

Grafting Copolymerization of Cationic Vinyl Monomer with Quaternary Ammonium Groups onto Polypropylene

Guangtian Liu^{*+•}

Hebei Provincial Key Laboratory of Applied Chemistry, Yanshan University, Qinhuangdao, 066004, P. R. CHINA

ABSTRACT: Grafting polymerization was a valuable method for the modification of the chemical and physical properties of polymer surfaces. In this paper, the grafting of cationic vinyl monomer with quaternary ammonium groups, methacryloxyethyltrimethyl ammonium chloride (DMC), onto the isotactic polypropylene (iPP) granule was performed by suspension solid-state grafting process. The technique offers new opportunities in modification of polyolefins, which had the advantages of solventless, lower process temperature. The grafted PP was systematically characterized by using various analytic tools including FT-IR, DSC and TGA. The FT-IR spectra of the grafted iPP confirmed that DMC was successfully grafted onto the iPP backbone. The influences of the reaction parameters such as the concentration of DMC, the dose of styrene, initiator concentration, swelling time, reaction time, reaction temperature were investigated. The optimum condition for the grafting of DMC onto the iPP granules was obtained within the range studied. Furthermore, the results of TGA and the hydrophilicity measurement indicated that the thermal stability of the grafted iPP was enhanced remarkably, and the hydrophilicity was also enhanced due to the addition of hydrophilic quaternary ammonium groups. This research is worthwhile and it can be foreseen with a great prospect in the developing of anti-static and antiseptic materials.

KEY WORDS: Polypropylene, Cationic vinyl monomer, Grafting yield, Hydrophilicity.

INTRODUCTION

Polypropylene (PP) is a widely used material due to an excellent performance-to-price ratio, and has become one of the largest and fastest growing olefin polymers. However, its application is restricted by its hydrophobic nature and lack of polar sites. This is especially true when it comes to dyeing, painting, adhesion or blending with other polar polymers or fillers. To overcome these limitations, free radical grafting of polar vinyl monomers

onto PP has become a widely used post-polymerization process as a chemical modification of PP without significantly changing its backbones and molecular architecture [1]. After the modification, the basic physical and mechanical properties of PP are retained.

A great number of reports on grafting polar monomer onto PP has been published by conventional solution, melt and solid-state grafting rout, such as maleic

* To whom correspondence should be addressed.

+ E-mail: gtl-desire@163.com

• Other Address: Institute of Environmental and Chemistry Engineering, Yanshan University, Qinhuangdao, 066004, P. R. CHINA
1021-9986/15/2/17 7/\$/2.70

anhydride (MAH)[2-8], acrylic acid (AA)[9], methacrylic acid [10-12], glycidyl methacrylate (GMA)[13-15], methyl methacrylate (MMA)[16, 17,18] and so on. In recent years, grafting polymerization becomes a valuable method for the modification of the chemical and physical properties of polymer surfaces. Some desirable properties such as biocompatibility[19], ion-exchange[20] and thermo-sensitivity [21,22] can be obtained on many polymer surfaces by the grafting method. However, up to now, the grafting of cationic vinyl monomers with quaternary ammonium groups such as methacryloxyethyltrimethyl ammonium chloride (DMC) onto surface of PP has seldom been reported in the literature.

This study is an attempt to modify the isotactic polypropylene (iPP) granule surface by means of the suspension solid-state grafting process, in which the cationic vinyl monomer with quaternary ammonium groups, methacryloxyethyltrimethyl ammonium chloride (DMC), is used as grafting monomer, where styrene is used as the second monomer. The suspension solid-state grafting polymerization being both economical and environmentally clean technique is a convenient method for the modification of physical and chemical properties of polymeric materials. The influences of the reaction parameters such as the concentration of DMC and St, swelling time, initiator concentration on the grafting yield were investigated. The optimum conditions for the grafting of DMC onto iPP granules were obtained within the range studied. Furthermore, the hydrophilicity and the thermal stability of the grafted iPP were investigated. This research is worthwhile and it can be foreseen with a great prospect in the developing of anti-static and antiseptic materials.

EXPERIMENTAL SECTION

Materials

Commercial iPP granules (PPH-XD-425, MFR=47.6g/10min) was provided by Jinjiang Petrochemical Co. Ltd. (Jilin, China); Methacryloxyethyltrimethyl ammonium chloride (Industrial grade DMC aqueous solution with 75 wt% solid content) was provided by Wuxi Chemical Reagents Company and was used as received, with schematic structures shown in Fig. 1; styrene (Fuxing Chemical Factory, Beijing, China) was used as received; Benzoyl peroxide (BPO) was recrystallized in methanol-chloroform mixture and dried at 60°C under vacuum.

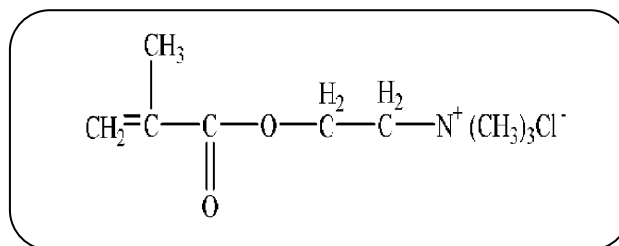


Fig. 1: The Schematic structures of Methacryloxyethyltrimethyl ammonium chloride (DMC)

Grafting procedure

In grafting polymerization, the industrial grade DMC aqueous solution with 75 wt% solid content was used, in which water can act as the medium of suspension, avoiding the recovery of organic solvent needed in the solution-state graft polymerization. Styrene has already been proved to be an appropriate candidate of coagent. It is capable of reducing the PP chain scission and increasing the grafting degree because styrene plays a “bridge” role in the grafting process. Additionally, styrene is also presented in our system as an interfacial reagent to swell the iPP granules, as well as medium for free radical, where benzoyl peroxide (BPO) was adopted as the initiator. Schematic of grafting reaction is showed in Fig. 2.

In the polymerization, the reaction temperature was well below the melting point of iPP, alleviating the side reactions of chain scission appeared in melt-state graft polymerization. Grafting procedure as follow:

The iPP granules (2.0g) were swollen in styrene solution containing BPO, and then were immersed in DMC aqueous solution in a 250 mL four-neck round bottom flask with a condenser and a stirring device. The system was deoxygenated by bubbling nitrogen for 1 h. The grafting reaction was carried out by placing the reactor in a homemade electronically controlled temperature oil bath under a nitrogen atmosphere. The grafted PP was carefully washed with boiling water for 0.5h removing DMC homo-polymer, and then were purified by Soxhlet extraction in acetone for 36h in order to eliminate polystyrene (PS), poly(styrene-co-DMC). Finally the purified samples were vacuum dried at 80°C for 24 h. The grafting yield was calculated by the following equation:

$$\text{Grafting yield (GY)(\%)} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

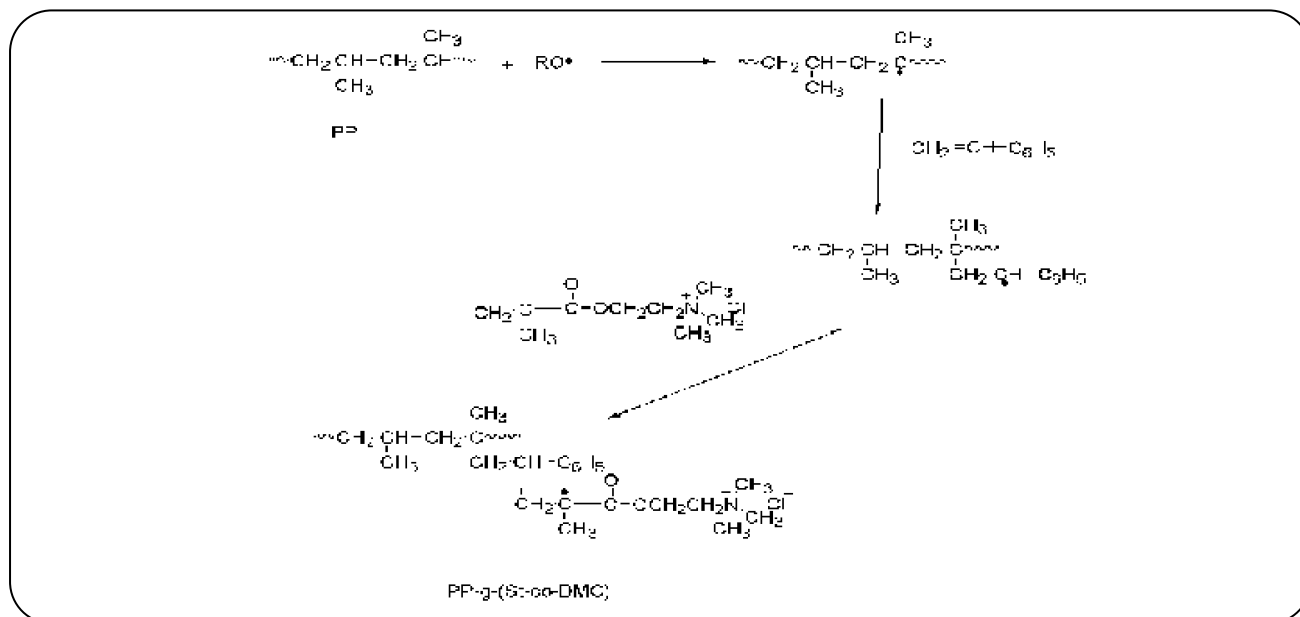


Fig.2: Schematic of grafting reaction.

Where W_0 and W_g are the weights of the sample before and after grafting, respectively.

FT-IR spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) of type Nicolet 380 spectrometer system (Nicolet company, U.S.A.) was used to study whether or not DMC was grafted onto iPP. Polymer samples were compression-molded to films at 200°C with a laboratory press.

Thermophysical properties of the pure iPP and PP-g-(St-co-DMC)

The samples were measured using a Perkin-Elmer DSC-7 thermal analyzer under ambient nitrogen atmosphere. The samples were heated up to 220°C at a rate of $10^\circ\text{C}/\text{min}$, afterwards the system was cooled down to room temperature at a rate of $20^\circ\text{C}/\text{min}$. Peak melting temperature (T_m) and melting enthalpy (ΔH_m) were measured.

The thermal stability of the pure iPP and the grafted iPP was investigated with a Perkin-Elmer Pyris6 ThermoGravimetric Analyzer (TGA). Thermogravimetric analysis was performed at a heating rate of $20^\circ\text{C}/\text{min}$ and a nitrogen flow rate of $20.0\text{ml}/\text{min}$.

Water-uptake measurement

In order to determinate gravimetrically the equilibrium water absorbency[23], the dry samples

were immersed into distilled water and kept for 24h at room temperature, the samples were taken out, the surface of the grafted sample was wiped with filter paper in order to remove the free water and then the swollen samples were weighed. The swelling percentage was determined by the equation:

$$\text{Swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

where W_s and W_d are weights of the swollen and initial samples respectively.

RESULTS AND DISCUSSION

Fig. 3 showed the FT-IR spectra of the pure iPP and the grafted iPP ($\text{GY} = 12.3\%$). Compared to the pure iPP, the typical absorption peak at 1720cm^{-1} represents the carbonyl group which originates from DMC, and the absorption peak at 1600cm^{-1} represented the backbone stretching of the aromatic ring of St. The peak at 2720cm^{-1} was attributed to the characteristic absorptions of the iPP skeleton. The results above provide the evidence of the iPP being grafted with DMC.

Table 1 summarized the grafting yield of PP-g-(St-co-DMC) with different reaction parameters. As the concentrations of the initiator BPO increased from 1.0 % to 5.0 %, the grafting yield first increased from 2.9% to 7.1%, and then decreased to 4.8%, as shown in Table 1 (S_{1-1} - S_{1-4}). In general, the grafting reaction was performed

Table 1: The influences of the reaction parameters on the grafting yield.

Samples	BPO (%)	Concentration of DMC (wt%)	St(mL)	Swelling time(hour)	Temperature($^{\circ}$ C)	Reaction time (hour)	Grafting yield (%)
S ₁₋₁	1.0	20	1.0	1	90	5	2.9
S ₁₋₂	2.0	20	1.0	1	90	5	7.1
S ₁₋₃	3.0	20	1.0	1	90	5	6.6
S ₁₋₄	5.0	20	1.0	1	90	5	4.8
S ₂₋₁	2.0	10	1.5	1	90	5	11.4
S ₂₋₂	2.0	15	1.5	1	90	5	12.0
S ₂₋₃	2.0	20	1.5	1	90	5	12.3
S ₂₋₄	2.0	25	1.5	1	90	5	13.2
S ₂₋₅	2.0	35	1.5	1	90	5	6.3
S ₃₋₁	2.0	20	0.5	1	90	5	2.6
S ₃₋₂	2.0	20	2.0	1	90	5	21.6
S ₃₋₃	2.0	20	3.0	1	90	5	17.8
S ₄₋₁	2.0	20	1.5	2	90	5	12.3
S ₄₋₂	2.0	20	1.5	4	90	5	12.4
S ₄₋₃	2.0	20	1.5	6	90	5	12.4
S ₅₋₁	2.0	20	1.5	1	80	5	0.1
S ₅₋₂	2.0	20	1.5	1	85	5	1.5
S ₅₋₃	2.0	20	1.5	1	95	5	12.0
S ₆₋₁	2.0	20	1.5	1	90	1	8.0
S ₆₋₂	2.0	20	1.5	1	90	2	11.5
S ₆₋₃	2.0	20	1.5	1	90	4	11.7
S ₆₋₄	2.0	20	1.5	1	90	6	12.3

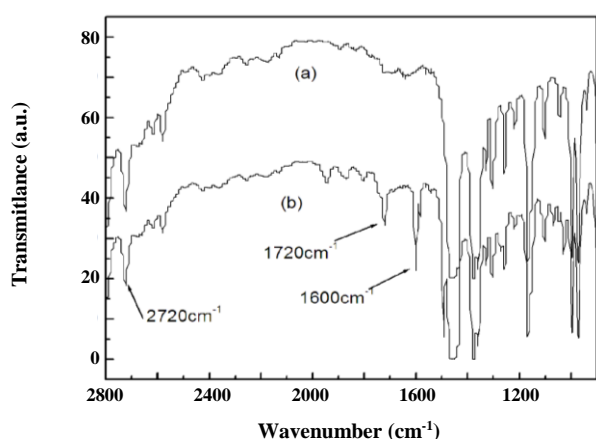


Fig. 3: FTIR of the pure iPP and PP-g-(St-co-DMC). (a) pure iPP (b) PP-g-(St-co-DMC) (GY=12.3%).

by initiating the macroradicals from the iPP skeleton, and then the addition of unsaturated monomers to the macroradicals. In the initial time, the most amount of BPO was consumed by the grafting reaction and the grafting yield therefore would remarkably increase. However, the grafting yield decreased after it went up to maximum at 2.0%. The reason for this could be attributed to the faster termination rate of free radical at higher free radical concentration, which resulted in the decrease of a net grafting yield.

The effect of concentration of DMC monomer on grafting yield of PP-g-(St-co-DMC) was given as S₂₋₁-S₂₋₅[5]. The grafting yield reached the maximum value 13.2% when the concentration of DMC was 25 wt%. However, a significant reduction in grafting yield

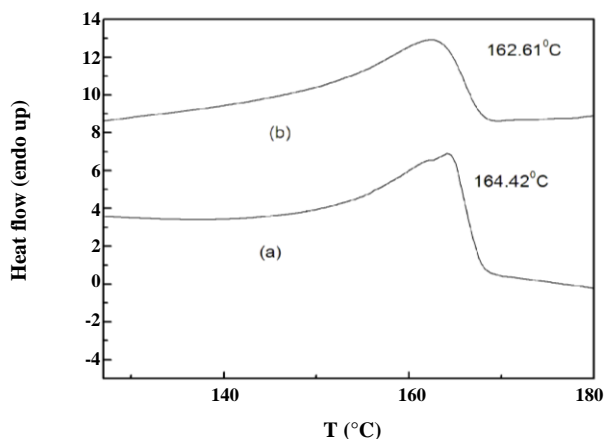


Fig. 4: The DSC melting thermographs of the pure iPP and PP-g-(St-co-DMC). (a) pure iPP (b) PP-g-(St-co-DMC) (GY=12.3%).

occurred when the monomer concentration was beyond the optimum condition. The reason should be due to the increase of DMC homopolymerization as the monomer concentration increased. Besides, at the later stage of polymerization the diffusion of the DMC monomers towards the polymeric matrix was additionally hindered by the increasing system viscosity due to the densification of DMC in the solution, the net result was a lower in the graft percentage.

In Table 1, S_{2,3}, S_{4,1}-S_{4,3} showed the effect of swelling time on grafting yield of PP-g-(St-co-DMC). It showed that the grafting yield varied slightly as the swelling time was over 1h. S_{2,3}, S_{5,1}-S_{5,3} showed that the grafting yield reached the maximum value when the reaction temperature was 90°C.

The effect of reaction time on grafting yield of PP-g-(St-co-DMC) was given as S_{2,3}, S_{6,1}-S_{6,4}, which showed that the grafting yield varied slightly as the reaction time was over 5h.

Addition of the second monomer St could greatly increase the grafting yield, as shown in Table 1 (S_{1,2}, S_{2,3}, S_{3,1}-S_{3,3}). The grafting yield reached the maximum value when the dose of St was 2.0ml. The reliable explanation was that the styrene, which was originally added as a swelling agent, reacted with iPP macroradicals much faster than DMC did, forming styryl radicals attached to the iPP backbone that were much more stable, then they readily reacted with DMC. However, a reduction in grafting yield occurred when the second monomer dosage

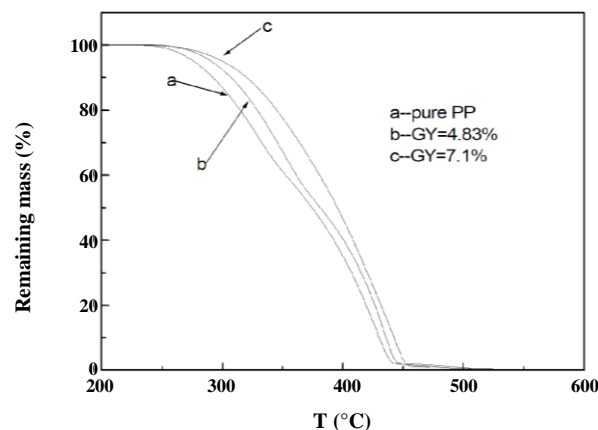


Fig. 5: The thermal stability of two PP-g-(St-co-DMC) samples and the pure iPP. (a) pure iPP (b) PP-g-(St-co-DMC) (GY=4.8%) (c) PP-g-(St-co-DMC) (GY=7.1%)

was over the optimum condition, which might be due to the increase in the homopolymerization of St.

Fig. 4 compared the DSC melting thermographs of the PP-g-(St-co-DMC) sample (b) (GY= 12.3%) with the pure iPP (a). As expected, it could be seen that grafted iPP (162.61°C) had a lower melting temperature than ungrafted iPP (164.42°C). Furthermore, the DSC result showed that the melting enthalpy of PP-g-(St-co-DMC) ($\Delta H_m=31.23\text{J/g}$) was lower than that of the pure iPP ($\Delta H_m=39.28\text{J/g}$). These might be due to destroying the ordered structure of the iPP crystals in grafting polymerization.

Fig. 5 showed the thermal stability of PP-g-(St-co-DMC). The samples with grafting yield of 4.8% and 7.1% were used to examine the thermal stability, respectively. In comparison with pure iPP ($T_d=275.9^\circ\text{C}$), 5% weight loss was found at 305°C (GY=7.1%), the thermal stability was enhanced remarkably because of the electrostatic interaction between quaternary ammonium groups grafted on iPP. In addition, from the TGA curve, 5% weight loss was found at 305°C for the sample c (GY=7.1%) and at 291.6°C for the sample b (GY=4.8%). The thermal stability was improved remarkably when the grafting yield increased from 4.8% to 7.1%. The higher the grafting yield was, the more quaternary ammonium groups in PP matrix were, so electrostatic interaction between quaternary ammonium groups became stronger.

Table 2 showed the hydrophilicity of the samples. It showed that the swelling percent increased gradually

Table 2: The hydrophilicity of the samples.

Grafting yield (%)	The swelling percentage (%)
0.0	0.0
4.8	1.6
12.0	3.1
12.3	5.3
13.2	7.4

with increasing the grafting yield, and therefore the hydrophilicity of the grafted samples is enhanced. The possible explanation is that quaternary ammonium groups on DMC chains is strongly hygroscopic, and the higher the grafting yield, the more quaternary ammonium groups exist in PP matrix, so the higher grafting yield samples are more hydrophilic. The results above also provided the evidence of the iPP being grafted with DMC.

CONCLUSIONS

In this paper, the DMC was successfully grafted onto the isotactic polypropylene (iPP) granule by suspension solid-state grafting processes. The optimum condition for the grafting polymerization was obtained. The hydrophilicity and the thermal stability of the iPP were enhanced remarkably after it was grafted with the methacryloxyethyltrimethyl ammonium chloride (DMC).

Received : Jun. 20, 2014 ; Accepted : Mar. 2, 2015

REFERENCES

- [1] Al-Malaika S., "Reactive Modifiers for Polymers", London: Blackie Academic & Professional, (1997).
- [2] Koji Miyauchi, Kyoichi Saito, High-Sensitivity Determination of Graft Ratio of Maleic Anhydride-Grafted Polyolefin by Anhydride Methylation in Supercritical Methanol Followed by ¹H NMR Spectroscopy, *Polymer*, **52**: 3519-3521 (2011).
- [3] Wulin Qiu, Takashi Endo, Takahiro Hirotsu, A Novel Technique for Preparing of Maleic Anhydride Grafted Polyolefins, *European Polymer Journal*, **41**: 1979-1984 (2005).
- [4] Chen HJ, Zhu YF, Zhang Y, Xu JR, Surface Enrichment of Polypropylene-Graft-Poly(methyl Methacrylate) on Polypropylene, *J Polym Res*, **14**: 489-496 (2007).
- [5] Shi D., Yang J.H., Yao Z.H., Wang Y., Huang H.L., Jing W., Yin J.H., Costa G., Functionalization of Isotactic Polypropylene with Maleic Anhydride by Reactive Extrusion: Mechanism of Melt Grafting, *Polymer*, **42**: 5549-5557 (2001).
- [6] Angel Contreras-García, Carmen Alvarez-Lorenzo, Cristina Taboada, Angel Concheiro, Emilio Bucio, Stimuli-Responsive Networks Grafted onto Polypropylene for the Sustained Delivery of NSAIDs, *Acta Biomaterialia*, **7**: 996-1008 (2011).
- [7] Zhang Yuncan, Chen Jinyao, Li Huilin, Functionalization of Polyolefins with Maleic Anhydride in Melt State Through Ultrasonic Initiation, *Polymer*, **47**: 4750-4759 (2006).
- [8] Zhu Lian chao, Tang Gong ben, Shi Qiang, Cai Chuan lun, Yin Jing hua, Neodymium oxide Co-Catalyzed Melt Free Radical Grafting of Maleic Anhydride Onto Co-polypropylene by Reactive Extrusion, *Reactive & Functional Polymers*, **66**: 984-992 (2006).
- [9] Tong Gang-sheng, Liu Tao, Zhao Ling, Hu Li-xia, Yuan Wei-kang, Supercritical Carbon Dioxide-Assisted Preparation of Polypropylene Grafted Acrylic Acid with High Grafted Content and Small Gel Percent, *The Journal of Supercritical Fluids*, **48**: 261-268 (2009).
- [10] Yessica S. Ram' rez-Fuentes, Emilio Bucio, Guillermina Burillo, Radiation-Induced Grafting of N-Isopropylacrylamide and Acrylic Acid onto Polypropylene Films by Two Step Method, *Nuclear Instruments and Methods in Physics Research B*, **265**: 183-186 (2007).
- [11] Wang Chyung-Chyung, Su Ching-Hua, Chen Jong-Pyng, Chen Cheng-Chi, An Enhancement on Healing Effect of Wound Dressing: Acrylic Acid Grafted and Gamma-Polyglutamic Acid/Chitosan Immobilized Polypropylene Non-Woven, *Materials Science and Engineering: C*, **29**: 1715-1724 (2009).
- [12] Shalini Saxena, Alok R. Ray, Bhuvanesh Gupta, Chitosan Immobilization on Polyacrylic Acid Grafted Polypropylene Monofilament, *Carbohydrate Polymers*, **82**: 1315-1322 (2010).
- [13] Zheng Yong, Liu Haiyan, V. Gurgel Patrick, G. Carbonell Ruben, Polypropylene Nonwoven Fabrics with Conformal Grafting of Poly(Glycidyl Methacrylate) for Bioseparations, *Journal of Membrane Science*, **364**: 362-371 (2010).

- [14] Al-Malaika S., Eddiyanto E., **Reactive Processing of Polymers: Effect of Bifunctional and Tri-Functional Comonomers on Melt Grafting of Glycidyl Methacrylate onto Polypropylene**, *Polymer Degradation and Stability*, **95**: 353-362 (2010)
- [15] Charu Tyagi, Lomas Tomar, Harpal Singh, **Glycidyl Methacrylate-co-N-vinyl-2-pyrrolidone Coated Polypropylene Strips: Synthesis, Characterization and Standardization for Dot-Enzyme Linked Immunosorbent Assay**, *Analytica Chimica Acta*, **632**: 256-265 (2009).
- [16] Hou Lianlong, Zhao Min, Liu Hongzhi, Yang Guisheng, **Novel Multimonomer-Grafted Polypropylene Preparation and Application in Polypropylene/poly(Vinyl Chloride) Blends**, *J. Appl. Polym. Sci.*, **107**: 2356-2363 (2008).
- [17] Tong Gang-Sheng, Liu Tao, Hu Guo-Hua, Zhao Ling, YuanWei-Kang, **Supercritical Carbon Dioxide-Assisted Solid-State Free Radical Grafting of Methyl Methacrylate Onto Polypropylene**, *Journal of Supercritical Fluids*, **43**: 64-73 (2007).
- [18] Hanjia, Chen Yafei, Zhu Yi, Zhang Jiarui, Xu R., **Surface Enrichment of Polypropylene-graft-Poly(Methyl Methacrylate) on Polypropylene**, *J Polym Res.*, **14**: 489-496 (2007).
- [19] Pinar Akkas, Kavakl, Cengiz Kavakl, Noriaki Seko, Masao Tamada, Olgun Güven, **Radiation-Induced Grafting of Dimethylaminoethylmethacrylate onto PE/PP Nonwoven Fabric**, *Nuclear Instruments and Methods in Physics Research B*, **265**: 204-207 (2007).
- [20] Hyun-Ju Park, Choon-Ki Na, **Preparation of Anion Exchanger by Amination of Acrylic Acid Grafted Polypropylene Nonwoven Fiber and Its Ion-Exchange Property**, *Journal of Colloid and Interface Science*, **301**: 46-54 (2006).
- [21] Angel Contreras-García, Carmen Alvarez-Lorenzo, Angel Concheiro, **PP Films Grafted with N-Isopropylacrylamide and N-(3-Aminopropyl) Methacrylamide by γ Radiation: Synthesis and Characterization**, *Radiation Physics and Chemistry*, **79**: 615-621 (2010).
- [22] Iván Meléndez-Ortiz H., Emilio Bucio, **Radiation Synthesis of a Thermo-pH Responsive Binary graft copolymer (PP-g-DMAEMA)-g-NIPAAm by a Two Step Method**, *Polymer Bulletin*, **61**: 619-629 (2008).
- [23] Yessica S. Ramírez-Fuentes, Emilio Bucio, Guillermina Burillo, **Thermo and pH Sensitive Copolymer Based on Acrylic Acid and N-sopropylacrylamide Grafted onto Polypropylene**, *Polymer Bulletin*, **60**: 79-87 (2008).