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GRAFT-COPOLYMERIZATION OF STYRENE ON POLYPROPYLENE IN THE SOLID PHASE

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Abstract : The graft-copolymerization of styrene on PP in the solid phase has been studied under various reaction conditions using a radical initiator. Polymerization kinetics were investigated by DSC experiments and reactions in glass ampoules. The conversion rate and grafting efficiency of styrene appeared to be strongly influenced by the presence of the PP matrix and the styrene/PP ratio. From reactions in a lab scale reactor the concentrations of styrene and initiator, the dosing rate and the temperature were investigated to be critical parameters determining the grafting efficiency and the average length and number of grafts. The phenomena observed were explained by describing the process in relative rates of diffusion and polymerization, including swelling of the polymer by styrene monomer and diffusion limitations (Trommsdorff effect).

INTRODUCTION

Various technologies are developed and applied in the area of polymerization catalysts and reactive processing for the production and modification of polyolefins. New materials become available by combining olefinic materials with non-olefinic polymers (Refs. 1, 2). The properties balance of PP-g-PS graft-copolymers allows targeting this material as potential ABS replacement and compatibilizer for PP-based blends. However, literature describing the polymerization kinetics and effects of process conditions on the characteristics of the graft-copolymers obtained is scarce. The graft-copolymerization process by radical initiation can be generally described by:

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$$\mathrm{I} \longrightarrow 2\,\mathrm{R}^{\bullet} \quad (1)$$

$$\mathrm{R}^{\bullet} + \mathrm{PP} \longrightarrow \mathrm{R\text{-}H} + \mathrm{PP}^{\bullet} \quad (2)$$

$$\mathrm{PP}^{\bullet} + n\mathrm{M} \longrightarrow \mathrm{PP\text{-}(M)}_{n}^{\bullet} \quad (3)$$

$$\mathrm{R}^{\bullet} + n\mathrm{M} \longrightarrow \mathrm{R\text{-}(M)}_{n}^{\bullet} \quad (4)$$

After decomposition of the peroxide initiator I (1), a radical R• can abstract a hydrogen from PP (2) or add to the monomer. Graft-copolymerization of styrene initiated by PP• radicals (3) and homopolymerization initiated directly by radicals of the initiator (4) may be competing processes. The growing PS chains, grafted or non-grafted, will terminate by recombination with another (macro)radical, chain transfer or disproportionation. The grafting efficiency is defined as the percentage of PS grafted of the total amount of PS formed. Process and material characteristics to be controlled include monomer conversion, grafting efficiency and the number and length of the grafts. In this study, kinetics of the graft-copolymerization of styrene on PP in the solid phase and the effects of styrene and peroxide concentrations, dosing rate and temperature on the grafting efficiency and graft-copolymer characteristics, were investigated.

RESULTS AND DISCUSSION

Kinetics

The conversion rate of styrene typically increased with the initiator concentration (Fig. 1a). When a higher fraction of the reaction medium consisted of PP, the overall conversion rate of styrene increased, despite constant initiator/monomer ratio (Fig. 1b). As the mobility of long chain radicals reduces if styrene is polymerizing at the PP surface and within the PP matrix and viscosity builds, this increase in reaction rate can be ascribed to a diffusion limited termination or Trommsdorff effect (Ref. 3). At increased initiator concentration the acceleration of the polymerization rate appeared to occur at lower conversion (Fig. 1c), indicating an effect of the viscosity of the reaction medium at lower conversion when more initiator was present. The decrease in reaction rate at high conversion at the highest initiator concentration used is probably a result of diffusion limitation of the monomer due to a higher viscosity of the reaction medium. The higher viscosity of the reaction medium was ascribed to more grafts formed at a higher initiator concentration, as no crosslinking of PP has been measured. A decrease in propagation at high conversion can also be due to a lower initiator efficiency and radical trapping.

The grafting efficiency of styrene on PP as a function of reaction time was investigated from graft-copolymerization reactions in glass ampoules at a medium initiator concentration. At low conversion (<15%) no graft-copolymerization was observed (Fig. 2a). The grafting efficiency increased at higher conversion (>70%) to a plateau level. The occurrence of preferred homopolymerization of styrene at low conversion may be ascribed to the preference of the initiator radical to react with the styrene monomer present at a relatively high concentration in combination with a higher diffusivity of the styrene monomer and styrene radical than the PP

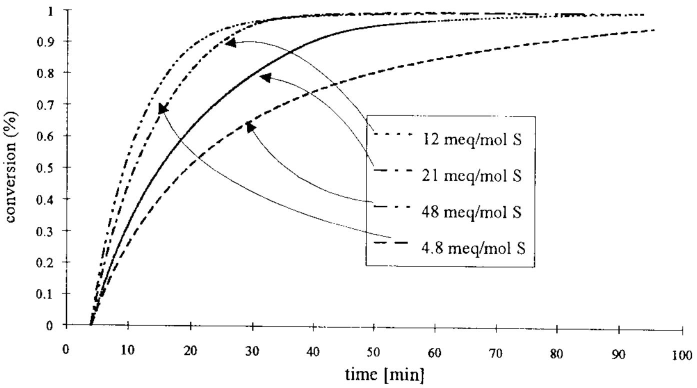

Fig. 1a. Styrene conversion, effect of initiator/styrene ratio; DSC, Isotherm 110°C, 0 wt% PP

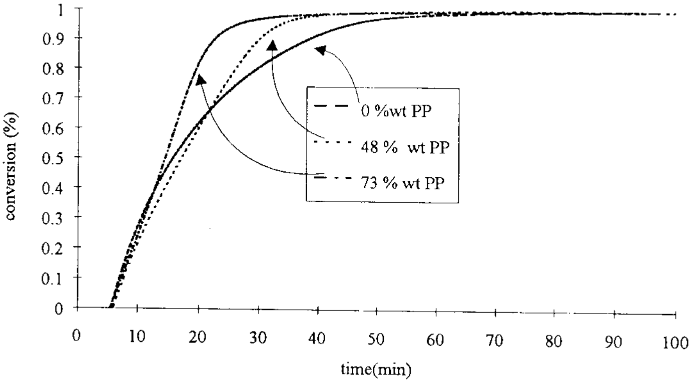

Fig. 1b. Styrene conversion, effect of wt% PP; DSC Isotherm 110°C, 13 meq initiator/mol styrene

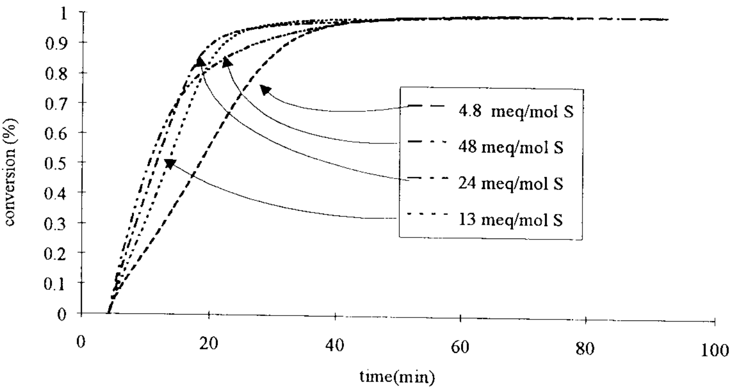

Fig 1c. Styrene conversion, effect of initiator/styrene ratio ; DSC, Isotherm 110 °C, 70 wt% PP

macromolecular chain. The initial Mw of the PS was typically high and decreased at low conversion at the reaction conditions used (Fig 2a). Reaction of the initiator radical with PP and subsequent initiation of graft-copolymerization of styrene may become competitive processes at increased conversion when the diffusivity of the styrene monomer and growing PS chains is reduced by the increased viscosity of the reaction medium. The Trommsdorff effect observed at higher conversion may correlate with the formation of graft-copolymers and increased viscosity of the reaction medium. This agrees with the increased molecular weight of the PS homopolymer extracted from the graft-copolymerization product at higher conversion (Fig. 2a). When more initiator is used, a higher level of graft-copolymerization at lower conversion would agree with the Trommsdorff effect occurring at lower conversion (Fig 1c). Alternatively, it may be speculated that part of the growing PS homopolymer chains are terminated by recombination with PP• radicals thus forming graft-copolymer chains at higher conversion. However this mechanism would conflict with the observed Trommsdorff effect indicating limitation of chain terminations due to increased viscosity of the reaction medium. Moreover, it cannot be excluded that the rate of swelling of PP by styrene plays also a role in the delayed formation of graft-copolymers. In addition, data obtained at short reaction times should be interpreted with caution as a time lapse may have to be accounted for equilibration of the temperature in the glass vials used.

The importance of the effect of swelling of PP by styrene is illustrated by experiments with varied styrene/PP ratio (Fig. 2b). The grafting efficiency decreased at styrene fractions of the reaction medium higher than 20-30 wt %, where visual examination confirmed the saturation swelling of PP by styrene and a layer of styrene remaining on the PP surface when more styrene was added. The Mw of the PS homopolymer showed an increasing trend at lower styrene fractions, probably due to the formation of higher molecular weight PS when more styrene is polymerized within the PP matrix.

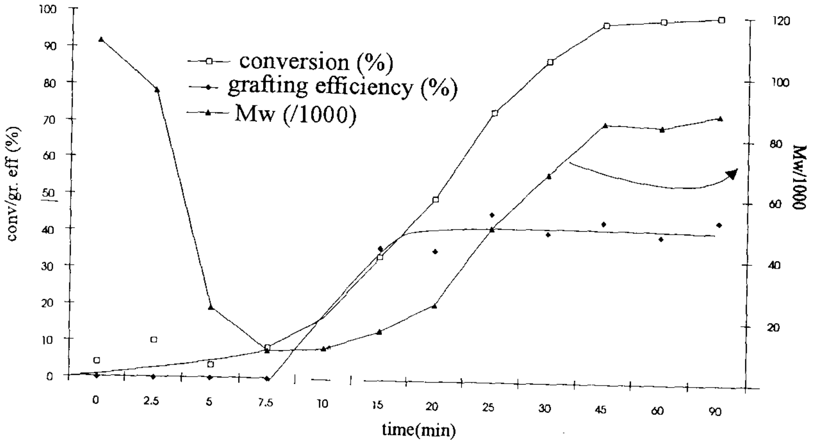

Fig. 2a. Effect of time on conversion, grafting efficiency of styrene on PP and Mw of PS
(13 meq, initiator/mole styrene, 70 wt% PP, 180°C)

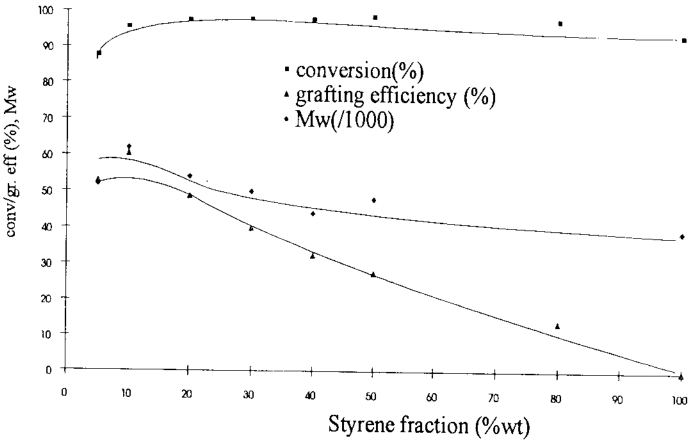

Fig. 2b. Effect of styrene on conversion, grafting efficiency of styrene on PP and Mw of PS (13 meq initiator/mol styrene, 110°C, 60 min)

The Influence of Process Variables

The effects of the process variables on the graft-copolymerization process and resulting copolymer characteristics have been studied from graft-copolymerization reactions in a lab scale reactor. After dosing of styrene and peroxide to hot PP powder, diffusion of styrene and peroxide into PP particles, decomposition of peroxide and polymerization of styrene, were taking place simultaneously. The PP particle can be considered to consist of a PP core and a shell swollen with styrene (Fig.3) (Refs. 2, 4). Polymerization will take place as well at the PP surface as in the swollen shell to a certain depth of penetration, depending on the relative rates of diffusion and polymerization. PS polymerized in an iPP matrix, in an equal amount to the amount of monomer absorbed, has been reported to be present in the non-crystalline phase of iPP and included in irregularities of crystallite surfaces (Refs. 2, 5).

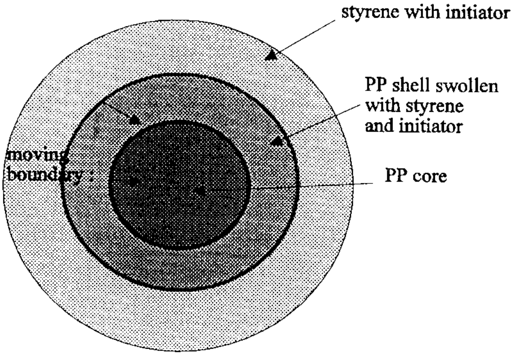

Fig 3, Core-shell system : PP particle and liquid styrene

Within this framework the influence was investigated of process variables including the concentrations of peroxide and styrene, the dosing rate, and the reaction temperature. Statistical analysis was used to study the influence of each process variable irrespective of and in combination with the other process variables on the grafting efficiency and the length and number of grafts.

Grafting efficiency

The grafting efficiency decreased when the dosing rate of the styrene/initiator mixture was increased. Accumulation of styrene and initiator around a PP particle would hinder the monomer to come into contact with PP allowing more homopolymerization to take place. The grafting efficiency increased when a large amount of styrene was added at low dosing rate (Fig. 4). This effect can be ascribed to swelling of PP and an increase in diffusivity of styrene and initiator in the PP matrix at a higher styrene concentration (Refs. 6, 7)
An effect of the temperature has been measured in combination with the dosing rate and the amount of styrene added (Fig. 5). At a high concentration of styrene, the grafting efficiency increased if the dosing rate was decreased, with a larger effect at lower temperature. The highest grafting efficiency was 70 % obtained at a relatively low temperature (95°C), a low dosing rate (0.45 pph/min) and a high concentration of styrene (40 wt %). The influence of the temperature on the grafting efficiency can be explained by the temperature dependence of the rate constants for diffusion and kinetics (Ref. 8). According to the Arrhenius relation both polymerization and diffusion are faster at higher temperature. When a large amount of styrene is added at a high dosing rate, more swelling and less accumulation occurs at higher temperature , increasing the grafting efficiency. Due to a higher activation energy, the polymerization rate decreases more at lower temperature than the diffusion rate, resulting in a higher grafting efficiency when a large amount of styrene is added at a low dosing rate, as more styrene is polymerizing in the PP phase. Further study is required to determine the influence of process variables on the polymer fraction of the total PP matrix which contains styrene graft-copolymers.

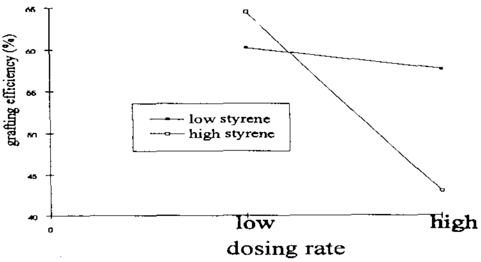

Fig.4. Effect of styrene concentration on grafting efficiency

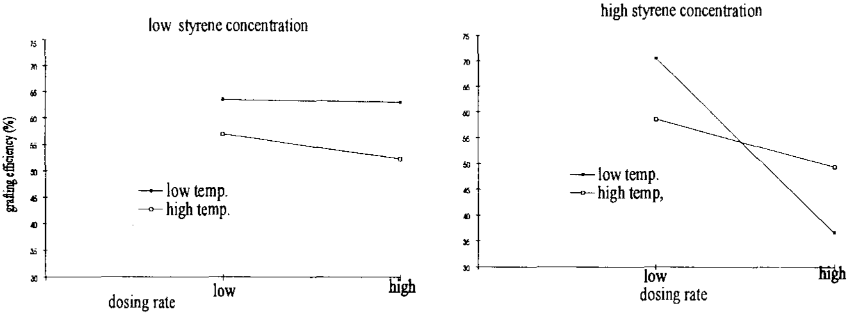

Fig. 5. Effect of temperature and dosing rate on grafting efficiency

Length and number of grafts

The Mw of the non-grafted PS homopolymer extracted from the graft-copolymerization product increased when less initiator and more styrene were added and when the temperature was decreased, as consistent with theory for the kinetic chain length in free radical polymerizations (Ref. 8). Mw also increased at process conditions at which diffusion was relatively fast with respect to polymerization and dosing rate of styrene and peroxide. The highest Mw was obtained at the same conditions as the maximal grafting efficiency, as both the rate of polymerization and the Mw of the PS homopolymer increase due to the Trommsdorff effect.

Within the PP matrix the polymerization of styrene is expected to be independent on the site of initiation (the PP• macro radical for the graft-copolymer or the initiator radical for the non-grafted PS homopolymer). Based on the assumption that the length of a graft would have the same length as the PS homopolymer extracted from the graft-copolymerization product, a calculation of the average number of grafts has been made. This number typically increased with the amount of initiator added and the temperature. The calculated number of grafts also increased when more styrene was added and at process conditions at which swelling of the polymer was expected. Then more grafts could be formed due to a higher diffusivity of styrene and initiator in the PP phase. It cannot be excluded that also at higher initiator concentration branched PS graft-copolymer or homopolymer chains are formed. More analytical study is needed to measure the number of graft sites and the distribution over the PP polymer by a direct method.

CONCLUSIONS

The phenomena observed suggest that the graft-copolymerization process of styrene on PP was controlled by the relative rates of diffusion and polymerization of styrene monomer, including diffusion limitations and the degree of swelling of the polymer. The conversion rate of styrene appeared to be strongly influenced by the presence of the PP matrix as a result of the Trommsdorff effect and diffusion limited propagation. The grafting efficiency increased in the course of the graft-copolymerization to a plateau level at higher conversion. The concentrations of styrene and initiator, the temperature and the dosing rate of styrene and peroxide were critical parameters determining the grafting efficiency, the length of grafts and the number of grafts.

Modelling based on polymerization kinetics and monomer diffusion rates will be useful in further study to describe and predict the influence of the process variables on the graft-copolymerization.

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EXPERIMENTAL PART

Materials

Hostalen PPU 0180 PP ex Hoechst (non-porous PP homopolymer powder, MFI = 18 g/10 min at 230 °C and 2.16 kg, density = 0.906 g/cm^3, particle size = 250 - 500 μm, m.p. = 170 °C, Mw = 430000), Styrol ex Merck, Art. 807679, Trigonox 21-C70, solution of 70 wt % tert.butylperoxy-2-ethylhexanoate in isododecane ex Akzo Nobel Chemicals, Dichloromethane ex Baker.

Experiments

Differential Scanning Calorimetry experiments have been carried out with mixtures of styrene, initiator and PP in Al crucibles 40μl Mettler ME-27331 on a Mettler DSC TA4000 Thermal Analysis System connected with a TC11TA processor using GraphWare TA72 for data evaluation.

Glass ampoules (10 ml Chrompack vials with Teflon cap) were filled with a mixture of styrene, initiator and PP and heated after one h our in an oil bath of 110°C. After various reaction times one ampoule was emptied in 20 ml of a solution of 2.5 litre dichloromethane, 25 gram n-butyl benzene and 6.25 gram BHT (2,6-di-tert-butyl-4-methyl-phenol, Topanol OC ex ICI). The conversion of styrene in the sample was determined using GC, the amount of non-grafted styrene was determined gravimetrically after a Soxhlet extraction, carried out several times in dichloromethane in a Soxtec system HT 2, 1045 Extraction Unit, Tecator.

Graft-copolymerizations at varying process conditions were carried out in a double walled glass reactor of 500 ml, equipped with a metal anchor stirrer and coiled condenser. Maintaining N_2-blanketing a mixture of styrene and peroxide was added to hot PP at a certain dosing rate using a Watson Marlow 101 U peristaltic dosing pump with Viton tubing. After the experiment the reactor content was dried for one night at 65°C under vacuum and the conversion was determined gravimetrically. The grafting efficiency was determined gravimetrically as well as using SEC. Process variables were varied according a full 2^4 vectorial design with added centre points. For each process variable a "-level", "+ level" and "0 level" were chosen in the range to be studied (table 1). Each combination of - and + levels represented an experiment.

Table 1. Process variables as used in the experiments.

Variables	Range	- level	0 level	+ level
Temperature (°C)	90 - 120	95	105	115
Styrene conc. (wt %)	16 - 44	20	30	40
Initiator conc. (meq/100g PP)	1.15 - 4.60	1.9	2.9	3.9
Dosing rate (pph/min)	0.25 - 1.50	0.45	0.85	1.25

Analysis

Molecular Weight Distributions of PS homopolymer have been determined using Size Exclusion Chromatography (SEC) on Waters 150 C with a 600*7.5 mm column, type mixed C, calibrated with narrow PS standards. Samples were dissolved in tetrahydrofuran prior to injection of 50 μl of 0.2% sample solutions. PP-g-PS graft-copolymers were analysed using SEC at a temperature of 140 °C . Samples were dissolved in 1,2,4-trichlorobenzene at 150°C with 0.15 % of BHT as antioxidant. All samples were filtered over 0.5 μm filters prior to injection by a build-in filtration system. The response peak area for a certain polymer is related to the concentration of the sample by a specific response factor. The relative concentrations of PS and PP have been calculated from:

$$A = R_{PS} * x + R_{PP} * (1 - x)$$

where x is the % wt PS, R_{PS} the RI response factor for PS, R_{PP} the RI response factor for PP and A the peak area.

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