

Flame Retardant Polypropylene Fibers with Good Dyeability

M. MUSKATELL,¹ L. UTEVSKI,¹ M. SHENKER,¹ S. DAREN,¹ M. PELED,¹ Y. CHARIT²

¹ Dead Sea Bromine Group, P.O. Box 180, Beer Sheva, Israel

² Israel Fiber Institute, P.O. Box 8001, Jerusalem, Israel

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ABSTRACT: Polypropylene has been grafted with pentabromobenzyl acrylate by reactive extrusion. The degree of grafting is about 4% by weight of the polypropylene independent of the weight of brominated monomer in the feed. Ungrafted monomer remains largely unreacted. Fibers spun from the grafted polypropylene display good mechanical properties and are easily dyed with anthraquinone type disperse dyes. The dyed cloths have good color stability even after laundering. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 601–606, 1997

INTRODUCTION

Polypropylene is one of the most versatile and cost-effective polymers available today. This is reflected in its growth in recent years. Its physical properties make it ideal for many applications including molded articles and spun fibers. The finished articles have good surface appearance and stain resistance. However, this same property makes it difficult to dye. Articles made from polypropylene and consequently polypropylene fibers are usually colored by the use of pigments.¹ However, the use of pigments is not trivial and often has a deleterious effect on other properties of the fibers. Dyeability of polypropylene can be improved somewhat by chemical modification with acrylic acids or esters,² aminoalkylacrylates,³ nylon blending,⁴ and maleic anhydride.⁵ In addition to the problem of dyeability, polypropylene does not possess adequate flame retardance for many applications including fibers. In view of its other desirable physical properties, it is of great interest to provide polypropylene fibers with greater flame retardancy and dyeability.

Traditionally, improvement of flame retardancy of polypropylene has relied on the use of additives such as decabromodiphenyl oxide, tetrabromobisphenol-A based epoxies, and magnesium hydroxide.⁶ However, a number of patents have related to the grafting of halostyrenes onto polypropylene to achieve flame retardance without loss of physical properties. A U.S. patent⁷ describes the grafting of bromostyrene or dichlorostyrene onto polypropylene and polyethylene in an extruder. A similar claim appears in a French patent.⁸ The radiation grafting of p-chloro- and bromo-styrenes onto polypropylene has also been claimed.⁹ Dibromostyrene has been grafted onto molten polypropylene in an extruder using a peroxide initiator.¹⁰ In practice, a mixture of grafted copolymer and nongrafted homopolymer (polydibromostyrene) was obtained.

The grafted polypropylene produced using dibromostyrene¹⁰ appeared to give satisfactory flame retardance but no mention was made of the dyeability of the products produced. Accordingly, there has remained a need for fire-retardant polypropylene compositions having good physical properties, processability, and dyeability. Pentabromobenzyl acrylate, FR1025M (Bromine Compounds Ltd.) behaves as a typical acrylate when

Correspondence to: Michael Peled.

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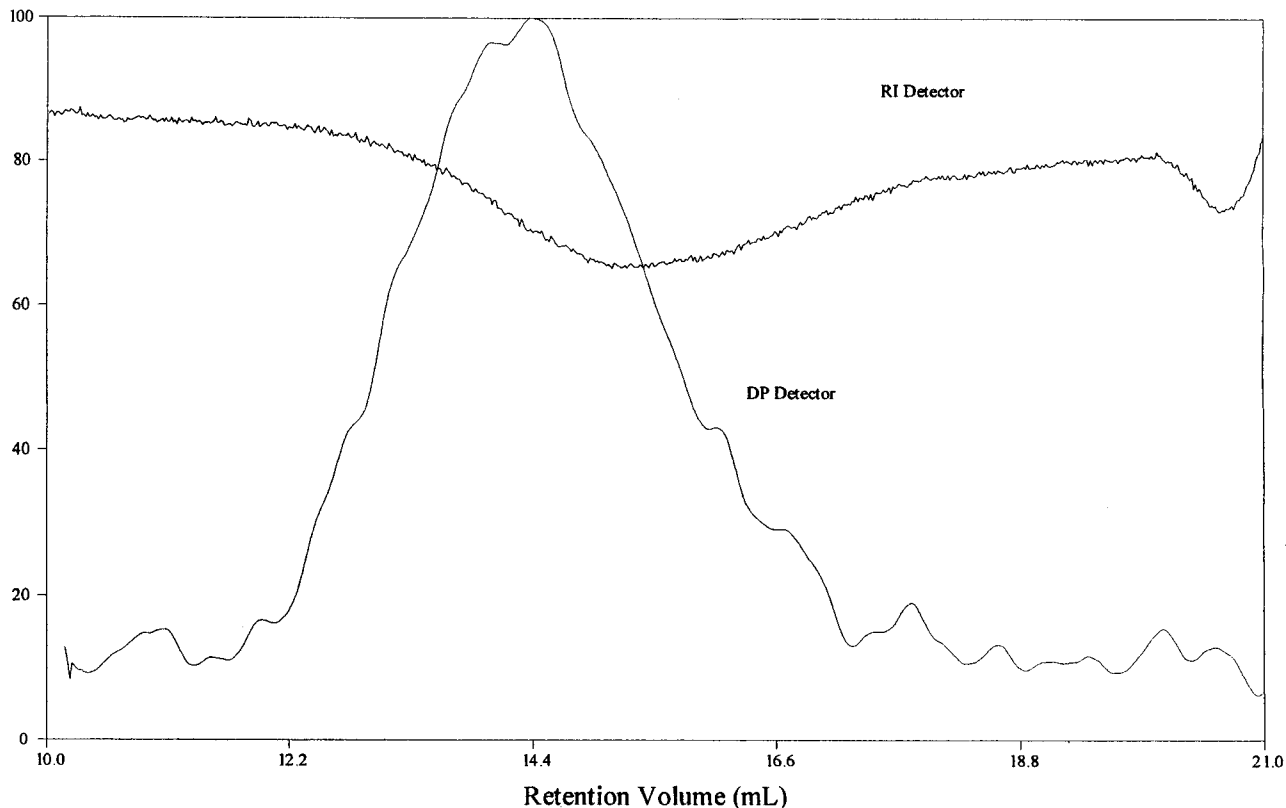


Figure 1 GPC of polypropylene A after granulation.

copolymerized in solution but its high melting point (120°C) allows it to also be polymerized or copolymerized by reactive extrusion.¹¹ It has also been shown that polypropylene, which was melt blended with FR1025M, was not only rendered flame retardant but also had a more reactive surface, which could be glued and colored.¹² In the present article a similar blend was used to produce flame-retarded polypropylene fibers with good dyeability. Such fibers could be very useful for the production of flame-retarded synthetic carpets and other household goods. It will also be shown that partial grafting of the FR1025M onto the polypropylene has also occurred.

EXPERIMENTAL

Materials

The materials used in this work were all commercially available technical products. Two types of polypropylene were used. Type A has a Melt Flow Index of 12.5 (ASTM D-1238) and an Elongation

at Break 30% (ASTM-D638). Type B was 12.0 and 9%, respectively. FR1025M (Bromine Compounds Ltd.) and Antimony Oxide (Ultrafine NA 9201 ex Laurel) were used as received.

Proving Existence of Grafting

Polypropylene (Type A) alone and polypropylene (Type A + 10% FR-1025M) were blended in a twin screw extruder at 160–210°C, extruded, cooled, and pelletized with no additional additives. The products were analyzed by GPC (Waters 150C) using bromobenzene at 120°C as eluent. The column was PL gel 5 and 10 μm . The eluent solutions were examined using both refractive index (RI) and pressure differential (PD) (Viskotek-150R) detectors. In the RI detector, PP appears as a negative peak (refractive index lower than the solvent) and in the PD as a positive peak (higher viscosity). (Fig. 1) FR-1025M monomer and polymer appear as positive peaks in both detectors. The pellets containing 10% FR-1025M after compounding still showed a negative PP peak in the

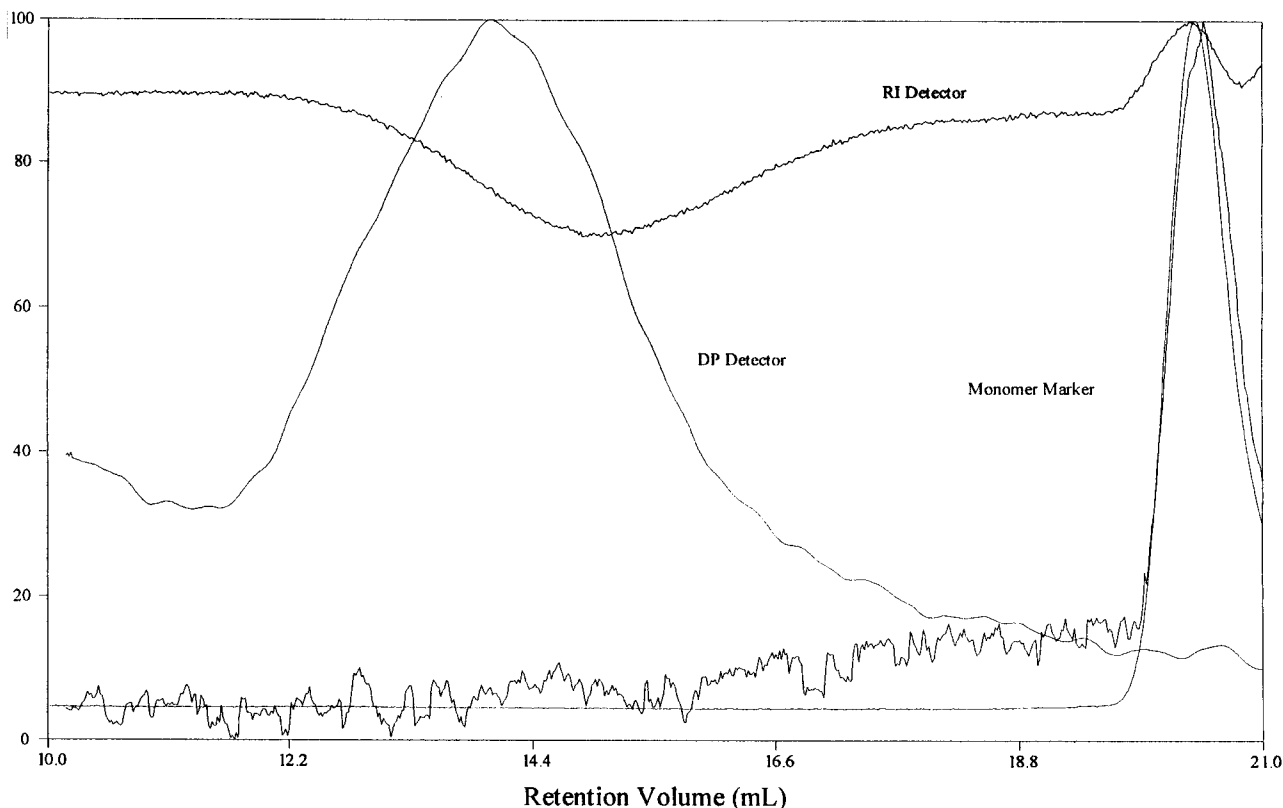


Figure 2 GPC of polypropylene A + 10% FR1025M after granulation.

RI detector (Fig. 2). A peak due to unreacted monomer was also observed.

Three grams of these pellets were dissolved in hot xylene and filtered via a heated sinter glass. No residue due to insoluble homopolymer was detected. (Note: the homopolymer FR1025P is only soluble in hot bromobenzene or bromonaphthalene.)

The polypropylene that precipitated from the xylene on cooling contained 2.8% bromine, corresponding to 3.9% by weight grafted FR-1025M. This value was checked from the opposite direction by determining the extractable monomer. Pellets (9.554 g) containing 0.955 g FR1025 in one form or another were refluxed for 24 h in chloroform to extract unreacted monomer. Under these conditions, the monomer was not likely to homopolymerise or graft. The chloroform extract was evaporated to dryness.

The chloroform insoluble polymer had a residual weight of 8.996 g (94% of original) and the dried extract weighed 0.601 g (6% of original). The Bromine content of the extract was 58.5%, i.e., 84% FR1025M corresponding to 0.505 g

monomer or 53% of the original FR1025M. This implies that 47% of the monomer has grafted, i.e., 4.7% in the product. The agreement between the two sets of measurements is excellent. Thus, of the original 10% FR-1025M monomer in the feed, about 4% has grafted onto the polypropylene and 6% has remained as unreacted monomer.

Preparation of Formulations for Fiber Spinning

A series of formulations containing from 0–16% bromine (0–23% FR1025M) were prepared in a twin screw extruder from appropriate master batches. Four typical examples are given in Table I.

The melt flow indices of FR-1025M-containing formulations were considerably higher than for the polypropylene alone. At 220°C MFI of $F_1 = 12.9$ g/10 min compared with 20.8 g/10 min for F_{12} . Thus, the presence of FR-1025M has improved the processability of the polypropylene.

Spinning of Fibers

The preparations were performed in Fourné pilot plant equipment according to the following pa-

Table I Formulations for Fiber Spinning

Materials	F ₁	F ₂	F ₃	F ₁₂	
PP-A	100			75.7	
PP-B		98.4	92.68		
FR-1025M			4.29	17.1	
Antimony Oxide			1.43	5.7	
Interox CC DFB		0.1	0.1	—	⁽¹⁾ Chimassorb 994
Chimassorb		1.0 ⁽¹⁾	1.0 ⁽¹⁾	1.0 ⁽²⁾	⁽²⁾ Chimassorb 119 FL
Irganox B-225		0.5	0.5	0.5	
Bromine Content %	0	0	3	12	

rameters: T melt before metering pump—172–182°C; T of hot plate for drawing—120–130°C; pressure of melt before metering pump—50–180 kp/cm²; pressure of melt before spinneret—50–150 kp/cm²; spinneret—12 holes; hole diameter—500 micron.

RESULTS AND DISCUSSION

A good balance of properties was achieved in most cases. The results are summarized in Table II.

Flammability of Fibers

Pieces of cloth were knitted using the four test fibers from Table I on a flat Walt 10/120 MOD QRT knitting machine. The first test was the Limiting Oxygen Index: The results are presented in Table III.

A significant increase in the percent oxygen required for burning (LOI) is obtained between zero (F₁ and F₂) and 3% bromine (F₃). Additional bromine does not appear to improve the LOI.

During burning the polypropylene melts and starts to flow. At these elevated temperatures, the residual monomer probably polymerizes. Because there is quite a big difference in melting points between polypropylene and the poly(pentabromobenzyl acrylate) homopolymer, 120 vs. 190°C, as well as in their melt viscosities, the two polymers separate and only that bromine that is chemically bound to the polypropylene remains in contact with it as the hot PP flows away from the flame. Thus, the improvement in oxygen index parallels the degree of grafting. Extra bromine neither increased the flame retardance nor, as we have shown, the degree of grafting.

Vertical Strip Test

This was performed on similar cloth samples in accordance with Federal Test Method 5905 Std. No. 191, which is intended for use in determining the resistance, among others, of textiles to flame propagation.

The results are summarized in Table IV.

The data from this table reveal that even 3%

Table II Preparation and Properties of Polypropylene Fibers

Conditions	F ₁	F ₂	F ₃	F ₁₂
Flow velocity of polymer (g/mm)	1.33	1.29	1.10	1.23
Winding velocity, m/min	68	87	88	75
Draw ratio	4.0	5.1	8.0	5.0
Yarn thickness (weight 9,000 m) denier	178	135	111	150
Filament thickness (denier)	14.8	11.3	9.3	12.5
Strength (g)	423	485	335	320
Tenacity at break (g/denier)	2.4	3.6	3.0	2.2
Elongation at break (%)	26.5	117.0	28.5	26.6
Yield force (g)	423	444	335	320
Yield stress (g/denier)	2.4	3.3	3.0	2.2
Knot strength (g)	416	484	416	436

Table III Limiting Oxygen Index of Fibers

Sample	LOI
F ₁	20.5
F ₂	20.1
F ₃	25.6
F ₁₂	26.0

bromine in the formulation, was sufficient to reduce the burning time to 0 s after removing the ignition source. The zero bromine samples, on the other hand, burnt continuously after an ignition time of 8–12 s. Thus, significant reductions in the flammability of polypropylene textiles have been achieved thanks to the addition of relatively small quantities of the brominated monomer.

Dyeability of PP-FR-1025M Fibers

The fibers obtained above were knitted into cloth and were tested with disperse dyes of the anthraquinone type. The cloths were dyed in 1% solutions, which were then heated from 50 to 98°C during 30 min and then boiled for 1 h. The dyed samples were then washed in hot and cold water and dried at room temperature. The Kubelka–Munk coefficients (K/S) were calculated from the reflection coefficient *R* as obtained from a Macbeth 1500 lightmeter.¹³ The wavelength measured was set in accordance with the respective dye. The results are described in Table V.

These results show improved dyeability of the PP fibers as the bromine content increases.

Laundering

The knitted samples were subjected to a laundering procedure according to the European Stan-

Table IV Results of the Vertical Strip Tests

Conditions	F ₁			F ₂			F ₃			F ₁₂		
	3	8	12	3 ^a	8 ^b	12 ^c	3	8	12	3	8	12
Contact Time with Flame, s												
After flaming time, s	52			16	17		0	0	0	0	0	0
Total burn	No	Yes	Yes	No	No	Yes				No burning		
Drips	Yes	Yes	Yes	Yes	Yes	Yes				No dripping		
Melt length, cm	18			9.5	17		4	6	7.5	4.5	8	9
Final result	Failed			Failed			Passed			Passed		

^a Testing done according to requirements of ASTM D3659-80 for textile products.

^b Testing done according to the requirements of the German Standard TL-8305-0135 for polyester textiles.

^c Testing done according to the requirements of ASTM D-626-55T for textile fabrics, MiL-C-83429B (1990) for Nomex, Fed. Test Method 5905-1978 Standard Method N 191A for cellulose fabrics.

Table V Intensity of Dying of Polypropylene Fibers

	% Br	K/S
		(wave length 600 nm)
<u>Cibacet Blue RF</u>	0	1.35
	4	2.16
	8	2.33
	12	2.53
	16	2.54
		(wave length 520 nm)
<u>Cibacet Red 3B</u>	0	0.9
	3	1.61
	4	1.64
	8	1.89
	10	1.88
	12	2.15
	16	2.15
		(wave length 520 nm)
<u>Terasil Yellow 2GW</u>	0	1.26
	3	1.54
	4	2.40
	8	2.49
	10	2.60
	12	2.63
	16	2.82

dard 1968/ISO-R-105. Although slight color changes were observed, the polypropylene fibers grafted with FR1025M had much more color stability than the untreated polypropylene fibers.

CONCLUSIONS

FR1025M has been grafted onto polypropylene to about 4% by weight. This amount is sufficient to

make significant improvements both to the dyeability and flame retardance of PP fibers. Additional monomer or polymer can further improve the dyeability but make no further improvement to the flame retardance. The grafted monomer may be acting to compatibilize the unbound homopolymer with the polypropylene backbone.

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