

Cationic Grafting from Plasma-Modified Polymer Surfaces

2. Preliminary Investigations with Polypropylene Fibers*

F. Denes¹, V. Percec¹, M. Totolin¹ and J. P. Kennedy²

¹ "Petru Poni" Institute of Macromolecular Chemistry, 6600 Jassy, Rumania

² Institute of Polymer Science, University of Akron, Akron, Ohio 44325, USA

Dedicated to Prof. C.I. Simionescu's 60th birthday

Summary

Polypropylene (PP) fibers have been surface-chlorinated by RF plasma process and used in conjunction with Et_2AlCl to initiate the cationic grafting of styrene. Although the extent of grafting was only 1.0 wt.%, the amount of grafted polystyrene completely covers the support. Grafting efficiencies were 10 - 35%. Scanning electron micrographs indicate incompatible polystyrene (PSt) sheets covering the PP fiber surfaces.

Introduction

Although numerous grafting systems have been developed in which liquid-phase grafting-from techniques were used (KENNEDY, 1977a, 1979), there is a dearth of information concerning grafting-from solids. Recently Vidal et al. (1977) grafted PSt and polyisobutylene, from poly(vinyl chloride) films and powders, and demonstrated surface grafting. In these experiments grafting was effected by swelling the solids in n-heptane/1,2-dichloroethane (70/30, v/v) mixtures and inducing grafting by introducing monomer and Et_2AlCl .

This communication concerns the first grafting of PSt from crystalline supports i.e., isotactic PP fibers, in the absence of swelling agents by the use of Et_2AlCl .

Experimental

n-Heptane (Fluka) was refluxed for several days first over sodium and then over CaH_2 , and fractionated under argon. 1,2-Dichloroethane (Reactivul Bucuresti)

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was refluxed several days over CaH_2 and fractionated under argon. The other chemicals were used as received (Reactivul Bucuresti). Styrene (Fluka) was refluxed over CaH_2 , distilled under vacuum and stored under argon in glass vials. Et_2AlCl (Fluka) was stirred over NaCl a few hours, diluted with *n*-heptane and stored in glass vials.

To remove ~4.5% textile-ingredients, the PP fibers were extracted successively with methanol, benzene, 1,2-dichloroethane and *n*-heptane at reflux temperature. According to spectral analyses (NMR, JEOL-C-60 HL, IR, Perkin-Elmer 577) these soluble ingredients are probably low molecular weight paraffins and soluble (probably atactic) PP.

Surface chlorinations were carried out in a continuous flow RF-plasma modification/grafting installation (Figure 1) which allowed the drawing of fibers with different speeds through the reaction chamber.

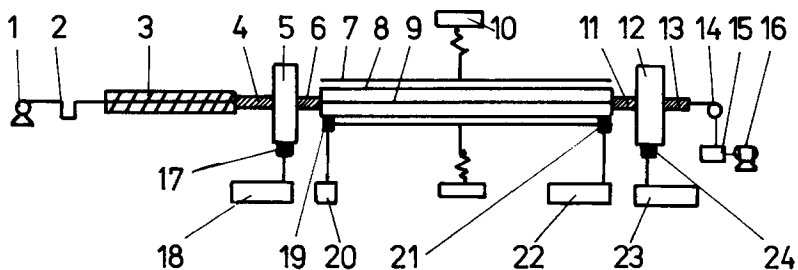


Figure 1. Schematic diagram of the plasma grafting and treatment device: 1-fiber holder; 2-monomer bath; 3-drying tunnel; 4,5,6,11,12,13-vacuum sealing system; 7-outside semi-cylindrical electrodes; 8-discharge tube; 9-polymer fiber; 10-RF generator; 14,15,16-fiber carrying system; 17,19,21,24-vacuum connections; 18, 22,23-vacuum pumps; 20-connection to the chlorine reservoir.

Glow discharge was started after having regulated the chlorine pressure in the discharge tube, the RF power on the outside silver-plated semi-cylindrical electrodes and the rate of fiber flow through the plasma reactor. After chlorination the PP fibers were thoroughly washed with water (until the pH of the washing-water reached 7.0) and methanol, and dried.

Table I summarizes chlorination conditions used with three samples.

Table I. Chlorination Conditions

Sample	Power (W)	Cl Pressure (mm Hg)	Flow rate of PP (m/h)
I	500	0.25	150
II	500	0.25	300
III	500	0.25	360

The labile chlorine content was evidenced by three different methods (3,4,5).

The presence of labile (mostly tertiary) chlorines was demonstrated by KENNEDY (1977b) THAME et al. (1972) and Robila et al.'s (1977) techniques.

Graft copolymerizations were carried out in stirred glass reactors at -16°C using n-heptane or n-heptane/1,2-dichloroethane (70/30 v/v) solutions. The reactor was charged with the surface chlorinated PP fiber (PP-Cl), then with glass vials containing the styrene and Et_2AlCl coinitiator, respectively (under argon and vacuuming cycles to remove traces of moisture), and finally with the solvent. After thermo-equilibrium was reached grafting was induced by breaking first the monomer vial and then the Et_2AlCl vial. Polymerizations were terminated by introducing MeOH/HCl mixtures. The products were purified by repeatedly washing with methanol and drying. Finally, ungrafted polystyrene was removed by extraction with refluxing benzene.

Simultaneously with grafting reactions control experiments were carried out. In these experiments the ingredients were mixed in the same proportions as in the grafting experiments, except that PP-Cl was omitted. Under these conditions, homopolymerization did not take place.

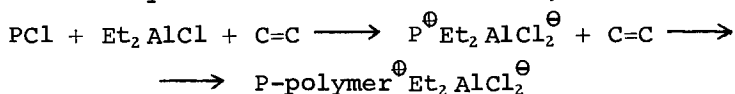
Scanning electron micrographs were obtained using a JEOL JSM 50A microscope.

Results and Discussion

Graft copolymerizations have been carried out within the concentration limits $\text{Et}_2\text{AlCl} = 1.35 \times 10^{-2} - 2.0 \times 10^{-3}\text{M}$, $\text{St} = 3.0 \times 10^{-2} - 1.5\text{M}$, $\text{PP-Cl} = 7.0 - 143.0 \text{ g/l}$. Representative data are shown in Table II.

Numerous examples have recently been published according to which active (tertiary, benzylic, allylic) halogens in conjunction with certain alkylaluminum compounds are able to initiate the polymerization of

cationically active monomers (KENNEDY, 1977a):



where PCl=active halogen containing compound and C=C = monomer. In case P=polymer, this technique gives rise to graft copolymers. Indeed a large number of novel graft copolymers have been prepared by the use of this principle. Recently this chemistry was also extended to grafting of surfaces (VIDAL et al., 1977).

Table II. Surface-grafting of Isotactic PP
Fibers with Styrene

Sample	Chlorine content (%)		Reaction time (hr)	PSt-grafted on PP, (wt, %)	Grafting efficiency (%)
	Total	Labile			
I	0.213	0.08	5.50	0.5	11.70
	0.213	0.08	7.00	1.1	34.10
II	0.073	-	3.50	0.2	12.90
	0.073	-	6.25	0.9	38.40
III	0.042	-	5.00	0.1	9.10
	0.042	-	7.00	0.4	19.31

PP-Cl = 143g/l; St = 1.5M; Et₂AlCl = 1.35x10⁻²M; -16°C; nC₇H₁₆/C₂H₄Cl₂ (70/30, v/v); total volume 200 ml.

Recently we postulated that active chlorines may also be mobilized by this chemistry and thus graft copolymers could be synthesized directly by the use of solids. Further, it was theorized that the necessary active chlorines could be generated by a recently developed RF plasma chlorination method (SIMIONESCU et al., 1979) on the surface of various crystalline or glassy polymers.

The grafted PP fibers have been exhaustively Soxhlet extracted by refluxing benzene, n-heptane and 1,2-dichloroethane for 48 hrs, or until a constant weight of the fiber has been attained. Subsequently the solvents were removed by vacuum evaporation and the remaining solids analyzed by IR and NMR spectroscopy. According to these investigations all the extracts contained both PP and PSt. Benzene and 1,2-dichloroethane are good solvents for PSt but do not dissolve isotactic PP. The presence of PP in these solvents may be due to the formation of PP-g-PSt and to the solubilization of insoluble PP backbones by

soluble PSt branches. That PP and PSt were detected in n-heptane (a nonsolvent for both PP and PSt) may be due to a slight PP degradation during plasma chlorination and to the "pulling-in-solution" of PSt branches by PP backbones. These selective solubility experiments strongly suggest successful grafting.

Surface-grafting has also been demonstrated by a new technique involving degradation of surface-grafted PP fibers by Ar plasma followed by fragment analysis by GC. Thus various samples of virgin PP, surface-chlorinated PP, surface-grafted PP-g-PSt, and PSt were placed in a small plasma reactor (6 cm long, 1 mm wide glass capillary), destroyed by Ar plasma and the gaseous fragments were analyzed by GC using a column (Apiezon L, 3 m long, 5 mm wide) sensitive only to the degradation products arising from PSt. According to the GC scans shown in Figure 3, the fragmentation pattern of PSt and that of surface-grafted PP were identical.

Figure 4 shows scanning electron micrographs of a) the original PP fiber; b) the chlorinated PP fiber and c) the surface-grafted product. While the original PP and surface-chlorinated PP exhibit smooth surfaces, the surface-grafted product shows a cracked cover-layer of PSt surrounding the PP core. Significantly, the fibers are completely covered by PSt and the PSt layer is partially detached of the PP support due to the polymer/polymer incompatibility.

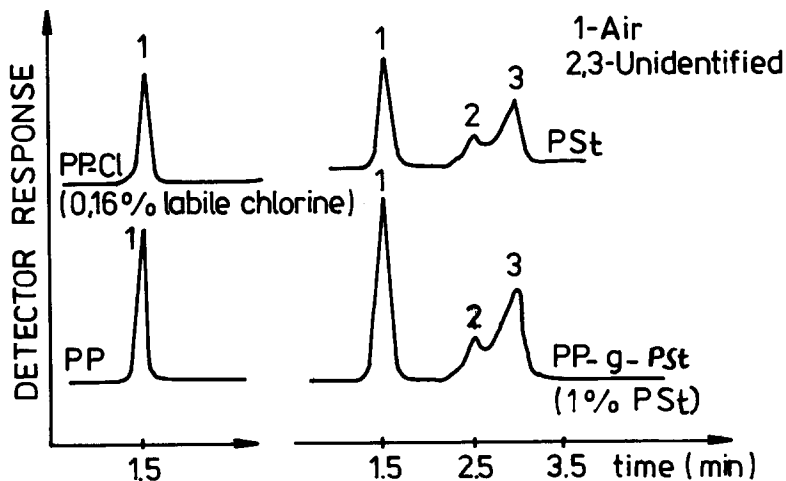
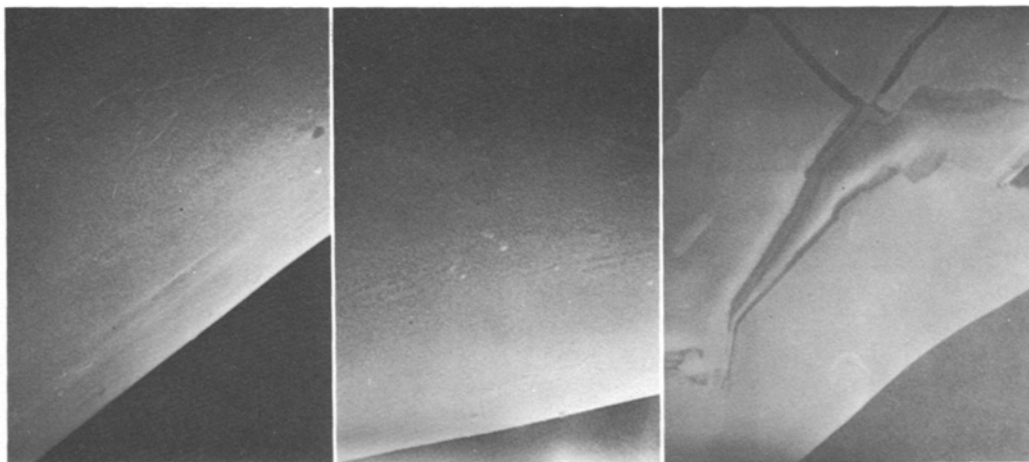


Figure 3. GC scans of the gaseous products obtained by Ar plasma destruction



x 3000 PP

x 3000 PPCI III

x 3000 PP-g-St III
(0.4%)

Figure 4. Scanning electron micrographs of standard PP, surface halogenated PP and PP-g-PSt

The apparently low grafting degree can probably be interpreted by the steric hindrance due to the low specific fiber surfaces ($3 \times 10^{-2} \text{ m}^2/\text{g}$) and by limited penetration of the monomers due to the morphology (crystallinity) of the isotactic PP.

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