

# Grafting of iPP Powder with Methacrylate Monomers in Water Medium

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**ABSTRACT:** The grafting of different methacrylates on iPP in the solid state has been studied under various reaction conditions using a radical initiation. Three peroxides and five grafting agents representing methyl-, ethyl-, butyl-, ethyl hexyl-, and dodecyl methacrylate were tested. The grafting efficiency (GE) performed in water medium (slurry) as possible heat transfer medium was compared with the GE obtained without using water. The iPP powder was first impregnated with monomer and peroxide initiator and then water solution of NaCl was added. Obtained GEs were

much higher for all peroxides and monomers used when compared with GE performed without water. Quantity of grafted monomer was determined by Fourier transform infrared spectroscopy (FTIR). The products were characterized by differential scanning calorimetry (DSC) and surface energies of grafted iPP films were measured. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2750–2758, 2011

**Key words:** graft copolymers; modification; poly(propylene) (PP); solid state structure

## INTRODUCTION

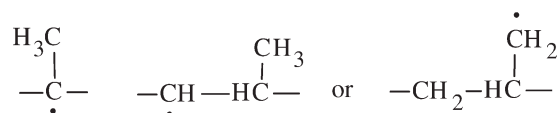
The search for effective methods for grafting isotactic polypropylene (iPP) evolved over the past fifty years.<sup>1,2</sup> The aim of this effort is, in most cases, to suppress the nonpolar character of iPP by attaching to it polar functional groups or chains. This has led to methodologies for preparing multi-component polymer systems based on iPP. Continued commercial applications for modified iPP such as nanocomposites containing dispersed nanoparticles, supports the need for further development. It should be mentioned that, currently, the iPP compatibilizer with highest efficiency in mixing with inorganic fillers and polar polymers is iPP grafted with maleic anhydride (MAH).<sup>3,4,5</sup>

Chemical modification of iPP is based practically exclusively on free radical processes. These processes can be initiated by peroxides,<sup>6,7</sup> mechanochemical, irradiation,<sup>8</sup> and also by plasma.<sup>9–15</sup> Plasma and excimer laser ablation are mostly used for surface modification of iPP in the shape of small particles or other more voluminous form of modified polymeric material.<sup>16–18</sup> The mechanism of MAH grafting on iPP as well as on 2,4-dimethyl pentane and squalane as model compounds of iPP has been studied.<sup>7,19</sup> The mechanism of iPP grafting is usually described in a simplified form

whereby free radical of initiator, I<sup>•</sup> reacts with a polymer chain, PPH, by hydrogen abstraction (reaction A):

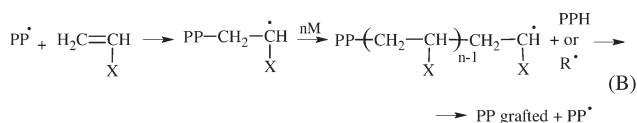


Solomon and coworkers<sup>19</sup> have found that reaction of poly(propylene) with tert-butoxy free radicals produces three kinds of free radicals:



of which the ratio of primary : secondary : tertiary free radicals is 5.6 : 1.5 : 1.

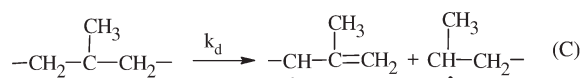
In reaction (B), any of the three types of free radicals (marked with the common symbol PP<sup>•</sup>) may react with monomer M of a different kind, for example, MAH, styrene, methacrylic acid, glycidylmethacrylate, flame retardants, etc.<sup>20–22</sup>:



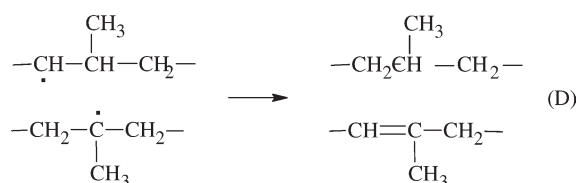
Double bonds are known to be present in PP. These may form during its preparation and also they may arise during the grafting process<sup>23,24</sup> as a result of the degradation reaction involving  $\beta$ -scission of the tert. PP<sup>•</sup> free radicals. This reaction proceeds also in the presence of vinyl monomer.<sup>23</sup>

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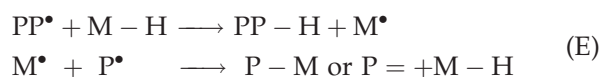
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This means that the rate of monomolecular destruction of the tertiary free PP<sup>o</sup> radical (reaction C) considerably competes with the grafting reaction (B). Double bonds in iPP arise also by a disproportion-termination reaction of two PP<sup>o</sup> free radicals e.g.:



Ivantchev et al.<sup>25</sup> observed a decrease of PP free radicals during irradiation of iPP in the presence of low molecular additives or monomers. These react with propagating free radicals in a transfer reaction (E). The arising low molecular free radicals which, with their greater mobility can easily find and react with "static" PP<sup>o</sup> free radicals in a termination reaction. Because the reaction proceeds at room temperature, this mechanism can be realized in the amorphous phase only.



By what ever means the double bonds in iPP arise, they function as effective free radical scavengers. They also capture propagating chains<sup>23,26</sup> that are formed by the direct polymerization of monomer initiated by low molecular weight free radicals. This contributes to increased grafting efficiency (GE).<sup>23,26</sup>

Reaction in the melt is the most wide-spread method for carrying out iPP modification and grafting.<sup>3,4,15,27</sup> Solution reactions<sup>28</sup> generally provide lower yields; e.g., grafting of iPP in xylene produced only 0.7 wt % dimethyl itaconate graft.<sup>17</sup> It should be mentioned that a recent novel method of iPP grafting utilized dissolution in super-critical CO<sub>2</sub> with peroxide initiation. This special method gave higher yields of grafted monomers (in the case of maleic anhydride nearly 5.2 wt %) at 125°C compared with that of the solid state reaction (nearly 2 wt %).<sup>29</sup>

In the last decades, interest in the less-used method of solid state grafting of iPP has increased. This method allows for better control of undesired side reactions—mainly degradation reactions—as well as easier elimination of low molecular weight by-product.<sup>15,25,30–35</sup> The base polymer can be used in the form of powder, granules, or film.

This work is a continuation of our studies of grafting in the solid state<sup>26,32,36</sup> with emphasis on the use of water as a heat transfer and dispersing medium. This contrasts with a medium of inert gas and monomer vapor, which has been used until now. The usual procedure for solid phase grafting involves heating a mixture of powdered iPP containing peroxide and monomer absorbed in the amorphous part of the iPP particles, where the main grafting reaction is realized.<sup>32,37</sup> This represents a heterogeneous material, in which heat transfer and thermal equilibration are established slowly. Therefore, in this study, we have used water as a heat transfer medium. Besides pure water, aqueous solutions of NaCl were used to decrease the solubility of monomer in water. The primary goals of this study are to evaluate the possible role of water as heat transfer medium and to investigate the influence of the alkyl chain in the ester group of a series of methacrylate monomers on the efficiency of iPP grafting and also on the hydrophilicity of the grafted iPP. Methyl-, ethyl-, butyl-, ethyl hexyl-, and dodecyl were examined as alkyl groups on the methacrylate monomers.

## EXPERIMENTAL

### Materials

The base polymer used for this investigation was a nonstabilized iPP, melt flow index 8.367 g/10 min at 230°C (Slovnaft a.s., Bratislava, Slovak Republic). The methacrylate monomers utilized were: methyl methacrylate—MMA (Merck-Schuchardt, Germany); ethyl methacrylate—EMA (Fluka AG, Buchs SG, Switzerland); butyl methacrylate—BMA 99% (Aldrich Chem. Co. Ltd., England); 2-ethyl hexyl methacrylate—EHMA 98% (Aldrich Chem. Co. Ltd., England); and dodecyl methacrylate—DMA 60–70% (Merck-Schuchardt, Germany). The peroxide initiators used were: tert-butyl peroxy-2-ethylhexanoate—TBPEH, Trigonox 21S, 97% (Akzo Nobel Polymer Chemicals bv., The Netherlands); tert. butyl peroxyvalerate—TBPPI, Trigonox 25-C75, 75% (Akzo Nobel Polymer Chemicals bv., The Netherlands); and dibenzoyl peroxide—BPO (Merck-Schuchardt, Germany). Other chemicals used such as sodium chloride, chloroform, xylene, granulated PMMA and distilled water, were of analytical purity.

Methacrylate monomers were washed with an aqueous solution of sodium hydroxide to remove the inhibitor, dried over MgSO<sub>4</sub> and distilled under reduced pressure.

### Preparation of iPP samples grafted with methacrylate comonomers having different alkyl chain length

Samples of grafted iPP were prepared in 10 g quantities. Powdered iPP and the appropriate

methacrylate monomer (in amount of 10, 20, or 30 wt %) were premixed with peroxide ( $1.39 \times 10^{-2}$  mol/100 g of PP mixture) and weighted into a round-bottom flask. The reaction mixture in the closed flask was stirred at room temperature using a magnetic stirrer. After 2 h homogenization and penetration, a solution of 5 g NaCl in 25 mL distilled water was added to the reaction mixture. A reflux condenser and a nitrogen inlet were attached and the mixture was heated in an oil bath at 94°C. The reaction time represented seven half-lives of peroxide decomposition (half-life of the peroxide decomposition for TBPPI -  $t_{1/2} = 0.1$  h at 94°C). The obtained grafted polymer was removed from the aqueous NaCl solution by filtration on a glass frit, followed by multiple washing with distilled water and then dried at 100°C until constant weight in a vacuum oven.

#### Separation of the grafted polymer from methacrylate homopolymer

About 1 g of dried sample containing the grafted iPP and alkylmethacrylate homopolymer was dissolved in 100 mL boiling xylene. Cooling the solution to room temperature caused the grafted polymer to precipitate so that it could be isolated from the xylene solution of alkyl methacrylate homopolymer by filtration on a fritted glass funnel. The grafted polymer on the funnel was then given multiple washings by xylene, and then vacuum dried to constant weight.

#### Preparation of the samples for FTIR measurements

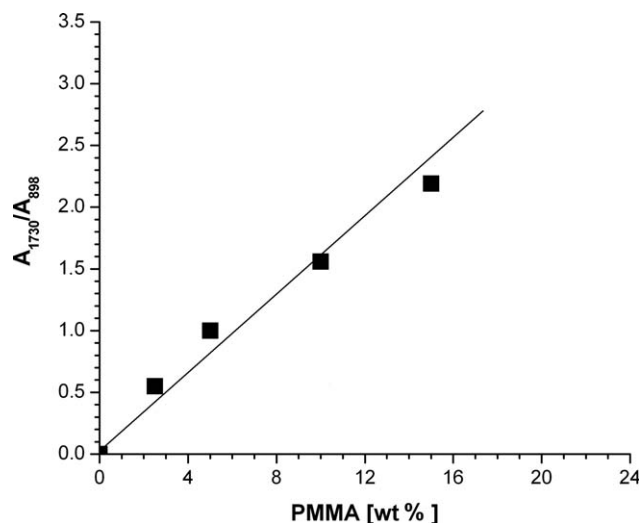
A sample of 0.3 g grafted polymer was preheated for 30 sec. and then pressed between two polyester sheets into about 0.1 mm film in an electrically heated laboratory press (Fontune Vlaardingen, The Netherlands) at 190°C under 1.3 MPa pressure for 1 min.

#### FTIR spectra measurements—Confirmation of the presence of grafted copolymer

Pressed films of grafted polypropylene were scanned with a Nicolet Impact 400 Infrared spectrometer with 32 scans and with differentiation  $4 \text{ cm}^{-1}$ . The spectra were evaluated directly with a program installed in the equipment (Omnic, Version 1.2). The ratio of carbonyl absorption peak at wavelength  $1730 \text{ cm}^{-1}$  and peak at wavelength  $898 \text{ cm}^{-1}$  was calculated. The content of corresponding polymethacrylate in grafted sample was determined from a calibration curve.

#### FTIR calibration graph for determination of amount of poly(methyl methacrylate) grafted onto iPP

Infrared absorptions of physical mixtures of PMMA and iPP were used to construct a calibration graph.



**Figure 1** Calibration graph for determination of amount of polymethylmethacrylate grafted onto iPP as determined by FTIR.

The mixtures were prepared by combining PMMA solutions in chloroform with powdered iPP. Thus, a solution of 2.5 g PMMA in 25 mL chloroform was prepared and mixed with powdered iPP in such amounts as to produce PMMA concentrations representing 2.5, 5, 10, and 15 wt % of the total 5 g of sample. The mixture of iPP and PMMA solution was stirred by magnetic stirrer to allow impregnation of PMMA and to complete the evaporation of chloroform. From the impregnated PP powder, about 0.1 mm thin film was pressed and the infrared spectrum was taken. A calibration curve was constructed (Fig. 1) using the ratio of carbonyl absorbance peaks from PMMA at wavelengths  $1730$  and  $898 \text{ cm}^{-1}$  (including a correction for iPP absorption due to variations in film thickness) on the  $y$ -axis and PMMA concentration in samples on the  $x$ -axis.

#### Differential scanning calorimetry measurements of grafted samples

DSC measurements were done using a Mettler-Toledo DSC 821 instrument under nitrogen atmosphere (gas-flow, rate  $50 \text{ mL N}_2/\text{min}$ ). Indium was used for calibration of temperature and heat of fusion. The samples of grafted PP were heated from 40 to 200°C at a heating rate of  $10^\circ\text{C}/\text{min}$ . After the first melting, the samples were cooled from 200°C to 40°C to get the crystallization temperature and then once more heated to 200°C (second melting) to reveal the effect of different thermal history of samples. The percentage crystallinity of various samples was calculated by using the following equation:

$$\% \text{ Crystallinity} = \frac{\Delta H_s}{\Delta H_0} \times 100$$

where  $\Delta H_0$  is the heat of fusion of 100% crystalline polypropylene which is considered to be 209 J/g.  $\Delta H_S$  is the heat of fusion obtained from the DSC measurement.

### Measurement of the surface energy

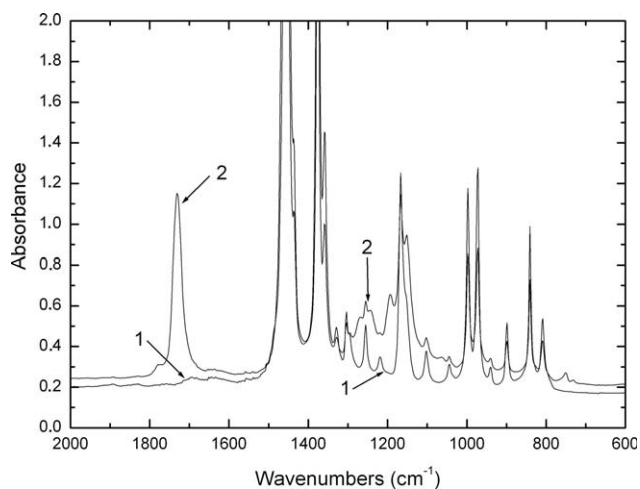
The surface energy of grafted iPP copolymer was determined via measurements of contact angles of a set of testing liquids (i.e., redistilled water, ethylene glycol, formamide, ethylene iodide, and 1-bromonaphthalene) using SEE (surface energy evaluation) system completed with a web camera (Masaryk University, Czech Republic) and necessary PC software. The drop of the testing liquid ( $V = 3 \mu\text{L}$ ) was placed with a micropipette (0–5  $\mu\text{L}$ , Biohit, Finland) on the polymer surface, and a contact angle of the testing liquid was measured.

## RESULTS AND DISCUSSION

### Comparison of the efficiency of iPP grafting with methacrylates in solid state and in water phase; selection of the optimal peroxide type

Because of the aqueous medium used in this study, the reaction temperature of iPP grafting is limited to  $\leq 100^\circ\text{C}$ . Seven half-lives of the used peroxide were chosen as sufficient time for complete peroxide decomposition. Therefore, the peroxides for these experiments were selected according to appropriate length of the half-life times of their decomposition at the required reaction temperature. For grafting of iPP with MMA, three different types of peroxides were tested: tert-butyl peroxyvalate (TBPPI), tert-butyl peroxy-2-ethylhexanoate (TBPEH), and dibenzoyl peroxide (BPO). The monomer, MMA was used for testing of peroxides in grafting attempts in both solid state and also in water suspension. The presence of grafted MMA in iPP was confirmed by FTIR spectroscopy.

Figure 2 shows the FTIR spectrum of the film prepared from initial iPP as well as the spectrum of the films prepared from grafted iPP. The absorption bands at  $1730 \text{ cm}^{-1}$  are due to the carbonyl group of the ester linkage in MMA and confirm the incorporation of this monomer on iPP chains. As can be seen in Table I, the GE was higher in all cases when carried out in water phase (NaCl/H<sub>2</sub>O) than in solid state (without liquid medium). However, grafting performed in the pure water (TBPPI as initiator) afforded lower efficiency than grafting in NaCl water solution. For 10 wt % of MMA in the mixture, reaction in pure water gave just 4.1 wt % grafting in comparison with 5.7 wt % grafting in NaCl solution. For 20 wt % MMA in the reaction mixture, the difference was even much greater, 8.2 wt % grafted in pure water and 17.3 wt % grafted in NaCl solution.



**Figure 2** FTIR spectra of pure iPP (1) and iPP grafted by methylmethacrylate (2).

These findings led us to perform all other grafting experiments in NaCl solution. One possible reason for the improved results in saline mixtures may be the relatively high solubility of MMA in water. This value represents 150 mmol/L at room temperature.<sup>38</sup> Surely, solubility will be much higher at the temperature we used in the grafting experiments. The solubility of MMA is expected to be less in saline solution due to the well-known “salting out” effect. Inorganic salts have been found to increase the grafting of methanol solutions of styrene to low-density polyethylene, polypropylene, and cellulose in the case of photografting and by ionizing radiation.<sup>39–41</sup> Partitioning of monomer into the backbone polymer was significantly improved and this effect is predominantly responsible for grafting enhancement.

Concerning the peroxide type, much higher GE was reached using TBPPI for all MMA concentrations. Moreover, the reaction time representing seven half-lives was too long (7 and 9.3 h) for TBPEH and BPO. However, for TBPPI this value represented just 45 min. Therefore, TBPPI was selected for the scheduled study of iPP grafting with different methacrylates.

### Grafting of iPP with methacrylate monomers in water dispersion

The influence of concentration and length of the alkyl chain in the ester group of methacrylic monomers on efficiency of grafting of iPP in water dispersion at  $94^\circ\text{C}$  were investigated. Methyl- (MMA), ethyl- (EMA), butyl- (BMA), ethylhexyl- (EHMA), and dodecyl- (DMA) methacrylate were evaluated. Samples of grafted iPP based on three different initial concentrations of each type of MA monomer (10, 20, and 30 wt%) relative to iPP and at constant concentration of peroxide of  $1.39 \times 10^{-2} \text{ mol}/100 \text{ g iPP}$  in water medium were prepared.

**TABLE I**  
**Comparison of Efficiency of Peroxide Initiators (tert. Butyl Peroxypivalate [TBPPI], tert.-Butyl Peroxy-2-ethylhexanoate [TBPEH], Dibenzoyl Peroxide [BPO]) for Grafting of iPP with MMA in Solid State and in Water Phase (5 g NaCl/25 mL water)**

Type of peroxide	Reaction conditions: temperature time	Conc. of MMA in the reaction charge (wt %) with respect to iPP	Grafting in solid state (without H <sub>2</sub> O)	Grafting in water phase (5 g NaCl/ 25 mL H <sub>2</sub> O)
			grafted MMA (wt %)	grafted MMA (wt %)
TRIGONOX 25 (TBPPI) $\tau_{1/2} = 94^\circ\text{C}/6 \text{ min}$	94°C, 45 min	10	4.2	5.7
		20	7.4	17.3
		30	13.7	22.3
TRIGONOX 21S (TBPEH) $\tau_{1/2} = 91^\circ\text{C}/60 \text{ min}$	91°C, 7 h	10	0.9	4.6
		20	7.6	11.3
		30	11.9	14.1
BPO $\tau_{1/2} = 90^\circ\text{C}/80 \text{ min}$	90°C, 560 min	10	0.7	1.8
		20	4.5	10.1
		30	9.6	18.6

The type of alkyl ester group in the monomers manifests itself in various ways in the grafting experiments. Homo-propagation rates, gel effects, self-transfer tendency, and relative solubility in water and iPP all interplay to produce the observed grafting efficiencies.

Samples prepared with 10 wt % monomer (MMA, EMA, BMA, EHMA and DMA) have shown that the yield of grafting slightly increases with the length of alkyl chain in the series MMA to BMA (Table II). With these monomers, the GE (see working equation below) was 57, 68, and 72%, respectively.

$$\text{GE} = \frac{\text{Mass of grafted XMA (g)}}{\text{Mass of feeding XMA (g)}} \times 100$$

However, with longer alkyl chains, EHMA and DMA, the GE was only 33 and 36.2%, respectively.

The longer alkyl chain in monomer ester group contributed to the easier diffusion of the monomer into the amorphous phase of the iPP. However, monomers with longer alkyl chains like EHMA and DMA have lower reactivity of propagating free radicals. From this, it follows, in the case of EHMA and DMA, the contribution of longer alkyl chain to better solubility of the MA monomer does not compensate for the lower reactivity of the propagating free radical on the growing MA chain attached to iPP.<sup>43</sup> The decrease of GE for monomers with longer alkyl chain can be caused by the higher probability of transfer reaction on the monomer. This is illustrated in Table II in which experiments using 10 wt % MA monomers showed the highest yield to be achieved was with BMA. This monomer can be considered as a compromise between higher compatibility of PBMA with iPP and lower reactivity of propagating BMA free radical.

**TABLE II**  
**Amount of Methacrylate Polymer Grafted Onto iPP in Water Phase Determined by FTIR Spectroscopic Method and Grafting Efficiencies (GE)**

Amount of methacrylate in reaction mixture (wt %)	Amount of grafted methacrylates (wt %) and grafting efficiencies GE (%)					DMA
	MMA (GE)	EMA (GE)	BMA (GE)	EHMA (GE)	DMA (GE)	Gel content (wt %)
10	5.7	6.8	7.2	3.3	3.7 <sup>a</sup>	2.0
	(57.0)	(68.0)	(72.0)	(33.0)	(36.2) <sup>b</sup>	
20	17.3	10.4	10.5	5.5	19.6 <sup>a</sup>	21.4
	(86.5)	(52.0)	(52.5)	(27.5)	(77.0) <sup>b</sup>	
30	22.3	17.0	9.4	13.0	29.5 <sup>a</sup>	34.7
	(74.3)	(56.6)	(31.3)	(43.3)	(64.2) <sup>b</sup>	

All runs are based on 10 g quantities of iPP and methacrylate mixture in aqueous medium (5 g NaCl/25 mL water) under TBPPI initiation.

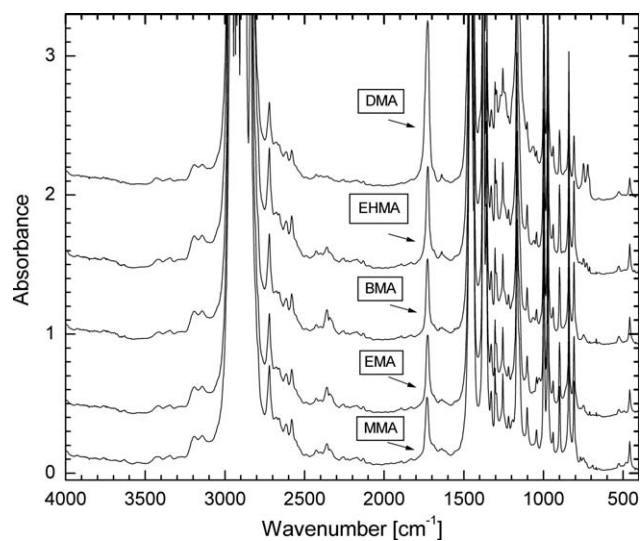
<sup>a</sup> Total amount of grafted DMA and gel content.

<sup>b</sup> The amount of gel content was subtracted for GE calculation.

At 20% monomer content, grafting to iPP is significantly increased in the case of MMA (86.5% efficiency) and DMA. However, the reason for grafting effectiveness was different for each monomer. In the case of MMA, the increase of grafted monomer may be attributed to the gel effect, which leads to a rapid increase in concentration of free propagating PMMA radicals. This should lead to a higher transfer of free radicals to iPP, and thus lead to a higher number of grafted PMMA chains. The gel effect is typical for MMA at this concentration of monomer, and also the iPP matrix should contribute to this phenomenon. In the case of DMA, chain transfer to monomer leads to crosslinking of DMA chains, as is observed also during its homopolymerization.<sup>36</sup> Grafting reactions using DMA produced insoluble gel that was found (Table II) to increase with increasing amounts of initially charged monomer. But for EMA and BMA, the GE was lower (about 50 %), and for EHMA grafting values were the lowest, with only about one fourth of the monomer being grafted.

At 30 wt % monomer content for MMA or EMA, the amount of grafting again increased, but the efficiency of grafting decreased because more homopolymer was produced. This can be understood by the fact that the local concentration of these monomers is greater on the surface of the less swollen iPP particles than with other monomers. On the other hand, the higher concentration of monomer on the surface of the iPP particles is considered also to be an advantage with a nonpolar monomer like styrene.<sup>30</sup> The higher surface concentration of monomer results in a greater probability of homo-propagation via the gel effect and a lower probability of transfer of free radical onto iPP chains, which is necessary for successful grafting. In regard to monomers with long-chain alkyl groups, we have obtained a grafting efficiency of 43.3% of EHMA onto iPP. However, the results obtained with DMA are obscured by the formation of crosslinked gel. DMA is known to undergo radical chain-transfer to monomer, which leads to uncontrolled crosslinking.<sup>36</sup> Figure 3 shows the FTIR spectra of the films prepared from grafted iPP at 30 wt % monomer contents.

In our experiments, the highest grafting efficiency was achieved using MMA, i.e., 22.3 wt % and it decreased in the order: MMA > EMA > EHMA > BMA (DMA is linked to the iPP chain in the form of crosslinked microgel particles of DMA). This order of grafting efficiency is approximately coincident with the intensity of the gel effect of the appropriate monomer, which is observed during its polymerization. It does not proportionally decrease with length of the alkyl group. To relate the influence of structure to reactivity of the individual monomers on grafting efficiency, one must take into the consideration the dissolving of the monomer into iPP and also

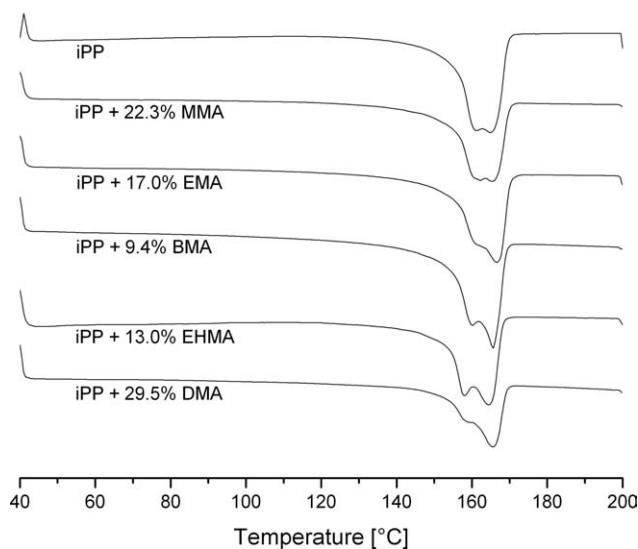


**Figure 3** FTIR spectra of the films prepared from grafted iPP at 30 wt % monomer contents.

the reactivity of the propagating free radical. Both factors can contribute to better transfer of free radicals to the iPP chains and so to more effective grafting, as could be the case with EHMA.

#### DSC measurements of thermal properties of the grafted iPP with MMA, EMA, BMA, EHMA, and DMA

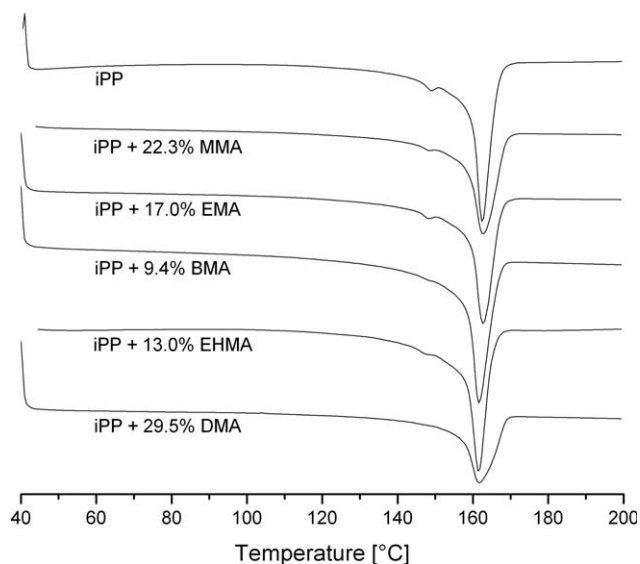
DSC measurements of pure iPP as well as iPP grafted with methacrylates containing different alkyl chain lengths in the ester group, showed during the first heating two melting endotherms (Fig. 4). The temperature of the first peak decreases as the length of the ester alkyl chain is increased. However, the value of the second peak practically does not change. The presence of two peaks in the thermogram can be caused by partial recrystallization, followed by melting of crystallites.<sup>44,45</sup> Melting, recrystallization, and remelting are possible if the reorganization of molecular structure occurs throughout the first run of DSC measurement, as well as during annealing below the melting point. Thinner and/or less stable lamellar structures of crystalline domains are melted at lower temperature. Usually, they recrystallize simultaneously during the growth of more uniform and/or more stable crystallinities having higher melting temperature. The increase of the temperature difference between the two melting peaks depends on the length of the alkyl chain of methacrylate monomer, in accordance with the expectations that the longer alkyl chains probably hinder the formation of more uniform and more stable crystalline structures. Consequently, the heats of fusion (the crystallinity) of all grafted iPP samples -except the DMA- show higher values than pure iPP. Samples of iPP grafted with the longest



**Figure 4** DSC thermograms of the first heating of the different grafted samples iPP/XMA.

alkyl chain in DMA monomer indicated a significant decrease of crystallinity (Table III). The presence of grafted chains on the one hand, contributes to an increase of the total melting heat presumably due to the chains acting, to a certain extent, like nucleating agents. On the other hand, iPP grafted with DMA exhibited a significant decrease of melting heat in comparison with iPP alone. This is likely caused by a suppression of chain movement of the polymer as a consequence of partially crosslinking of iPP which takes place concurrent with grafting. Entire removing of gel as well as partially crosslinked iPP resulted in the heat of fusion  $\Delta H_{m1} = 110 \text{ J/g}_{\text{PP}}$ . This value approaches to the heats of fusion of all other samples.

During the second heating of the samples (Fig. 5), the shifting of melting temperature of the first peak to the lower temperatures (150°C) was observed. For the sample iPP-g-DMA, the first peak was not observed. The temperature of the main melting peak shifted toward the melting temperature of pure iPP and did not change with the increase of the alkyl



**Figure 5** DSC thermograms of the second heating of grafted samples of iPP/XMA.

length in MA units. The heat of fusion at the second heating, after controlled crystallization during first cooling, is higher for all samples in comparison with the first melting; again the lowest value was registered for the iPP-g-DMA sample.

### Surface energy measurements

Contact angles have been shown to be very sensitive to the nature of the functional groups present within a few angstroms of the upper layer on the surface of functional polymers. The functionalized iPP in this work had essentially two types of functional groups: a polar portion contributed by the grafted monomers and a nonpolar portion contributed by the iPP units. The methods implemented in the used program allow for the determination of the surface energy of solids from contact angle data.

The surface energies of the grafted copolymer were evaluated by Owens-Wendt-Rabel-Kaelble (OWRK) equation modified by the least squares method<sup>46-48</sup>:

**TABLE III**  
DSC Measurements of Grafted Samples of iPP with 30 Wt % Methacrylate and  $1.39 \times 10^{-2} \text{ mol TBPPI/100 g PP Mixture}$

Comonomer in the sample	Grafted MA (wt %)	$T_{m1}$ (°C)	$\Delta H_{m1}$ (J/g PP)	% cryst. in PP <sup>a</sup>	$T_{m2}$ (°C)	$\Delta H_{m2}$ (J/g PP)	% cryst. in PP <sup>a</sup>
pure PP	–	165.9	89.1	42.6	162.7	107.6	51.4
MMA	22.3	165.3	112.8	53.9	162.7	124.4	59.5
EMA	17.0	166.6	113.0	54.0	162.8	133.2	63.7
BMA	9.0	165.5	125.7	60.1	161.6	143.3	68.5
EHMA	13.0	164.6	121.9	58.3	161.5	138.6	66.4
DMA	29.5	165.6	70.3	33.6	161.7	81.6	39

<sup>a</sup>  $\Delta H = 209 \text{ J/g}$  for 100% crystallinity.<sup>42</sup>

**TABLE IV**  
Surface Energy and Polar Fraction of Testing Liquids  
(WORK Method)

Testing liquid	Surface energy (mJ/m <sup>2</sup> )	$x_L^p$
Water	72.8	0.701
Ethylene glycol	48.3	0.393
Formamide	58.2	0.321
Methylene iodide	50.8	0.045
$\alpha$ -Bromo naphthalene	45.3	0

$$\frac{(1 + \cos \theta)\gamma_{LV}}{2} = (\gamma_{LV}^d \gamma_s^d)^{1/2} + (\gamma_{LV}^p \gamma_s^p)^{1/2} \quad (1)$$

$$\gamma_{LV} = \gamma_{LV}^p + \gamma_{LV}^d \quad (2)$$

$$\gamma_s = \gamma_s^p + \gamma_s^d \quad (3)$$

where

$\Theta$  = contact angle of the testing liquid (deg);

$\gamma_{LV}$  = surface energy of the testing liquid (mJ/m<sup>2</sup>);

$\gamma_{LV}^d, \gamma_{LV}^p$  = dispersion component (DC) and polar component (PC) of surface energy of the testing liquid (mJ/m<sup>2</sup>);

$\gamma_s$  = surface energy of the polymer (mJ/m<sup>2</sup>);

$\gamma_s^d, \gamma_s^p$  = DC and PC of surface energy of the polymer (mJ/m<sup>2</sup>).

The tabulated values of the surface energies for the testing liquids at 23°C are given in Table IV.

Table V shows the contact angle of redistilled water, surface energy, its polar and dispersion component of pure iPP, and grafted iPP containing various amount of methacrylic comonomers. The contact angles of redistilled water decrease after grafting with acrylic monomers from 90° (pure iPP) up to 77° for iPP-MMA copolymer. From the content in wt % of grafted MA monomer onto iPP, the amount of carboxylic groups —COO— in mol/kg could be calculated.

**TABLE V**  
Contact Angle of Water, Surface Energy, Its Polar and Dispersion Component of Pure iPP and Grafted Propylene-Methacrylate Copolymers with Various Amounts of Methacrylic Comonomers

Monomer	iPP grafted		Contact angle of water (deg)	$\gamma_s^D$ (mJ/m <sup>2</sup> )	$\gamma_s^P$ (mJ/m <sup>2</sup> )	$\gamma_s$ (mJ/m <sup>2</sup> )	$x_s^p \times 10^2$	$\frac{x_s^p}{[-COO-]} \times 10^2$
	Grafted monomer (wt %)	$[-COO-]^a$ (mol/kg)						
Pure iPP	—	—	90	30.0	1.4	31.4	4.45	—
MMA	22.3	2.22	77	32.4	4.6	37.0	12.43	5.59
EMA	17.0	1.49	85	31.2	3.2	34.4	9.30	6.24
BMA	9.4	0.66	84	30.8	3.0	33.8	8.87	13.4
EHMA	13.0	0.65	83	31.8	2.8	34.6	8.09	12.4
DMA	29.5	1.16	83	31.3	2.6	33.9	7.67	6.6

<sup>a</sup> Concentration of —COO— groups in mol/kg in grafted iPP.

$\gamma_s^D$  = Dispersion component of surface energy;  $\gamma_s^P$  = Polar component of surface energy;  $\gamma_s$  = Total surface energy.

Also, the polar fraction  $x_s^p$  for individual MA monomer grafted on iPP was calculated according to:

$$x_s^p = \frac{\gamma_s^p}{\gamma_{total}}$$

The value obtained from the ratio  $x_s^p / [-COO-]$  characterizes the polarity, which is caused by the grafted MA in the iPP sample at comparable grafted amounts of all monomers. The polarity of the surface of grafted copolymers does not decrease with increasing of the alkyl chain length as would be expected. The values of the column  $x_s^p / [-COO-]$  show, that the highest polarity has been obtained with BMA and EHMA. EMA and MMA reach similar polarity in grafted iPP. This can be caused by much higher attractive interactions between the grafted PMMA or PEMA chains and so the polar groups of the PMMA and PEMA chains tend to be pulled from the surface and from among the chains just under the surface. On the other hand, with DMA, the polarity of grafted copolymer decreased rapidly in comparison with BMA and EHMA, which may be related to crosslinking of the grafted DMA.

## CONCLUSIONS

- Efficiency of powdered iPP grafting with methacrylate monomers (with various length of alkyl chain ester group) in water medium (grafting in slurry) was achieved at a twofold higher level than obtained without using a water medium.
- The peroxide initiator, tert-butyl peroxy pivalate, TBPPI, was found to be the most effective in these grafting reactions.
- The degree of grafting onto iPP is not a simple function of the alkyl chain length. Monomer



reactivity, chain transfer and solubility in iPP play a role.

- The highest influence on degree of grafting was observed at conditions corresponding to the gel effect of MMA and EMA (at levels of 20 to 30 wt % of the monomer).
- Grafting of iPP with DMA resulted in a partial crosslinking of the grafted polymer chains.
- An increase of surface energy was found due to grafting of methacrylic monomers.
- The highest polarity was achieved in the case of iPP grafted with BMA and EHMA.

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