoven was under a small level with the AA monomer concentration less than 25%, while the graft copolymerization was obvious when the AA monomer concentration was over 25%. The grafting rate increased with the increasing of monomer concentration at first, and then the curves got to the maxim, then decreased. It may be because the graft copolymerization was more important than the homopolymerization in the lower concentration monomer solution, resulted from the competition between graft copolymerization and homopolymerization. With the AA monomer concentration enhancing, the grafting rate at high AA concentration decreased. It also may owe to the high reactivity of the AA monomer, resulting in the excess formation of the homopolymer. The excessive formation of the homopolymer must have also reduced the possibility of the AA monomer reaching the PPS surface.[10]

Effect of plasma treatment time on grafting rate

The data in Figure 2 indicated that as the N_2 plasma pretreatment time increased, the curves of the grafting rate of approached their respective optimum values of 120 s of N_2 plasma pretreatment time, and then went down. This fact may be explained as that with the plasma treatment time elapsing, the impact of high-energy plasma on the surface of PPS nonwoven leads to the production of large amount of free radicals, which make the grafting rate increase. However, long-playing plasma pretreatment may cause un-
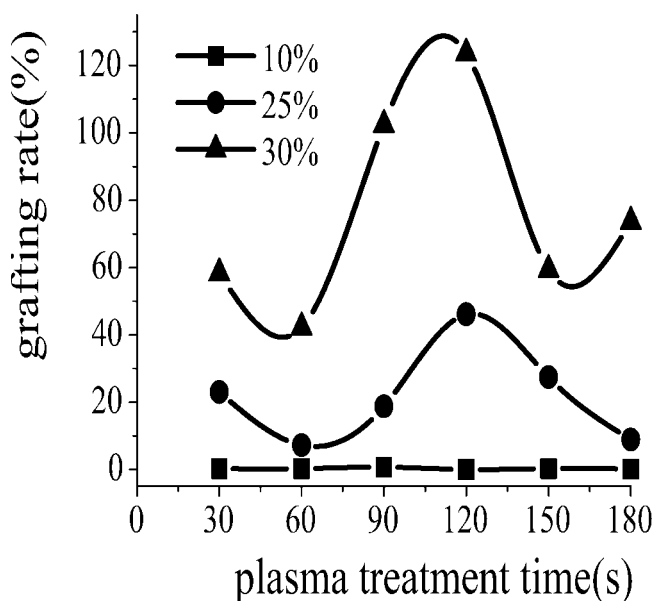
Figure 2 Effect of plasma treatment time on grafting rate under different monomer concentration plasma power (50 W), temperature (80°C), and space between electrodes (1.5 cm).
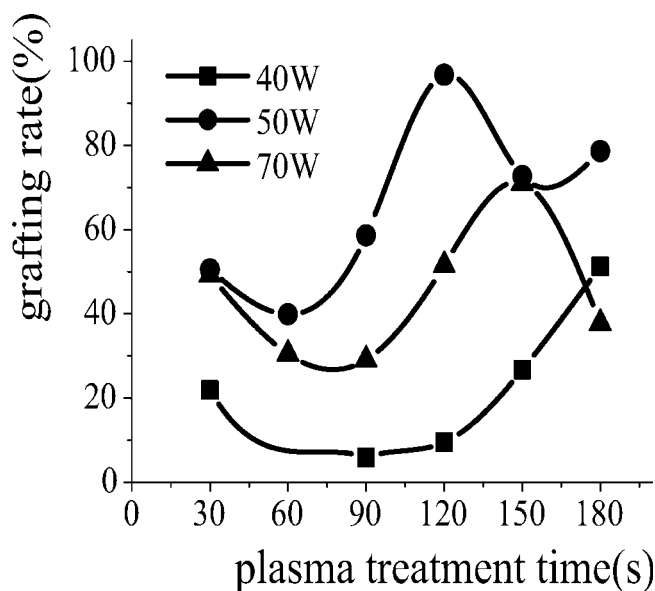
Figure 3 Effect of plasma power on grafting rate monomer concentration (35 wt %), temperature (80°C), and space between electrodes (1.5 cm).

favorable etching, crosslinking, and/or degradation of the substrate surface, resulting in no net gain of the surface activated species for the subsequent graft copolymerization. It can be found that there was no copolymerization, as the AA monomer concentration was 10%, which also agrees with the conclusion from Figure 1.

Effect of plasma power on grafting rate

The dependence of the grafting rate of the PPS nonwoven on the plasma power, ranging from 40 to 80 W in Figure 3, suggests that with the plasma power strengthening from 40 to 50 W, the grafting rate was fairly large correspondingly. But when the plasma power range from 50 to 70 W, the grafting rate becomes smaller, which may be rooted from the change of electron density. The electron density is increased with the strengthening of plasma power, resulting in the more formation of free radical and the increase of the grafting rate. If the free radical concentration reached to a specific degree, however, the probability of collide and scavenging activity of the free radical increased too, so too large plasma power goes against the grafting rate.[11,12]
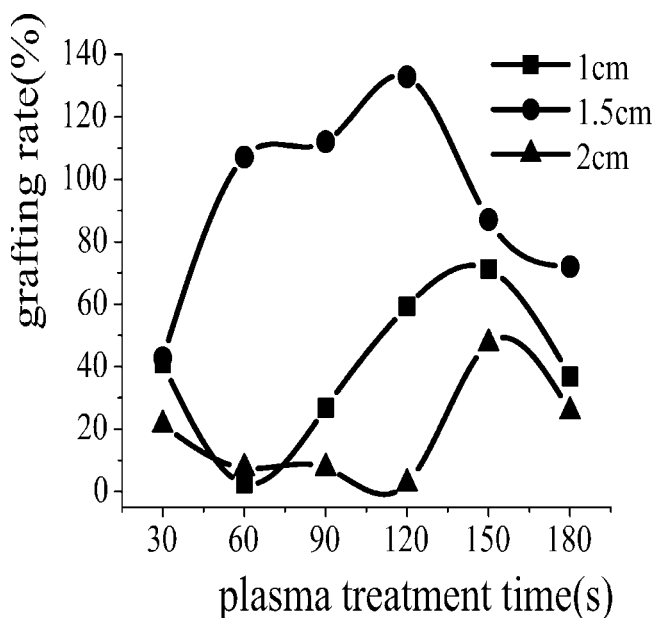
Effect of space between electrodes on grafting rate

With the space between electrodes extending from 1 to 1.5 cm, the grafting rate increased, but at 2 cm the grafting rate declined (Fig. 4). It was because the distributions of potentials and particle were not uniform, leading to the change of the grafting rate following the enlargement in the space between electrodes. When the space between electrodes was 2 cm, PPS nonwoven was irradiated in the positive column of the RF low temperature plasma surface treat, where the potentials and the electron density were low, which produced the little free radical, and resulted in the low grafting rate. When the space between the electrodes was 1 cm, low grafting rate was seen owing to the increase of the probabilities of collide and scavenging activity of the free radical. When the space between the electrodes was 1.5 cm that was the best place for making the free radical and the potentials, and at the same time the electron density was moderate, so the grafting rate was the highest.

SEM photos of grafted PPS

The morphology of grafted PPS nonwoven was investigated with SEM. It can be seen that there is difference in the morphology of grafted PPS nonwoven, with the grafting rate changing. The PPS nonwoven is the smoothest and they are the smallest grains on the fiber, as the graft yield is 9.8%, which suggest that the grafting rate is evident at the section of fiber. It is because that the section of fiber is very loose, supplying enough room for graft copolymerization. It can be learned from Figures 5(c,d) that the monomer was grafted on the surface of the PPS nonwoven and there was no graft copolymerization in the interior of the PPS nonwoven. It was because the graft copolymerization initiated by radiation takes place only on the surface of the fiber. It can be con-

Figure 4 Effect of space between electrodes on grafting rate monomer concentration (35 wt %) and temperature (80°C).
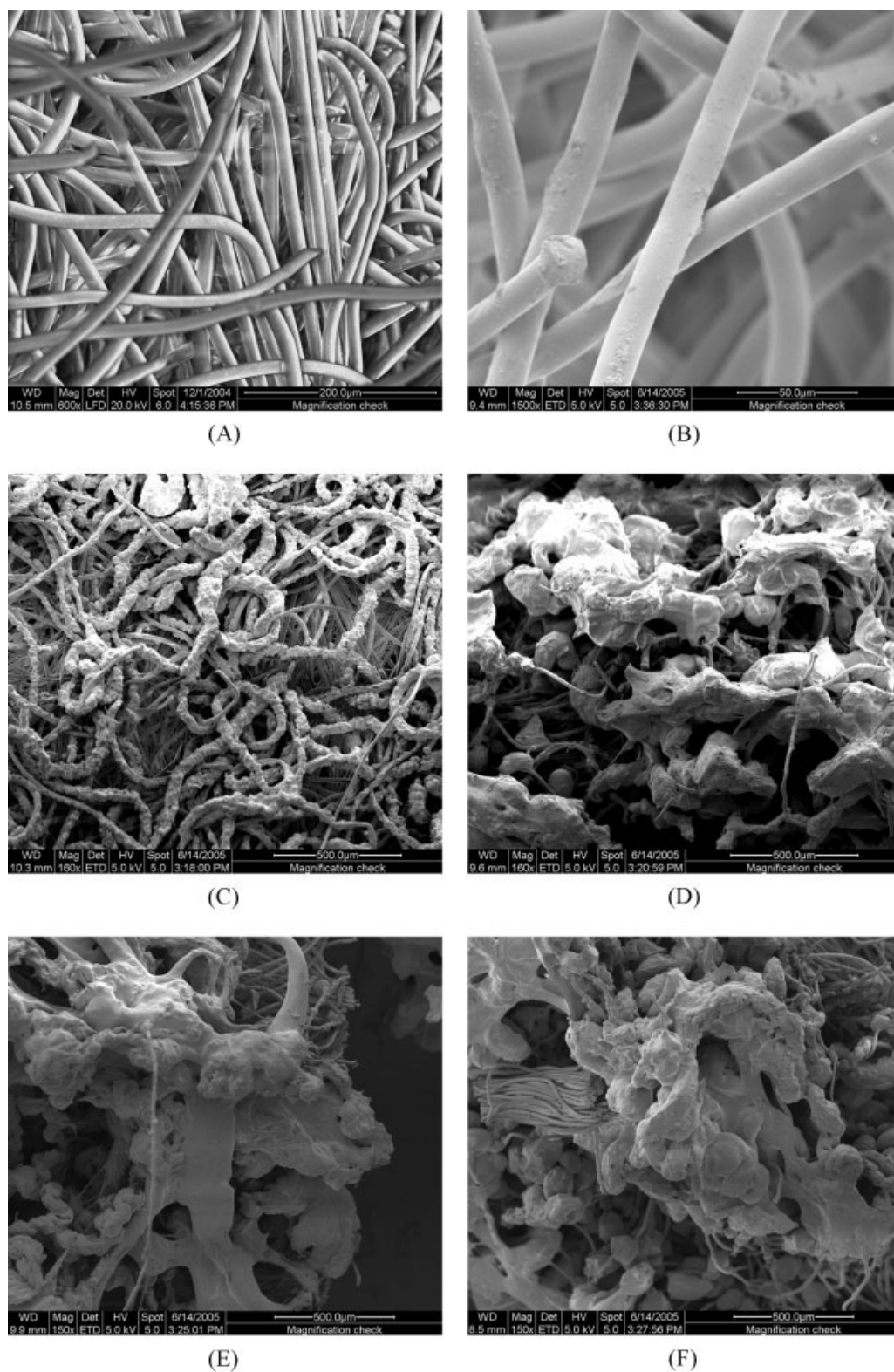
Figure 5 (a) SEM photo of ungrafted PPS (×600); (b) SEM photo of grafted PPS nonwoven with grafting rate 9.8% (×1500); (c) SEM photo of grafted PPS nonwoven with grafting rate 18.76% (×160); (d) SEM photo of grafted PPS nonwoven with grafting rate 26.90% (×160); (e) SEM photo of grafted PPS nonwoven with grafting rate 38.2% (×150); (f) SEM photo of grafted PPS nonwoven with grafting rate 59.3% (×150).

cluded that from (e) and (f), the free radical on the surface could not bring high graft rate, while the graft copolymerization is obvious. It is because of the chain transfer that goes with the graft copolymerization, which makes the free radical transfers to the longer chain.

TABLE I
The XPS Results of PPS with Different Grafting Rate

Sample numbers	The percentage of peak area (%)						Grafting rate (%)
	C1s	S2p	O1s	N1s	C1s/O1s	S2p/O1s	
P-1	81.0	2.2	13.9	0.6	5.83	0.16	0
P-2	77.5	2.0	16.8	1.6	4.61	0.12	2.0
P-3	75.4	1.0	20.2	1.6	3.73	0.05	6.7
P-4	69.9	0.8	26.4	1.6	2.65	0.03	13.9

The experiments of facial element analysis of partial samples were carried on with PHI-1600 photoelectron spectrometer from PE company of America. The results of XPS are shown in Table I and Figure 6. The XPS of PPS nonwoven with grafted AA in Figure 6 showed that there is only one peak in chart C1s of nongrafted samples, of which the position is 284.73 eV, and this peak is the characteristic one of aroma rings. There are two peaks in chart C1s of grafted samples, the positions are near 284.76 and 288.88 eV, separately. The peak near 288.88 eV proved the existence of —COOH. With the increasing of grafting rate, the area of the peak increased correspondingly, which were 5.8%, 7.61%, and 12.85%. Table I showed that after treating of N_2 plasma, the group with nitrogen was produced on the surface of PPS nonwoven. The peak area of N1s did not change with that of the grafting rate. There was some oxygen existing on the surface of PPS nonwoven before grafted, which maybe resulted from the oxidation reaction in the process of high temperature molding of PPS fiber. With the increasing of grafting rate, the proportion of the peak areas of the C1s/O1S and S2p/O1S reduced. It was further indicated that although the PPS is radiation-resistant, it can be grafted PAA according to the
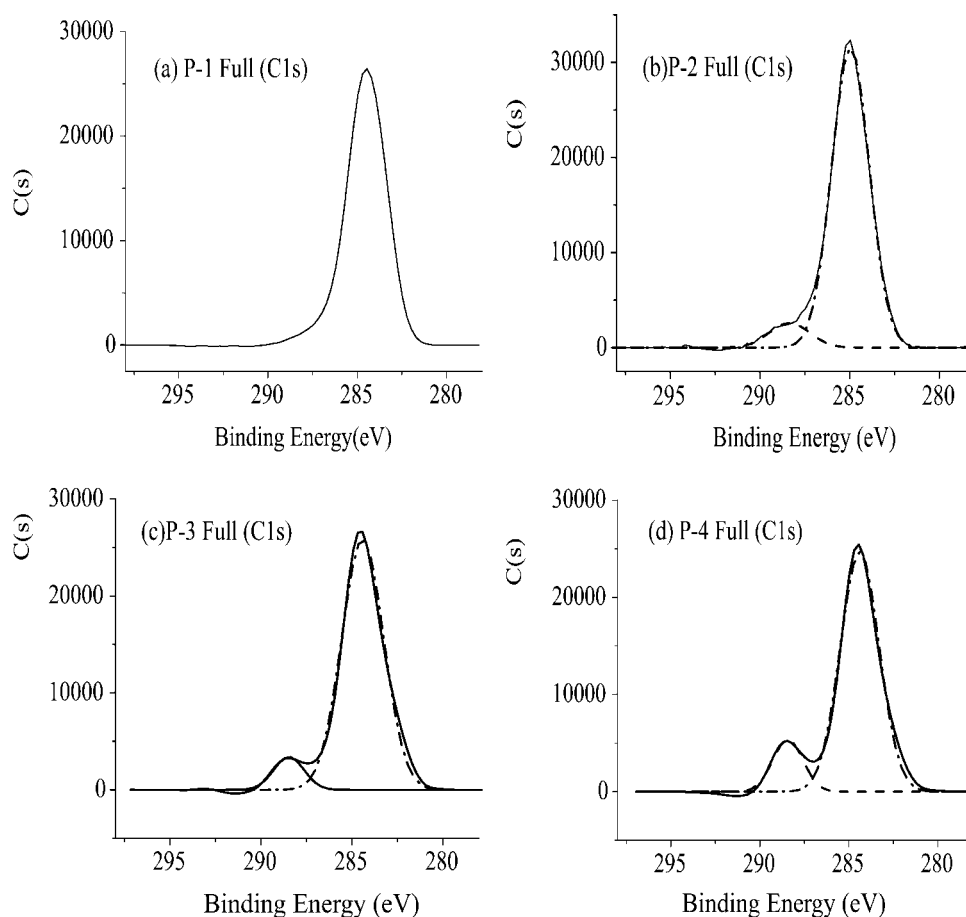
Figure 6 (a) C1s peaks of p-1 PPS nonwoven; (b) C1s peaks of p-2 PPS nonwoven; (c) C1s peaks of p-3 PPS nonwoven; (d) C1s peaks of p-4 PPS nonwoven.

manner of free radical reaction after the treatment of low temperature plasma under appropriate conditions.

CONCLUSIONS

1. PPS nonwoven surfaces, when pretreated with N_2 plasma, have been found to be susceptible to RF low temperature plasma induced graft copolymerization with AA.
2. The PPS nonwoven surface graft reaction could be optimized by the following processing conditions: 120 s of plasma treatment time, 50 W of plasma power, 1.5 cm of space between electrodes, 30% of monomer concentration, and 50°C of temperature of graft polymerization.
3. SEM results showed that there is difference in the morphology of grafted PPS nonwoven, with the grafting rate changing. Because graft copolymerization initiated by radiation takes place only on the surface of the fiber, we confer that the chain transfer goes with the graft copolymerization.

4. Measurement of XPS showed that the peak of C1s of graft polyacrylic acid were existed, and the peak area increased with the increase of the grafting rate

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