

Properties and Application of Novel Amphoteric Polypropylene Fabrics

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ABSTRACT: The properties and characterization of a novel series of amphoteric polypropylene fabrics were done by γ -preirradiation followed by grafting methacrylic acid and then amination using (3-chloro-2-hydroxyl propyl)ammonium derivatives. The new amphoteric grafted PP fabrics have an increase in moisture regain up to 5.5% and 100% reduction in growth of *Staphylococcus aureus* and *Klebsiella pneumoniae*. Also, the dyeability was improved using acid and basic dyes. These new amphoteric textiles properties were studied using differential scanning calorimetry (DSC)

and thermogravimetric analysis including TGA and DTA. A slight decrease in the crystallinity was observed by DSC and X-ray diffraction. The modified PP fabrics can be used for the development of upholstery and medical fabrics with antimicrobial properties. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2373–2379, 2005

Key words: amphoteric poly-(propylene) (PP); thermal; antibacterial; dyeing properties

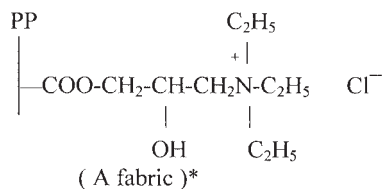
INTRODUCTION

Nowadays, polypropylene (PP) is extensively used in international markets due to its low cost, low density, and good thermal stability. Polypropylene fibers possess some drawbacks such as hydrophobicity, poor moisture absorption, static charge formation by fiber friction, and easy soils adhesion. In addition, the absence of hydrophilic reactive groups in PP macromolecules prevents its dyeability. These drawbacks have been successfully overcome by chemical modification of PP involving oxidation, chlorination, sulfonation,^{1,2} or modification by irradiation technique^{3,4} (electron beams, γ rays, or plasma treatment) followed by grafting selected monomers containing reactive groups.

Literature review revealed that Kim and Sun⁵ reported on the functional modifications of nylon to prepare durable and renewable antimicrobial nylon fabrics. They used a quaternary ammonium salt having an alkyl chains of C₁₂, which was similar to that used in the present investigation such as *N*-(3-chloro-2-hydroxylpropyl)-*N,N*-dimethyldodecylammonium chloride. They used a finishing method to bind the quaternary groups to the acid dyed nylon fibers (used as bridges) and salts bonds were formed, resulting in

different add-ons to the dyed fabrics, thus contributing to the durability of the antimicrobial functions. Le Thuaut and coworkers^{6,7} obtained novel materials by graft-copolymerization of glycidyl methacrylate onto PP. This was done and achieved by electron beam technique, followed by reaction of cyclodextrin to the linked epoxide group of the glycidylmethacrylate. The structure configuration of the resulting PP materials is characterized by Fourier transform infrared spectroscopy, solid state nuclear magnetic resonance, chemical differential scanning calorimetric, thermogravimetric, and optical microscopic analysis. Graft copolymerization of methacrylonitrile and its binary mixture with 4-vinyl pyridine in aqueous medium onto preirradiated isotactic polypropylene fibers was studied⁸ and the optimum conditions for the maximum grafting were evaluated. The rate of grafting (R_g) was determined as a function of the initial monomer concentration. The grafted copolymers were characterized by IR spectroscopy and thermogravimetry analysis. Mukherjee and Gupta^{9,10} grafted methacrylic acid onto PP fibers using simultaneous irradiation techniques, which were evaluated by thermogravimetric analysis and differential scanning calorimetry. The presence of polymethacrylic acid in the polymer was determined by infrared spectroscopy. The crystallinity of grafted fibers was deduced from the X-ray diffraction pattern, which showed that it decreased with the increase in graft level of the fibers. This behavior has been attributed to the dilution of the PP crystalline fraction by the incorporation of amorphous poly-

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Structure 1

methacrylic acid chains in the fiber matrix. The density of the grafted samples showed a continuous increase with the increase of percentage graft. However, the diameter did not change up to 16% graft content, after which an increase in the diameter was observed. This increase in diameter has been related to the sharp increase in disperse dye uptake of grafted fibers at higher levels of grafting. Acrylic acid¹¹ was grafted onto PP fabric by a preirradiation method using γ rays. The effects of irradiation dose, reaction temperatures, reaction time, and storage time were studied. The effect of ferrous ion addition and sulfuric acid on the degree of grafting were determined. Various AA-PP metal salt grafted fabrics were prepared¹² and evaluated for their antibacterial activity. Armostrong and Waleh¹³ grafted PP with various vinyl monomers using the γ -radiation method, which improved moisture regain, dyeability, and thermal properties without significantly altering the original fabrics properties. Shukia et al.¹⁴ grafted PP with 2-hydroxyethyl methacrylate using UV in the presence of three different photo initiators, uranyl nitrate, ceric ammonium nitrate, and benzoin ethyl ether, separately. The parameters of grafting were optimized for the maximum graft add-on. The moisture regain of grafted PP increased in proportion to the graft add-on. Dyeing with reactive dye gave only a light color with the grafted fibers.

In the present study, chemical modification technique was adopted. First PP fabric was γ -preirradiated followed by grafting with methacrylic acid and then amination of the produced fabric. This method resulted in changing and improving the hydrophobic character of the PP fabric by introduction of the above new hydrophilic groups.

A novel series of amphoteric PP fabrics was previously prepared¹⁵ and characterized. These fabrics contain in their chemical constitution cationic sites such as quaternary and secondary ammonium groups and anionic sites of methacrylic acid besides other reactive groups such hydroxyl and ester groups.

This article involves the study of the physical and chemical properties and application on some of the novel synthesized amphoteric PP fabric.

The produced amphoteric PP fabric can be used as ion-exchange filters. These are easily dyed with both acid and basic dyes compared to the unmodified PP, which cannot be dyed by the usual conventional methods due to the lack of reactive groups in its chemical constitution. The moisture regain was analyzed and the antibacterial effects of the amphoteric PP fabrics were also determined.

Amphoteric PP fabrics are then analyzed using several methods such as differential scanning calorimetry (DSC), thermogravimetric analysis (DTA, TGA), and X-ray.

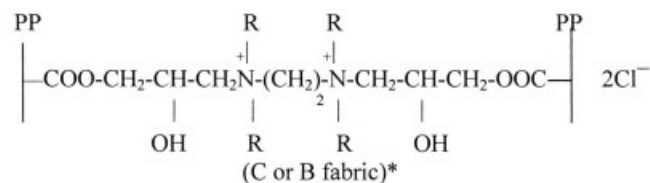
EXPERIMENTAL

Amphoteric PP-MA-ester-condensation fabrics were previously prepared in our laboratory according to described procedures.¹⁵ The PP-MA grafts of a specified graft yield were immersed in a flask containing the freshly prepared cationic agents and refluxed in alkaline medium at 90 °C for 1 h with continuous stirring. The fabric was then washed with water and acetone and finally dried at room temperature and over P₂O₅ in a vacuum desiccator and the weight increase was determined.

Some of these fabrics were chosen for this study. The chemical structure configurations of these fabrics are based on PP-MA ester condensation with selected amines and are shown in Structures 1 and 2.

Fabric A is PP-MA-ester (2-hydroxyl propyl)triethyl ammonium chloride (A); Fabric B is PP-MA-ester(2-hydroxylpropyl)tetramethylethylenediamine dichloride (B); and Fabric C is PP-MA-ester(2-hydroxylpropyl)ethylenediamine dichloride (C).

PP-MA fabric is polypropylene grafted with methacrylic acid.



Where R=H (for C fabric)* or Where R=CH₃ (for B fabric)*

*Fabric A, PP-MA-ester (2-hydroxyl propyl)triethyl ammonium chloride (A)

Structure 2

TABLE I
Moisture Regain of Amphoteric PP Fabrics

PP-MA-Graft (%)	PP-MA-ester AHE condensate	Weight increase by cationic agent (%)	Moisture regain of PP-MA-graft (%)	Moisture regain of PP-MA-ester AHE condensate (%)
20.5	PP-MA-ester(2-hydroxypropyl)triethylammonium chloride (A)	26	2.48	5.5
20.04	PP-MA-ester(2-hydroxypropyl)tetramethylethylenediamine dichloride (B)	22.16	2.47	5.3
21.5	PP-MA-ester(2-hydroxyl-propyl)ethylenediamine dichloride (C)	12.31	2.66	4.46

Moisture regain

The samples were conditioned at room temperature for 4 days in a desiccator containing a saturated solution of sodium nitrite to achieve a relative humidity of 65%. The samples were weighed and dried. The moisture regain was calculated as follows.

$$\text{Moisture regain (\%)} = \frac{W - W_0}{W_0} \times 100,$$

where W and W_0 are the conditioned and oven dry weights of the sample, respectively.

Nitrogen analysis

The nitrogen content was determined according to the micro-Kjeldahl method.¹⁶

DSC method

A sample of 6–10 mg was accurately weighed on a thermogravimetric mettler balance in a small 40- μ L aluminum crucible. The crucible cover was perforated with a pin to allow the evaporation of the decomposed vapors. It was compressed to the crucible by means of a special compression machine. The crucible was put together with an empty reference crucible in a calorimetric oven (DSC 30 Mettler) connected to a TC 10A Mettler processor control unit and a printer. The processor programmed and the temperature was raised from 0 to 450 °C in a nitrogen atmosphere. The DSC melting peak gives the heat of fusion of the sample. By integration of the peak area, the crystallinity is computed by dividing the specific heat of fusion of the

sample ΔH_f by the heat of fusion of 100% crystalline PP, ΔH_{cryst} is 149 J/g.

TGA and DTA analysis

TGA studies were carried out on a Shimadzu TGA-30 at a heating rate of 10 °C/min over a heating temperature range from room temperature to 500 °C.

The differential thermal analyzer used was DTA-50 Shimadzu.

X-ray diffraction(XRD)

The XRD patterns were measured with a Shimadzu diffractometer XD-DI series, which was automatically operated.

Antibacterial tests

The antibacterial properties were quantitatively determined according to the experimental normalization XPG 39–010 published by the Afnor concerning textiles and polymeric surfaces having antibacterial properties.¹⁷ The bacteria used were Gram-positive *Staphylococcus aureus* (ATCC 6538) and Gram-negative *Klebsiella pneumonia* (ATCC 4352).

After 5 min, amphoteric PP fabrics (five samples) and control fabrics(three samples) cut into small pieces (4 cm²) were put on the surface of a Petri dish containing Müller Hinton agar, which was inoculated with 1 mL suspension of 1×10^6 to 3×10^6 CFU/mL of colonies forming units of the previous bacteria culture. To ensure sufficient contact between the fabric

TABLE II
Nitrogen Content of Amphoteric PP Fabrics

PP-MA-AHE condensates	Nitrogen (%)
PP-MA-ester(2-hydroxylpropyl)triethylammonium chloride (A)	1.2
PP-MA-ester(2-hydroxylpropyl)tetramethylethylenediamine dichloride (B)	1.38
PP-MA-ester(2-hydroxylpropyl)ethylenediamine dichloride (C)	1.1

TABLE III
Differential Scanning Calorimetry (DSC) of Amphoteric Fabrics

Fabric	Specific heat of fusion, ΔH_f (J/g)	Crystallinity ^a (%)	Melting temp. (°C)
PP fabric nonirradiated	96.95	65.1	163.8
PP-MA-ester (2-hydroxylpropyl)tetramethylethylenediamine dichloride (B)	62.54	42.0	162.5

$$^a \text{Crystallinity \%} = \frac{\Delta H_f}{\Delta H_{\text{cryst}}(149)} \times 100.$$

and the agar medium, a sterilized glass disc (200 g) was placed into the top of the fabric with the purpose of pressing them for 1 min. The resulting fabrics containing the adherent bacteria were placed into a sterilized Petri dish, taking into account that the inoculated face is placed upward to the air and further incubated at 37 °C for 24 h in a humid atmosphere. The fabric samples were then extracted with 20 mL of neutralization broth and vigorously shaken for 1 min. A 1-mL aliquot of the suspension mixture was added to 9 mL of a dilution solution and serially decimal diluted (10^2 , 10^3 , and 10^4). Then it was plated onto 20 mL of nutrient agar and kept at 37 °C for 24 h. Viable colonies of bacteria were counted by the spread plate method:

Percentage reduction in numbers of bacteria growth

$$= \frac{A - B}{A} \times 100,$$

where A is the number of bacteria counted for untreated fabrics (control) and B is the number of bacteria counted for treated amphoteric PP fabrics.

Reduction of the bacteria growth was determined at the beginning of the experiment at t_0 and after 24 h.

Dyeing procedure

The dyeing bath was prepared by addition of the dyestuff solution (Acid Red 1or Basic Red 8 ,0.2 g/L) and a nonionic surfactant such as nonyl phenol ethoxylate (0.2 g/L). The pH was about 4–5. The fabric to liquor ratio 1 : 100.

Dyeing was started at 50°C and the temperature was gradually raised to boiling in half an hour. The dyed sample was removed from the dye bath and washed with fresh water. Unfixed dye was removed by extraction of the wet sample with 50% aqueous dimethylformamide (DMF).

The color strength (K/S) of the dyed sample after extraction with DMF solution was determined using a spectrophotometer (Perkin-Elmer Lambda 3(b)) and applying the Kubelka–Munk equation¹⁷ as follows:

$$K/S = \frac{(1 - R)^2}{2R} - \frac{(1 - R_0)^2}{2R_0},$$

where K = absorption coefficient, S = scattering coefficient, and R , R_0 are the reflectance fractions of the dyed and undyed samples, respectively.

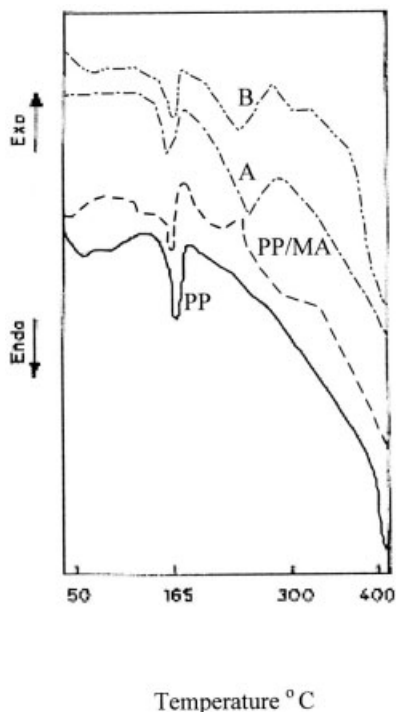


Figure 1 DTA thermograms of (—) polypropylene (PP) fabric, (---) polypropylene grafted with methacrylic acid, (-.-) PP-MA-ester(2-hydroxylpropyl)triethylammonium chloride (A), and (- - -) PP-MA-ester(2-hydroxylpropyl)tetramethylethylenediamine dichloride (B).

TABLE IV
Weight Loss (%) at Different Decomposition Temperatures for PP Fabric, PP-MA Grafted Fabric, and Amphoteric Fabrics

Fabric	Weight loss (%)		
	350°C	400°C	450°C
PP	30	96	100
PP-MA	30	77	92
A	45	66	92
B	30	65	88

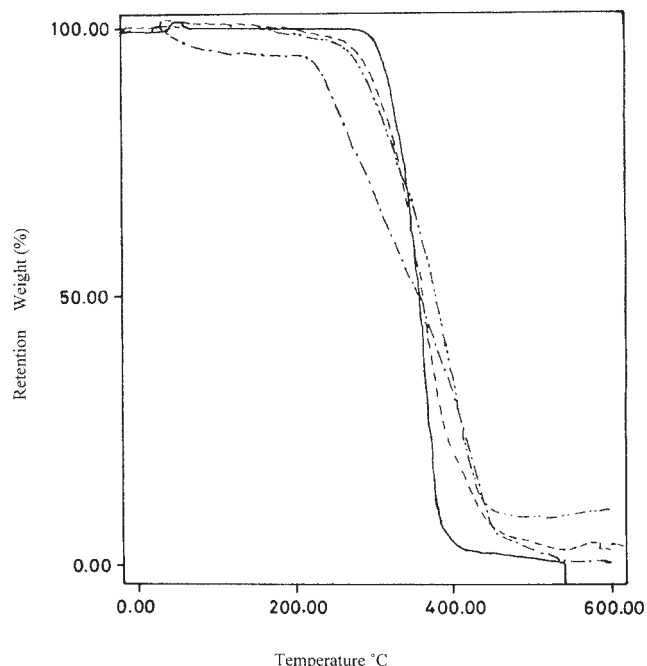


Figure 2 TGA thermograms of (—) polypropylene (PP) fabric, (---) polypropylene grafted with methacrylic acid, (-·-) PP-MA-ester(2-hydroxylpropyl)triethylammonium chloride (A), and (-·-·) PP-MA-ester(2-hydroxylpropyl)tetramethylethylenediamine dichloride (B).

RESULTS AND DISCUSSION

Moisture regain

The moisture regain of the amphoteric PP fabrics was improved due to the formation of hydrophilic groups by grafting MA and subsequent amination. Thus, it attained an increase of 5.5, 5.3, and 4.4%, respectively, for the amphoteric PP fabrics A, B, and C compared to nil for the untreated PP as shown in Table I.

Nitrogen analysis

The analysis of the nitrogen content for the amphoteric PP (A, B, and C) confirmed the amination reaction completion for grafted MA as shown in Table II.

DSC

DSC of the samples is demonstrated in Table III. The melting point of amphoteric fabric was slightly decreased compared to the untreated PP fabric. The crystallinity of Fabric B was decreased from 65.1 to 42%. The decrease in crystallinity and the disordered structure of amphoteric PP fabric becomes more easily accessible to water, and dye diffusion and the dyeability of the fabrics are improved.

DTA

A single peak is shown in Figure 1 (PP, PP/MA, A, B) and it is the melting point of PP fabric detected at 165°C, which is in agreement with that observed in DSC (163.8°C).

The profile curve for PP-MA shows two peaks occurring at 165 and 215°C. The second peak may be due to loss in weight.

The second peak for A and B, occurring at 250°C, is due also to weight loss.

TGA

Thermal stability measurements of PP fabric, grafted with MA and amphoteric PP fabrics containing mono- and diquaternary ammonium salt and secondary diamine groups, was carried out by TGA in the temperature range of 200–600°C under a nitrogen atmosphere. Thermal stability of the samples is an important factor for their durability during practical use. The percentage weight loss was determined at three elevated temperatures, 350, 400, and 450°C, as shown in Table IV and Figure 2. After grafting, the fibers exhibit higher weight retention in the temperature range of 350–600°C compared to the untreated PP fabric.

X-ray diffraction

The X-ray pattern of the control PP is characterized by a diffraction scattering angle 2θ at 13°, which remains at this value regardless of the grafting reaction.

The decrease of the scattered intensity is due to the grafting of MA or the introduction of amino group

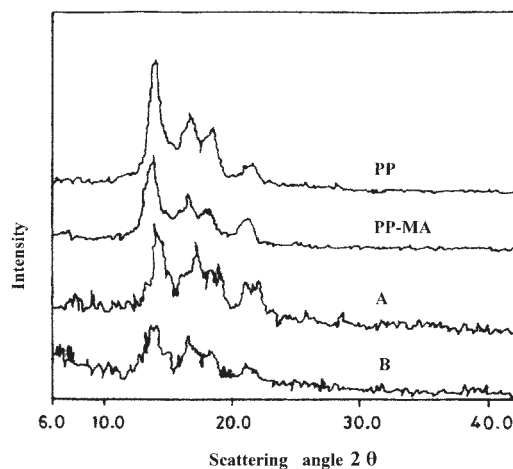


Figure 3 X-ray diffractograms of polypropylene fabric (PP), polypropylene grafted with methacrylic acid (PP-MA), PP-MA-ester(2-hydroxylpropyl)triethylammonium chloride (A), and PP-MA-ester(2-hydroxylpropyl)tetramethylethylenediamine dichloride (B).

TABLE V
Effect of PP Quaternization Reaction on the Ratio of Unreact MA to Initial MA Graft

Fabric (%)	MA graft (%)	Quaternization reaction completion	Reacted MA	Unreacted MA	Ratio of unreacted MA to total grafted MA (%)
				%	
Control PP-MA	40	—	—	—	1
(C)	15	34.9	5.24	9.77	0.65
(A)	20.5	49.34	10.12	10.38	0.51
(B)	20	61.4	12.28	7.72	0.39

into PP-MA graft occurring into the amorphous region which is shown in Figure 3 (PP/MA, A, B). The scattered intensity for A and B became broader and thus indicates the increase of the amorphous region relative to the crystalline one.

Antibacterial effect

The tested fabrics are amphoteric polypropylene (PP) containing grafted, untreated methacrylic acid, mono- and diquaternary ammonium salts, and secondary diamine groups. The hydrophobic nature of PP fabric prevents good contact between the aqueous medium of the agar containing bacteria and PP surface. The results shown in Table V indicated that the fabric (PP-MA) grafted with only 40% methacrylic acid is very effective in reducing the growth of bacteria by >99%. The fabric grafted and crosslinked by the secondary diamine groups proved to be a biocidal fabric since its reduction growth of bacteria was >99% (Fabric C).

It is shown in Tables IV and V that the presence of the carboxylic acid groups in the fabric play an important role in complexation of the microcations of the nutrient agar medium required by the bacteria. Thus, they form the corresponding carboxylate salts; being hydrophilic, they are oriented toward the surface and are in intimate contact with the bacteria, providing a biocidal action. This finding is in agreement with the previous published investigations.¹² It seems that the structural configuration of the secondary amino nitrogen (protonated groups) of the diamino containing

onto the treated (Fabric C) has an effect due to the presence of a lone pair of electrons on the nitrogen available for metal complexation. The tetramethylethylenediamine fabric (Fabric B) was ineffective.

However, the initial reagents used for quaternization of the PP fabric were tested and they provided no biocidal effects on the above-tested bacteria. The fixed counts at t_0 compared to those after 24 h incubation might refer to no antibacterial action for A and B fabrics as shown in Table VI.

Dyeing properties

The color strength (K/S) of untreated fabric is very low compared to that of the PP-MA grafted and amphoteric PP fabrics as shown in Table VII.

In the dyeing of PP-MA grafted fabrics using a basic dye, the dye reacted with the carboxyl groups present in the grafted chains. Dyeing of amphoteric PP fabrics with a basic dye should also react with the carboxyl groups available on the amphoteric fabrics as unreacted MA.

Interactions of acid dye with the quaternary ammonium salt groups contained in the amphoteric fabric resulted in the formation of strong ionic bonding of the anionic sulfonate groups of the dyes and cationic quaternary ammonium onto the grafted fabric. Thus, modification and production of amphoteric PP achieved dyeability with both basic and acid dyes.

The authors express their great gratitude to Prof. M. Abdel Samie for his interesting antibacterial discussion.

TABLE VI
Effect of Amphoteric PP Fabrics on the Reduction Growth of Bacteria

Fabric	Ratio of unreacted MA to grafted MA	<i>Staphylococcus aureus</i>		<i>Klebsiella pneumonia</i>		Reduction growth of bacteria (%)	
		E_0	E_{24}	E_0	E_{24}	<i>Staphylococcus aureus</i>	<i>Klebsiella pneumonia</i>
		(CFU/ml)		(CFU/ml)			
PP Control	0	1×10^3	1×10^3	1×10^3	1×10^3	0	0
PP-MA	1	1×10^3	0	1×10^3	0	>99%	>99%
C	0.65	1×10^3	0	1×10^3	0	>99%	>99%
A	0.51	1×10^3	1×10^3	1×10^3	1×10^3	0	0
B	0.39	1×10^3	1×10^3	1×10^3	1×10^3	0	0

TABLE VII
Dyeing^a Properties for PP Fabric, PP-MA Grafted
Fabric, and Amphoteric Fabrics

Fabric	Color strength (K/S)	
	Dyed fabric: acid dye	Dyed fabric: basic dye
PP	0.234	0.1482
PP-MA	0.311	8.12
A	7.96	7.8
B	8.12	7.5
C	7.65	6.61

^a Dyes: acid dye, C.I. Acid Red 1, CIBA-GEIGY, and basic dye Basic Red 18.

References

- Carreher, C. E. *Polymer Chemistry*, 4th ed.; Dekker: New York, 1996; p 451.
- Rouette, H. K. *Encyclopedia of Textile Finishing*; Springer-Verlag: New York, 2001; Vol. 2, p 1673.
- Gawish, S. M.; Kantoush, A.; El Naggar, A. M.; Mosleh, S. *J Appl Polym Sci* 1992, 1671.
- Gawish, S. M.; Kantoush, A.; El Naggar, A. M.; Mosleh, S. *J Appl Polym Sci* 1995, 57, 45.
- Kim, Y. H.; Sun, G. *Textile Res J* 2000, 70, 728-.
- Le Thuaat, P.; Marel, B.; Crinic, G.; Maschke, U.; Coqueret, X.; Morcellet, M. *J Appl Polym Sci* 2000, 77, 2118.
- Marel, B.; Le Thuaat, P.; Morcellet M.; Maria, N. A.; Maschke, U.; Bertini, S.; Vecchi, C.; Coqueret, X.; Torri, G. *J Appl Polym Sci* 2000, 77, 1869.
- Kaur, I.; Barsola, R.; Misra, B. N. *J Appl Polym Sci* 1994, 55, 329.
- Mukherjee, A. K.; Gupta, B. D. *J Appl Polym Sci* 1985, 30, 2253.
- Mukherjee, A. K.; Gupta, B. D. *J Appl Polym Sci* 1985, 30, 3479.
- Chen, J.; Nho, Y. C.; Park, J. S. *Radiat Phys Chem* 1998, 52, 201.
- Park, J. S.; Kim, J. H.; Nho, Y. C.; Hyun Kwon, O. H. *J Appl Polym Sci* 1998, 69, 2213.
- Armstrong, A. A.; Walsh, W. K. *Modification of Textile Fiber, Polymer by Radiation Induced Graft-Co-polymerization*, Office of Technical Services, Dept. of Chemistry, Washington, DC, 1962.
- Shukia, S. R.; Athalye, A. R. *J Appl Polym Sci* 1994, 51, 1567.
- Mosleh, S.; Gawish, S. M. *J Appl Polym Sci* 2003, 88, 2504.
- Vogel, A.F. *Elementary Practical Organic Chemistry, Quantitative Organic Analysis*, 2nd ed.; Longman Group: London, 1958; p 652.
- Afnor, French Normalisation, XPG39-010 May (2000) *Fabric & Polymeric Surfaces with Antibacterial Properties*.
- Kubelka, P.; Munk, F. *Z Technol Phys* 1981, 12, 593.