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Synthesis of graft copolymers of polyethylene: grafting of fluorinated model compound oligomers

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Abstract

The condensation reaction of perfluorinated amines on to (succinic anhydride)–HDPE (high-density polyethylene) graft copolymer have been studied. Four different amine structures have been synthesized which have been analyzed by ^1H NMR spectroscopy GC–MS methods. Model structures of succinimide and succinamic acid have been synthesized with each amine and analyzed by FT-IR spectroscopy in order to determine the structure of the copolymer obtained. A scale of reactivity has been deduced as a function of the amine structure. Grafting levels of copolymer have been determined by elemental analysis of fluorine.

Introduction

Polyolefins such as polyethylene (PE) and polypropylene (PP) are very often modified chemically in order to improve their intrinsic properties. Thus, polar groups, e.g. CO_2H, SO_3H, F, etc., are introduced into their backbones in order to confer special behaviour such as lyophobicity.

Such modifications can be achieved either during the synthesis of the polymer by using copolymerization or by chemical modification of the polymer. As an example of the first method, Gouarderes and Schlund [1] prepared copolymers of ethylene and fluorinated monomers such as vinyl fluoride. The main interest of this technique is that low or high functional group levels can be introduced into the polymer. The technique has been widely developed and cannot be summarized in this paper. The second major method consists in the modification of polymers by reagents. Different kinds of polymers can be modified. Thus, Gerhardt and Lagow [2] introduced fluorine into polyethers such as polypropylene oxide. These modifications can be realized by grafting functional monomers via a reaction initiated by the thermal decomposition of organic peroxides [3–12]. Modified polyolefins can also be synthesized by the condensation reaction of functionalized polymers (e.g. polyolefins modified with maleic anhydride) with reactive oligomers [13].

It is well known that the introduction of fluorine into polyolefins increases the chemical resistance and thermal properties [12] and decreases the surface tension [13]. The products have many applications as textile fibres [14–18] or as ion-exchange membranes possessing linear or crosslinked fluorinated chains [19–33].

Graft fluoropolymers of polyethylene and polypropylene have been synthesized in our laboratory [34]. Two methods of synthesis have been studied. Firstly, the graft copolymerization of perfluorinated acrylate or methacrylate monomers on to PE or PP macroinitiators obtained by ozonization. Secondly, the condensation reaction of perfluorinated monofunctional monomers (carboxylic acid, epoxide) with PE or PP graft copolymers containing reactive groups such as epoxide, alcohol or carboxylic acid [34].

In the present paper, we report an investigation of the condensation of perfluorinated amines with a (succinic anhydride)–polyethylene graft copolymer.

Results

Grafting maleic anhydride (MA) on to high-density polyethylene (HDPE)

The grafting reaction of MA on to HDPE has been studied by Gaylord and coworkers [35–37]. The general technique employed uses organic peroxide to initiate the grafting reaction of MA on to HDPE. More recently, Ganzeveld and Janssen studied this reaction in an extruder [38]. They showed that very low concentrations

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of initiator led to a grafting reaction. The grafting levels obtained were between 0.5% and 2% depending on the experimental conditions employed.

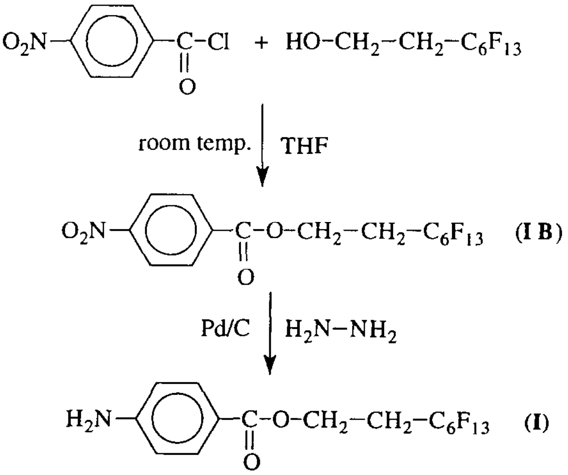
In our case, (succinic anhydride)–polyethylene (SA–PE) graft copolymer has been prepared without the use of a free-radical initiator. The grafting of MA is initiated solely by thermomechanical treatment in a Brabender batch mixer at 250 °C over a period of 8 min with a roller speed of 100 rpm. An increase of viscosity was noticed during the reaction brought about by coupling of macroradicals of PE or PEgMA (polyethylene graft maleic anhydride). This phenomenon was also observed by Gaylord *et al.* However, the copolymer obtained was still totally soluble in refluxing toluene and was therefore not crosslinked. The unreacted MA was eliminated by dissolution in dry acetone.

The FT-IR spectrum of the purified copolymer exhibited absorption bands at 1865 and 1788 cm^{-1}, characteristic of succinic anhydride. Volumetric titration of the anhydride content using a KOH solution led to an estimate of 3% grafting (by weight). This result is comparable with the results of Ganzeveld and Janssen who obtained grafting values of 0.5% to 2% over temperatures within the range 160–210 °C and initiator concentration flows between 0.26 ml min^{-1} and 1.5 ml min^{-1}.

Synthesis of fluorinated amines

Perfluorinated amines with different chemical structures and hence different basicities and reactivities have been prepared.

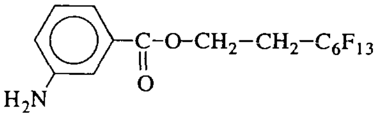
Aromatic amine with the ester group in the para *position*



In the initial step, the reaction was carried out in anhydrous THF at room temperature and the resulting nitro intermediate reduced by the action of hydrazine in the presence of palladium on activated carbon as a catalyst [39].

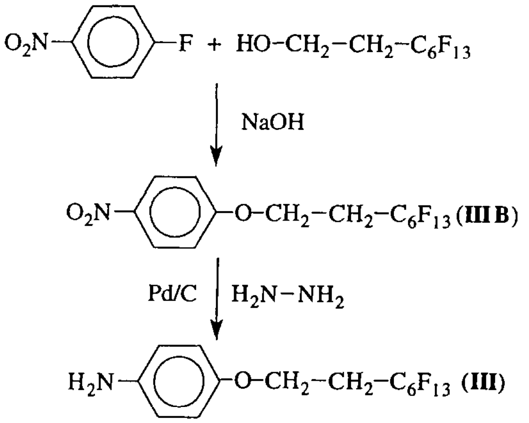
Aromatic amine with the ester group in the meta *position*

The same reactions were carried out with 3-nitrobenzoyl chloride, The fluorinated amine **II** was obtained.



(II)

Aromatic amine with the ether group in the para *position [40]*



The nitro intermediate was synthesized by the reaction of fluoronitrobenzene with the polyfluorinated alcohol. The reduction reaction was carried out as for compound **IB** above.

Aliphatic amine [41]

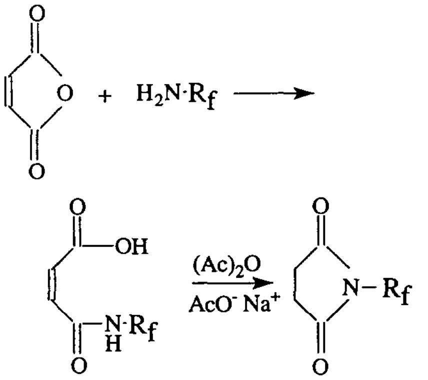
$$IC_2H_4C_6F_{13} \xrightarrow{NaN_3} \underset{\textbf{(IVB)}}{N_3C_2H_4C_6F_{13}} \xrightarrow[NH_4OH]{\text{triphenyl phosphine}}$$

$$\underset{\textbf{(IV)}}{H_2NC_2H_4C_6F_{13}}$$

The aliphatic amine was obtained in two steps. The iodofluoro derivative was first transformed to the azide by the action of sodium azide and the resulting intermediate **IVB** reduced to the aliphatic amine **IV**.

Modelling the perfluorinated amine/succinic anhydride reaction

Reaction between succinic anhydride grafted on to polyethylene and an amine may lead to different chemical structures, i.e. residual succinic anhydride, succinamic acid and succinimide. In order to characterize our graft copolymers, we prepared different model structures under similar conditions as in our other experiments. Thus, we reacted the prepared amines **I**, **II**, **III** and **IV** with succinic anhydride:

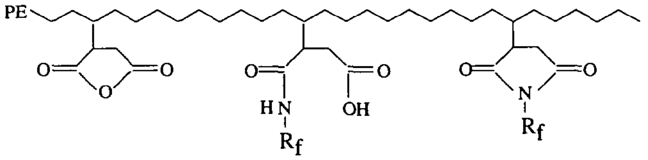


We have employed FT-IR analysis as a means of analyzing the graft copolymers thus obtained. The characteristic vibration bands for each compound are reported in Table 1.

Reaction between PE–AS copolymer and fluorinated amines

Grafting reaction

This was carried out in refluxing anhydrous toluene over a period of 12 h. Excess amine (×2/succinic anhydride) was employed. After completion of the reaction, different possible structures such as succinimide, succinamic acid and anhydride may be present in the final product.



The copolymer obtained was purified by precipitation in dry acetone and filtration. Excess amine was eliminated with the filtrate.

Analysis of graft copolymers

The graft copolymers were analyzed by elemental analysis for fluorine (Table 2) and FT-IR spectroscopy (Table 3) in order to establish the structures obtained.

Discussion

Aromatic amines with *para* ether groups did not lead to a graft copolymer since elemental analysis showed the complete absence of fluorine. This is probably due to the instability of this structure which decomposes before reaction can commence. Such behaviour has been demonstrated by differential scanning calorimetry and thermal gravimetric analysis which showed that decomposition of amine **III** commenced at 100 °C. However, the FT-IR spectrum showed an absorption band at 3331 cm^{-1} corresponding to a secondary amine vibration band. Thus, it was deduced that the fragment with the amine group had reacted with the succinic group of the copolymer.

The grafting yield for other graft copolymers synthesized with the fluorinated amines **I**, **II** and **IV** depended on the structure of the amine. Thus, aromatic amines with an ester group led to a grafting yield which depended on the position of the ester. Substitution in the *para* position led to a grafting yield of 7% while substitution in the *meta* position gave a grafting yield of 22%. This can be explained by the stabilization effect induced by the ester group in the *para* position (**I**) leading to deactivation of the amine.

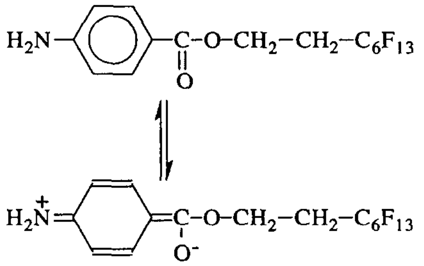


TABLE 1. Characteristic infrared vibration bands (cm^{-1}) for model structures

Model structure	Succinimide or succinamic acid	Amine	Hydroxyl
Succinic anhydride	1865; 1788	–	–
V: succinamic acid with **I**	1728; 1697	3302	3500–3000
VI: succinimide with **I**	1728; 1709	–	–
VII: succinamic acid with **II**	1720; 1697	3366	3500–3000
VIII: succinimide with **II**	1720; 1707	–	–
IX: succinamic acid with **III**	1715; 1697	3380	3500–3000
X: succinimide with **III**	1715; 1707	–	–
XI: succinamic acid with **IV**	1697(s)[a]	3380	3500–3000
XII: succinimide with **IV**	1707(s)	–	–

[a] s = strong.

TABLE 2. Fluorine content and grafting yield of graft copolymers

Grafted copolymer amines	Fluorine content of copolymer (%)	Grafting yield (%)
I	0.6	7
II	1.8	22
III	0	0
IV	3.3	44

TABLE 3. Characteristic infrared vibration bands (cm^{-1}) for graft copolymers

Grafted copolymer amines	Infrared absorption bands observed
I	1720; 1786; 3330
II	1724; 1786; 3335
III	1711; 1780; 3331
IV	1711; 1780; 3300

When the ester group is in the *meta* position (amine **II**), a similar stabilization effect is not induced so that the basicity of the amine is enhanced and the grafting yield is improved. Finally, the highest grafting yield (44%) is obtained with amine **IV** which is more basic and more reactive. In all cases, infrared analysis of the copolymers shows the presence of vibration bands characteristic of amide and acid groups. The N–H vibration observed 3300 cm^{-1} shows that cyclization did not occur in the reaction with no succinimide being formed. Bands at 1780 cm^{-1} due to residual succinic anhydride were observed in all cases.

Experimental

FT-IR spectra of copolymers (film) were recorded using a Nicolet 510P spectrophotometer. ^1H NMR spectra were recorded using a Bruker WP 200 apparatus. GC–MS analyses were undertaken using a Hewlett Packard 5890A Chromatograph equipped with a 25 m ×0.23 mm silica column grafted with polydimethylsiloxane. Mass spectra were recorded using a Hewlett Packard quadrupole MS system (model 5970) with 70 eV for electron impact.

Synthesis of IB

4-Nitrobenzoyl chloride (0.01 mol) in 20 ml of anhydrous THF was added to a stirred solution consisting of 0.01 mol of 1,1,2,2-tetrahydroperfluoro-octanol in 50 ml of anhydrous THF containing 0.01 mol of pyridine. The reaction was performed at 25 °C for 12 h when the pyridinium salt formed was eliminated by filtration and the THF solution distilled under vacuum. The product was dissolved in ether and extracted three times with 50 ml of an aqueous solution of HCl (pH 6). The organic fraction was then dried over sodium sulphate and evaporated to give **IB** in 80% yield. ^1H NMR (200 MHz) (acetone-D_6) δ: 8.2 (s, 4H, arom.); 4.8 (t, 2H); 2.6 (m, 2H) ppm. MS (*m/e*, rel. int.): 513 (5); 363 (2); 167 (28); 150 (100); 119 (5); 69 (22).

Synthesis of I

Hydrazine monohydrate (10^{-2} mol) in 20 ml of MeOH was added to 20 ml of an ethanol/THF (80:20) solution containing 5×10^{-3} mol of **Ib** and 5% of Pd/C (10% Pd). The reaction was performed at room temperature over a period of 90 min, and the temperature then raised to 80 °C for 8 h. The Pd/C was eliminated by filtration and the solvents distilled under vacuum. Product **I** was obtained in 90% yield. ^1H NMR (200 MHz) δ: 7.8 (d, 2H, arom.); 6.6 (d, 2H, arom.); 4.6 (t, 2H); 2.6 (m, 2H) ppm. MS (*m/e*, rel. int.): 483 (30); 120 (100); 92 (20); 69 (10).

Synthesis of IIB

3-Nitrobenzoyl chloride (0.01 mol) in 20 ml of anhydrous THF was added to a stirred solution consisting of 0.01 mol of 1,1,2,2-tetrahydroperfluoro-octanol in 50 ml of anhydrous THF containing 0.01 mol of pyridine. The reaction was performed at 25 °C over a period of 12 h. The pyridinium salt formed was then eliminated by filtration and the THF solution distilled under vacuum. The product was dissolved in ether and extracted three times with HCl solution (pH 6). The organic fraction was dried over sodium sulphate and evaporated to give **IIB** in 90% yield. ^1H NMR (200 MHz) (acetone-D_6) δ: 8.8 (t, 1H, arom.); 8.5 (qd, 2H, arom.); 7.9 (t, 1H); 4.8 (t, 2H); 2.7 (tt, 2H) ppm. MS (*m/e*, rel. int.): 513 (5); 363 (2); 167 (30); 150 (100); 119 (5); 69 (20).

Synthesis of II

Hydrazine monohydrate (10^{-2} mol) in 20 ml of MeOH was added to 20 ml of an ethanol/THF (80:20) solution containing 5×10^{-3} mol of **IIB** and 5% of Pd/C (10%). The reaction was performed at 20 °C over a period of 90 min, and the temperature then raised to 80 °C for 8 h. The Pd/C was eliminated by filtration and the solvents distilled under pressure. Product **II** was obtained in 90% yield. ^1H NMR (200 MHz) δ: 7–7.4 (m, 3H, arom.); 6.9 (m, 1H, arom.); 4.6 (t, 2H); 3.4 (m, 1H); 2.5 (m, 2H) ppm. MS (*m/e*, rel. int.): 483 (80); 120 (100); 92 (60); 69 (10).

Synthesis of IIIB

1,1,2,2-Tetrahydroperfluoro-octanol (0.03 mol) and 6×10^{-3} mol of tetrabutylammonium hydrogen sulphate were added to 0.202 mol of *p*-fluoronitrobenzene. Sodium hydroxide (27 ml of a 25 N solution) was then added slowly to the mixture, following which the temperature was raised to 40 °C for 48 h. Water was then added and the solution obtained extracted with dichloromethane. After purification, product **IIIB** was obtained in 70% yield. ^{1}H NMR (200 MHz) ($CDCl_3$) δ: 8.2 (d, 2H, arom.); 6.95 (d, 2H, arom.); 4.3 (t, 2H, arom.); 2.6 (tt, 2H) ppm.

Synthesis of III

Hydrazine monohydrate (10^{-2} mol) in 20 ml of MeOH was added to 20 ml of an MeOH/THF (80:20) solution containing 5×10^{-3} mol of **IIIB** and 5% of Pd/C (10% Pd). The reaction was performed at 20 °C over a period of 90 min and the temperature then raised to 80 °C for 8 h. The Pd/C was eliminated by filtration and the solvents removed by distillation under pressure. Product **III** was obtained in 40% yield. ^{1}H NMR (200 MHz) ($CDCl_3$) δ: 6.75–6.65 (m, 4H); 4.25 (6, 2H); 3.5 (m, 2H); 2.6 (tt, 2H) ppm.

Synthesis of IVB

NaN_3 (0.06 mol) in 12 ml of water, 0.03 mol of *F*-hexyl-2-ethyl iodide and 0.6075 g of Aliquat 336 were reacted at 90–100 °C over a period of 12 h with stirring. The azide was obtained by decantation. Yield, 96%. ^{1}H NMR (200 MHz) ($CDCl_3$) δ: 3.6 (t, 2H); 2.4 (tt, 2H) ppm. MS (*m/e*, rel. int.): 389 (9); 119 (5); 69 (30).

Synthesis of IV

Triphenylphosphine (0.02 mol) was added slowly (exothermic reaction) to 0.01 mol of **IVB** in 8 ml of *N*-methylpyrolidone. After stirring for 2 h, 0.685 ml of a 28% solution of ammonia was added and the product distilled under reduced pressure (52 °C/20 mmHg). Yield, 90%. ^{1}H NMR (200 MHz) (acetone-D_6) δ: 3.0 (t, 2H); 2.2 (tt, 2H); 1.2 (s, 2H) ppm. MS (*m/e*, rel. int.): 361 (80); 169 (5); 119 (25); 69 (100).

Synthesis of V

A solution consisting of 0.01 mol of succinic anhydride in 20 ml of chloroform was added to 0.01 mol of **I** in 20 ml of chloroform at -20 °C. Product **V** precipitated from the solution and was filtrated. Yield, 75%. ^{1}H NMR (200 MHz) δ: 9.5 (m, 1H); 8.0 (d, 2H); 7.8 (d, 2H); 4.65 (t, 2H); 2.8 (tt, 2H); 2.65 (s, 4H) ppm. MS, (*m/e*, rel. int.): 565 (30); 483 (10); 202 (100); 119 (10); 69 (10).

Synthesis of VI

Compound **V** (9×10^{-3} mol), 0.09 of acetic anhydride and 0.065 mol of sodium acetate were reacted at 90 °C over a period of 2 h. The mixture was precipitated in cold water and the succinimide isolated in 80% yield by filtration. ^{1}H NMR (200 MHz) δ: 8.2 (d, 2H); 7.5 (d, 2H); 4.65 (t, 2H); 2.9 (s, 4H); 2.6 (tt, 2H) ppm. MS (*m/e*, rel. int.): 565 (20); 202 (100); 483 (10); 119 (10); 69 (10).

Synthesis of VII

Same procedure as for compound **V** but with amine **II**. Yield, 75%. ^{1}H NMR (200 MHz) δ: 9.5 (m, 1H); 8.4 (s, 1H, arom.); 7.9 (d, 1H, arom.); 7.7 (d, 1H, arom.); 7.45 (t, 1H, arom.); 4.6 (t, 2H); 2.9 (tt, 2H); 2.6 (s, 4H) ppm. MS (*m/e*, rel. int.): 565 (40); 483 (10); 202 (100); 119 (10); 69 (10).

Synthesis of VIII

Same procedure as for compound **VI** but with succinimic acid **VII**. Yield, 80%. ^{1}H NMR (200 MHz) δ: 8.0 (m, 2H); 7.6 (m, 2H); 4.6 (t, 2H); 2.8 (tt, 2H); 2.8 (s, 4H) ppm. MS (*m/e*, rel. int.): 565 (40); 483 (10); 202 (100); 119 (10); 69 (10).

Synthesis of IX

Same procedure as for compound **V** but with amine **III**. Yield, 80%. ^{1}H NMR (200 MHz) δ: 9.1 (s, 1H); 7.6 (d, 2H); 6.9 (d, 2H); 4.3 (t, 2H); 2.7 (tt, 2H); 2.6 (s, 4H) ppm. MS (*m/e*, rel. int.): 555 (15); 363 (5); 100 (8); 119 (10); 69 (40).

Synthesis of X

Same procedure as for compound **VI** but with succinimic acid **IX**. Yield, 30%. ^{1}H NMR (200 MHz) δ: 7.0 (d, 2H); 7.2 (d, 2H); 4.4 (t, 2H); 3.0 (s, 4H); 2.8 (tt, 2H) ppm. MS (*m/e*, rel. int.): 537 (100); 510 (5); 455 (20); 119 (10); 69 (20).

Synthesis of XI

Same procedure as for compound **V** but with amine **IV**. Yield, 80%. ^{1}H NMR (200 MHz) δ: 7.5 (m, 1H); 3.5 (m, 2H); 2.5 (tt, 2H); 2.5 (m, 4H) ppm. MS (*m/e*, rel. int.): 445 (15); 119 (10); 100 (10); 69 (10).

Synthesis of XII

Same procedure as for compound **VI** but with succinimic acid **XI**. Yield, 60%. ^{1}H NMR (200 MHz) δ: 3.8 (t, 2H); 2.7 (s, 4H); 2.4 (tt, 2H) ppm. MS (*m/e*, rel. int.): 445 (15); 112 (35); 119 (10); 69 (10).

Reaction between PE–SA and fluorinated amine

PE–AS (2 g) was dissolved in 100 ml of refluxing anhydrous toluene. When dissolution was complete, a solution consisting of 1.2×10^{-3} mol of fluorinated amine in 20 ml of anhydrous toluene was added. After 12 h, the solution was precipitated into 500 ml of dry acetone. The copolymer obtained was filtered and washed with acetone and ether. It was then dried at 110 °C over 12 h before analysis.

Synthesis of HDPE–succinic anhydride graft copolymer

HDPE (Stamylan 6621 from DSM – Melt Flow Index=0.16 measured at 190 °C under a strength of 21.2 N) (50 g) and 5 g of maleic anhydride were introduced into a Brabender batch mixer at 250 °C and mixed for 8 min. The roller speed was 100 rpm. The copolymer obtained was dissolved in dry toluene and precipitated from dry acetone. After filtration, it was dried and analyzed by volumetric titration.

Analysis of HDPE–succinic anhydride copolymer

Copolymer (5 g) was dissolved in refluxing toluene and the temperature then raised to 90 °C. The solution was titrated using a solution consisting of 0.05 M KOH in isopropanol in the presence of phenolphthalein as indicator.

Conclusions

In this work, we have investigated the reaction of different fluorinated amines with PEgSA [polyethylene–(succinic anhydride) graft] copolymer. The most active reactive amine was an aliphatic amine which led to 44% grafting. The copolymer obtained had a 3.3 wt.% fluorine content. Aromatic amines lead to low grafting yields and a reactivity scale has been established as a function of their structure. It has been shown that aromatic amines with *para* ether groups do not lead to graft copolymers because of the instability of the structure.

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