Chem. Mater. **1992**, *4*, 1027-1032

Functionalization of Poly(organophosphazenes). 2. Modification of Poly[bis(4-*sec*-butylphenoxy)phosphazene] by Free-Radical-Initiated Grafting of Maleic Anhydride

Mario Gleria,[†,*] Francesco Minto,[†] Marco Scoponi,[‡] Fiorella Pradella,[‡] and Vittorio Carassiti[‡]

Istituto di Fotochimica e Radiazioni d'Alta Energia del Consiglio Nazionale delle Ricerche, Sezione di Legnaro, Via Romea 4, 35020 Legnaro, Padova, Italy, and Centro di Studio sulla Fotochimica e Reattivita' degli Stati Eccitati dei C.C., Dipartimento di Chimica dell'Università, Via Borsari 46, 44100 Ferrara, Italy

Received March 5, 1992. Revised Manuscript Received June 23, 1992

In this paper we report the modification of poly[bis(4-*sec*-butylphenoxy)phosphazene] by solution grafting of maleic anhydride molecules promoted by radical initiators, in order to develop a new class of functionalized poly(organophosphazenes). Grafting reactions and yields, evaluated by FTIR spectroscopy, are investigated as a function of the different experimental conditions, such as maleic anhydride and benzoyl peroxide concentrations, temperature of the process, and grafting time. The new phosphazene materials show improved adhesion strength on the metal surfaces in the melt state as compared to that of the pristine poly[bis(4-*sec*-butylphenoxy)phosphazene], which is related to the content of succinic anhydride residues grafted onto the polymer.

Introduction

During the past 30 years there has been a growing demand for specialities and tailor-made polymeric materials for advanced applications. This interest has essentially been fulfilled in two ways, i.e., developing new polymers[1] and using multicomponent polymeric blends formed by already known and characterized macromolecules.[2]

As far as the first point is concerned, poly(organophosphazenes) (POPs) are relatively new macromolecules, first disclosed by Allcock in 1965,[3,4] and their importance has continuously increased in the past 2 decades due to their scientific interest,[5] outstanding properties,[6] and versatility.[7]

These exciting qualities of POPs originate from three facts.

The first is the almost unique synthetic approach used for their preparation:[3,4,8] poly(dichlorophosphazene), $(NPCl_2)_n$, in fact, the very reactive polymeric precursor from which POPs are obtained by replacement of the reactive chlorines with nucleophiles, is used to bind a large variety of different substituents, so imparting to POPs a remarkable series of intersting and valuable properties (self-extinguishibility,[9,10] flame retardancy,[11] biocompatibility,[12] water repellency[13] or affinity,[14] photoactivity,[15] etc.). The second is the copolymerization process, i.e., the simultaneous substitution on the same polyphosphazene skeleton of two (or more) different nucleophiles,[16] thus obtaining phosphazene materials containing mixed substituents, showing modified physical[17,18] and chemical[19-21] properties as compared with those of the original homopolymers. The third is the modification of the POP side substituents by introducing suitable chemical functionalities in these groups.[22] The above-mentioned experimental approaches can be used to synthesize phosphazene homopolymers, copolymers, and functionalized polymers of predictable structures, therefore showing a priori selected characteristics.

Despite of the great versatility of POPs, however, these substrates show poor miscibility either with conventional, carbon-backboned polymers[23] or with other phosphazene macromolecules.[24,25] This behavior may be attributed, in part, to the considerably high molecular weight of POPs (usually $>10^6$)[26] and to their remarkably low interfacial energy.[27] These limitations can be overcome either by decreasing the molecular weight (MW) of POPs, for instance by better controlling the polymerization process of

---

[†] Istituto di Fotochimica e Radiazioni.

[‡] Centro di Studio sulla Fotochimica e Reattivita'.

(1) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.

(2) Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: New York, 1978.

(3) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.

(4) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1965**, *5*, 1016.

(5) Gleria, M. *Chim. Ind.* (*Milan*) **1988**, *70*, Suppl. to Nr. 11, p 15.

(6) Penton, H. R. In *Inorganic and Organometallic Polymers*; ACS Symposium Series No. 360; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; American Chemical Society: Washington, DC, 1988; Chapter 21, p 277.

(7) Allcock, H. R. In ref 6, Chapter 19, p 250.

(8) Austin, P. E.; Riding, J. H.; Allcock, H. R. *Macromolecules* **1983**, *16*, 719.

(9) Quinn, E. J.; Dieck, R. L. *J. Fire Flammability* **1976**, *7*, 5.

(10) Quinn, E. J.; Dieck, R. L. *J. Fire Flammability* **1976**, *7*, 348.

(11) Lieu, P. J.; Magill, J. H.; Alarie, Y. C. *J. Fire Flammability* **1980**, *11*, 167.

(12) Allcock, H. R. In *Biodegradable Polymers as Drug Delivery Systems*; Chasin, M., Langer, R., Eds.; Marcel Dekker: New York, 1990; Chapter 5, p 163.

(13) Singler, R. E.; Schneider, N. S.; Hagnauer, D. L. *Polym. Eng. Sci.* **1975**, *15*, 321.

(14) See, as an example: Montoneri, E.; Gleria, M.; Ricca, G.; Pappalardo, G. C. *Makromol. Chem.* **1989**, *190*, 191.

(15) Gleria, M.; Bortolus, P.; Flamigni, L.; Minto, F. In *Inorganic and Organometallic Polymers with Special Properties*; Laine, R. M., Ed.; NATO ASI Series E 206; Kluwer Academic Publishers: Dordrecht, 1992; p 375.

(16) Rose, S. H. *J. Polym. Sci., Part B* **1968**, *6*, 837.

(17) Allcock, H. R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 147.

(18) Allcock, H. R.; Connolly, M. S.; Sisko, J. T.; Al-Shali, S. *Macromolecules* **1988**, *21*, 323.

(19) Gleria, M.; Minto, F.; Flamigni, F. Italian Patent No. 21293, 1989.

(20) Minto, F.; Flamigni, F.; Bortolus, P.; Gleria, M. *J. Inorg. Organomet. Polym.* **1991**, *1*, 53.

(21) Gleria, M.; Minto, F.; Flamigni, L.; Bortolus, P. *J. Inorg. Organomet. Polym.* **1992**, *2*, 329.

(22) See, as an example: Medici, A.; Fantin, G.; Pedrini, P.; Gleria, M.; Minto, F. *Macromolecules* **1992**, *25*, 2569.

(23) Gleria, M., Minto, F., unpublished results.

(24) Beres, J. J.; Schneider, N. S.; Desper, C. R.; Singler, R. E. *Macromolecules* **1979**, *12*, 566.

(25) Gleria, M.; Minto, F.; Bortolus, P.; Porzio, W.; Meille, S. V. *Eur. Polym. J.* **1990**, *26*, 315.

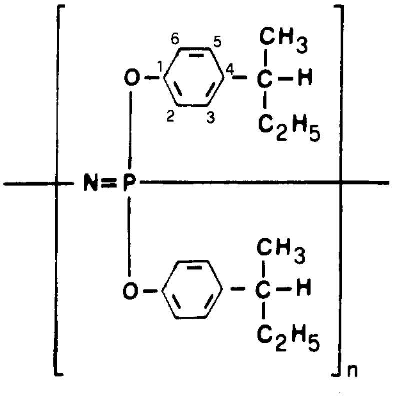
(26) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972.

(27) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982; p 122.

0897-4756/92/2804-1027$03.00/0

the phosphazenes,[28] or by chemical[27] or photochemical[29] attachment of functional groups which are particularly effective for achieving maximum reduction of interfacial tension.

Following this last approach, we chose to chemically functionalize poly[bis(4-*sec*-butylphenoxy)phosphazene], $\{NP[O\text{-}C_6H_4CH(CH_3)(C_2H_5)]_2\}_n$, (PsBPP), given both the industrial relevance of 4-*sec*-butylphenoxy-containing phosphazene copolymers[28] and the high reactivity of the tertiary hydrogen bonded to the *sec*-butyl group of the side phenoxy substituent.[29] We also considered maleic anhydride (MA) as a chemical function to be grafted onto PsPOP, due to the peculiar characteristics that this molecule is able to impart to polymeric materials once chemically attached to them as succinic anhydride (SA) residues, i.e., high chemical reactivity towards $-NH_2$ or $-OH$ end-capped (nylon or polyesters, respectively) polymeric materials (reactive blending processes) to generate compatibilizing agents for blending processes[30,31] and excellent capability of polar anhydride functions to enhance the surface properties of polymeric substrates.[32]



Poly[bis(4-secbutylphenoxy)]phosphazene

The low tendency of MA towards homopolymerization,[33] moreover, facilitates the grafting of monomeric anhydride residues onto PsBPP.

Accordingly, in this paper the chemical modification of PsBPP by reaction with maleic anhydride (MA) will be discussed, as a preliminary step to the use of modified phosphazene copolymers as compatibilizing agents in blending processes. The enhancement of adhesion properties to metal surfaces in the melt state of the modified POP will also be addressed.

Experimental Section

Materials. *sec*-Butylphenol was an Aldrich product and was dried by distillation of the water/toluene azeotrope immediately prior to use. Succinic anhydride (SA), maleic anhydride (MA), benzoyl peroxide (BP), and sodium hydride 60% oil dispersion (Aldrich) were used as received.

Tetrahydrofuran (THF), toluene, xylene, dioxane, and methylene chloride were C. Erba solvents, analytical grade; 1,1,1-trichloroethane was a Merck solvent, analytical grade. When necessary, they were purified and dried by standard techniques.[34]

Hexachlorocyclophosphazene, $(NPCl_2)_3$, was purchased from Shin Nisso Kako (Japan), and purified by vacuum sublimation until constant melting point was reached (113 °C).[26] Poly(dichlorophosphazene), $(NPCl_2)_n$, was obtained by ring-opening polymerization of hexachlorocyclophosphazene at 250 °C in vacuum[3,4] and was freed from the residual, unpolymerized trimer by vacuum sublimation at 60–70 °C.

The polypropylene-*g*-succinic anhydride (PP-*g*-SA) sample for adhesion experiments was kindly supplied by Himont Italia s.r.l. and used as received. The content of SA in this polymer was 0.4% w/w. Other characteristics of this polymer are as follows: weight average molecular weight 280000; $[\eta] = 20.0$ mL/g; isotacticity index 95%; crystallinity content 55%.

Equipment. ^{31}P, ^{1}H, and ^{13}C NMR spectra were carried out with a Varian FT 80 and with a Bruker AC 200 spectrometers. IR spectra were recorded by means of a Perkin-Elmer spectrophotometer Model 287 and with a Bruker FTIR instrument Model IFS 88.

Weight average molecular weights (MW) of the polymers were measured by the light-scattering technique using a Sophica spectrogoniodifussimeter.

T_g measurements were performed with a DSC Mettler calorimeter Model TA72.

Grafting experiments with PsBPP and maleic anhydride were carried out in an CEAST oven Model 1175, with forced hot-air circulation, at temperatures ranging between 95 and 139 ± 0.5 °C.

Adhesion Experiments. Joints for the adhesion tests were obtained by pressing a film of modified PsBPP containing variable percentages of SA between two aluminum foils, previously degreased with boiling 1,1,1-trichloroethane. The pressure used was 4 tons/cm^2, pressing time 2 min, and temperature 130 °C. The adhesion peeling tests were measured with an Instrom 1195 by 180° peeling joints and an extension speed of 10 mm/min. The width of the strips was 15 nm. The reported values per units of width, *P*, representing the mean of six measurements, are obtained with the following formula:[35]

$$P = 2F/W$$

where *F* is the applied force and *W* the width of the test aluminum strip.

For the adhesion tests for polypropylene-*g*-SA copolymers, the same experimental conditions are used, with $T = 180$ °C, as above described for PsBPP-*g*-SA.

Synthesis and Functionalization. *Synthesis of Poly[bis(4-sec-butylphenoxy)phosphazene], PsBPP.* The polymer was prepared by modification of a previously reported procedure;[9] all the manipulations concerning its preparation were carried out under a flux of dry nitrogen and using carefully dried solvents.

In a three-necked, round-bottomed flask, equipped with an efficient mechanical stirrer and with a condenser, 11.5 g (=9.91 × 10^{-2} mol) of poly(dichlorophosphazene) dissolved in 200 mL of dioxane was treated with a boiling solution (previously filtered via Shlenck technique) of *sec*-butylphenoxide obtained by reacting 59.70 g (=0.39 mol) of *sec*-butylphenol with a suspension of 19.03 g (=0.47 mol) of a sodium hydride 60% oil dispersion in 200 mL of dioxane. After this was refluxed overnight, 2 g of tetrabutylammonium bromide was added to improve the chlorine substitution in the poly(dichlorophosphazene),[8] and reflux was continued for a total of 48 h. After this time, the reaction suspension was allowed to cool to room temperature. The PsBPP, precipitated directly from the solvent, was collected by decantatation of the superior liquor. PsBPP so isolated was purified by dissolution in hot THF and precipitation in water (three times) in *n*-heptane (twice), and in methanol (twice); yield 25.0 g of polymer (73.52%). Elemental analysis (calculated values in parentheses): C, 69.93 (69.47); H, 7.74 (7.58); N, 4.13 (4.08); Cl, 0.3 (0).

The characterization data of this material are reported in Table I.

Functionalization Reaction of PsBPP with Maleic Anhydride (MA). In a 10-mL Pyrex tube, 50 mg of PsBPP was dissolved in 1 mL of xylene. This solution was treated with variable

---

(28) Potin, P.; De Jaeger, R. *Eur. Polym. J.* **1991**, *27*, 341.

(29) Minto, F.; Gleria, M.; Bortolus, P.; Daolio, S.; Facchin, B.; Pagura, C.; Bolognesi, A. *Eur. Polym. J.* **1989**, *25*, 49.

(30) Ide, F.; Hasegawa, A. *J. Appl. Polym. Sci.* **1974**, *18*, 963.

(31) See, as an example: De Vito, G.; Lanzetta, N.; Maglio, G.; Malinconico, M.; Musto, P.; Palumbo, R. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1325.

(32) Bratawidjaja, A. S.; Gitopadmoyo, I.; Watanabe, Y.; Hatakeyama, T. *J. Appl. Polym. Sci.* **1989**, *37*, 1141.

(33) Sneller, J. A. *Mod. Plast. Int.* **1985**, 42.

(34) Vogel, A. J. *A Textbook of Practical Organic Chemistry*; Longmans: London, 1970.

(35) Skeist, I. *Handbook of Adhesion*, 3rd ed.; Van Nostrand Reinhold: New York, 1980.

Table I[a]

PsBPP	PsBPP-*g*-SA
IR	
3050 (νCH aromatic);	3050 (νCH aromatic)
2970–2880 (νCH aliphatic);	2960 (νCH aliphatic)
	1865, 1785 (νC=O)
1610–1510 (νC–C of the aromatic ring)	1605–1500 (νC–C of the aromatic ring)
1250–1200 (asym ν of —P=N—)	1250–1200 (asym ν of —P=N—)
950 (νP–O–Ph).	950 (νP–O–Ph)
^{1}H NMR $(CDCl)_3$	
δ 6.84–6.72 (m) CH aromatic	δ 6.60–7.00 (m) CH aromatic
δ 2.34 (br) CH of the *sec*-butyl group	δ 2.35 C–H of the *sec*-butyl group
δ 1.38 (s, br) CH_2 of the ethyl moiety in the *sec*-butyl group	δ 1.39 (br), CH_2 of the ethyl ethyl moiety in the *sec*-butyl group
δ 1.02 (s, br), CH_3 of the *sec*-butyl group	δ 1.04 (br), CH_3 of the *sec*-butyl group
δ 0.80 (s, br), CH_3 of the ethyl moiety in the *sec*-butyl group	δ 0.70 (br), CH_3 of the ethyl moiety in the *sec*-butyl group
^{13}C NMR (CD_2Cl_2, {^{1}H})	
Aromatic Ring	
δ 149.93 C_1	δ 149.37–120.98 aromatic
δ 143.30 C_4	
δ 127.69 ($^1J_{CH}$ = 158.41 Hz, $C_{3,5}$)	
δ 121.48 ($^1J_{CH}$ = 162.99 Hz, $C_{2,6}$)	
sec-Butyl Group	
δ 41.30 ($^1J_{CH}$ = 125.30 Hz CH)	δ 40.67 (–CH– groups)
δ 31.61 ($^1J_{CH}$ = 126.13 Hz, CH_2 of the ethyl group)	δ 30.96 ($-CH_2-$ groups)
δ 21.91 ($^1J_{CH}$ = 124.92 Hz, CH_3 of the methyl group)	δ 21.44 ($-CH_3$ of the methyl group)
δ 12.44 ($^1J_{CH}$ = 124.38 Hz, CH_3 of the ethyl group)	δ 11.94 ($-CH_3$ of the ethyl group)
Succinic Anhydride Group	
	δ 171.73 ($-CH_2$–CO– carbonyl)
	δ 169.00 (–CH–CO– carbonyl)
	δ 42.13 (–CH–)
	δ 29.09 ($-CH_2-$)
^{31}P NMR ($CDCl_3$)	
δ –18.74 (s)	δ –18.98 (s, br)
Weight Average Molecular Weight (MW)	
2.3×10^6	9.4×10^5

[a] IR values in cm^{-1}; NMR values (δ) in ppm.

amounts of maleic anhydride (MA) and benzoyl peroxide (BP), at temperatures ranging between 95 and 139 °C, for different periods of time. Using these conditions, the reaction takes place by radical addition to the double bond present in the MA, followed by grafting of succinic anhydride (SA) onto the polyphosphazene matrix in an amount up to 7% w/w depending on the adopted experimental conditions.[32]

After the grafting reaction was completed, the functionalized polymer (PsBPP-*g*-SA) was recovered by precipitation in chilled methanol, quickly washed with two portions of fresh CH_3OH, and eventually dried in vacuum.

The characterization data of the functionalized PsBPP-g-SA are reported in Table I.

Although ^{1}H NMR spectra of the PsBPP and PsBPP-*g*-SA polymers reported in the table I are almost superimposable and are therefore not diagnostic for the grafting of SA groups onto the phosphazene polymer (the signals of the $-CH_2-$ protons of the free SA at 1.05 ppm are covered by signals at 1.02 ppm of the $-CH_3$ protons of the methyl group present in the PsBPP), IR and ^{13}C and ^{31}P NMR data unequivocally support the success of the grafting reaction of SA moieties onto the PsBPP matrix.

It is possible that during purification of PsBPP-*g*-SA by precipitation of the polymer in chilled methanol, a side reaction of SA groups with the solvent takes place, leading to a decrease of the anhydride content in the functionalized polymer. This reaction, however, although possible, is a negligible process under our experimental conditions as confirmed by the absence in the IR spectrum of the recovered PsBPP-*g*-SA polymer of peaks located at 1735 and 1710 cm^{-1} assigned to the vibrations of the $-COOCH_3$ ester and –COOH carboxylic acid groups,[36] respectively.

The IR vibrations at 1785 and 1865 cm^{-1} assigned to the anhydride groups in PsBPP-*g*-SA were used successively for the quantitative determination of the amount of the SA grafted onto the polyphosphazene matrix (vide infra).

Quantitative Determination of the Succinic Anhydride (*SA*) *Grafted onto PsBPP.* Quantitative determination of the SA grafted onto PsBPP under variable experimental conditions was carried by comparing the IR spectra of PsBPP-*g*-SA polymers with those of unmodified PsBPP/SA mixtures.

Accordingly, in a 10-mL Pyrex glass tube, 50 mg of PsBPP was dissolved in 2 mL of freshly distilled methylene chloride together with variable amounts of SA (from 0.1 to 10% w/w); 0.5 mL of this solution was successively evaporated on a NaCl window, and the residual solid analyzer by IR spectroscopy. The actual concentration of SA grafted onto the polyphosphazene matrix was determined by plotting the ratio between the band absorbance at 1785 cm^{-1} of the anhydride moiety and the band absorbance at 1605 cm^{-1}, attributed to the stretching of the aromatic ring of the phenoxy substituent of PsBPP taken as reference band (this could be possible because this band is unaffected both in position and in intensity by varying the amount of SA grafted onto PsBPP), vs the w/w percentage of SA used for each experiment.

The calibration plot obtained is reported in Figure 1.

Results and Discussion

The grafting functionalization reaction of preformed organic macromolecules (P) with maleic anhydride (MA) is a process widely investigated by several authors.[30,31,37] It is generally agreed[30] that the thermally induced breaking of the peroxide initiator R–R produces radicals which are able to abstract hydrogens from the polymer, producing macroradicals P$^\bullet$. These species can react successively with the MA double bond, thus inducing the formation of succinic anhydride radicals on the polymer (P-*g*-SA$^\bullet$) that eventually disappear by abstracting hydrogen from the

---

[36] Silverstein, R. M.; Bassler, C. G.; Morrill, T. C. *Spectrophotometric Identification of Organic Compounds*; Wiley: New York, 1974; p 86.

[37] Cimmino, S.; D'Orazio, L.; Greco, G.; Maglio, G.; Malinconico, M.; Mancarella, C.; Martuscelli, E.; Palumbo, R.; Ragosta, G. *Polym. Eng. Sci.* 1984, *24*, 48.

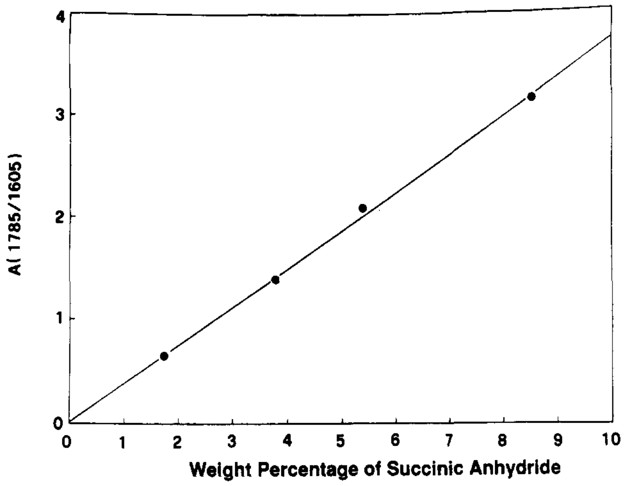
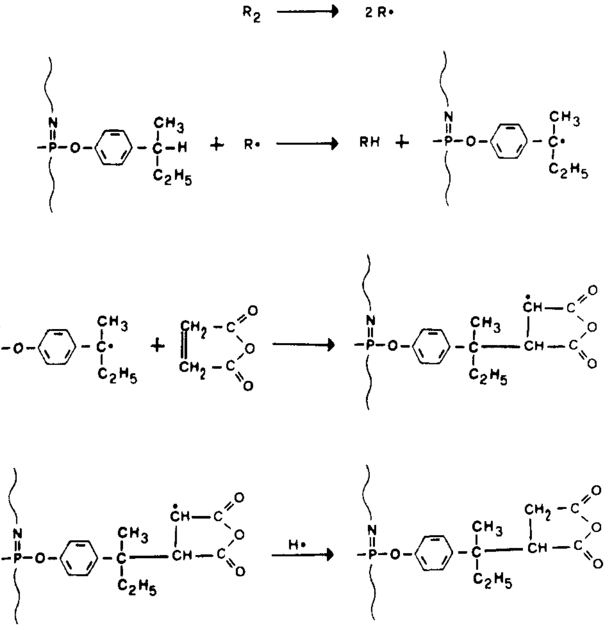


Figure 1. Calibration plot for determination of the percentage of succinic anhydride residues grafted onto the PsBPP matrix.

Scheme I



solvent, polymer or impurities, to form stable SA molecules randomly grafted onto the polymeric matrix (P-*g*-SA).

On the basis of this previous literature, we assume that the same reaction mechanism is also operative in the case of the functionalization reaction of PsBPP with MA, due to the presence of easily abstractable hydrogen atoms in this material. Moreover, we consider the tertiary hydrogen present in the *sec*-butylphenoxy side substituent of the polymer as a suitable functionalization site for PsBPP, given both the energy requirements for the C–H bond cleavage[38] (the splitting of the tertiary hydrogen in the PsBPP should take place much more easily than that of the secondary and the primary ones) and our previous findings on the photoreactivity[29] of PsBPP and poly[bis(4-isopropylphenoxy)phosphazene] (PIPP).[25,29]

Accordingly, the most reasonable reaction mechanism that can be put forward for the functionalization process of PsBPP with MA is represented in Scheme I.

As reported in Scheme I, benzoyl radicals are formed first by thermally induced breaking of the benzoyl peroxide initiator. Subsequently, phosphazene macroradicals, produced by hydrogen abstraction from the 4-*sec*-butylphenoxy residues by benzoyl radicals, react with MA, opening the ethylene double bond of this molecule and allowing SA groups to be grafted onto the polyphosphazene side substituents.

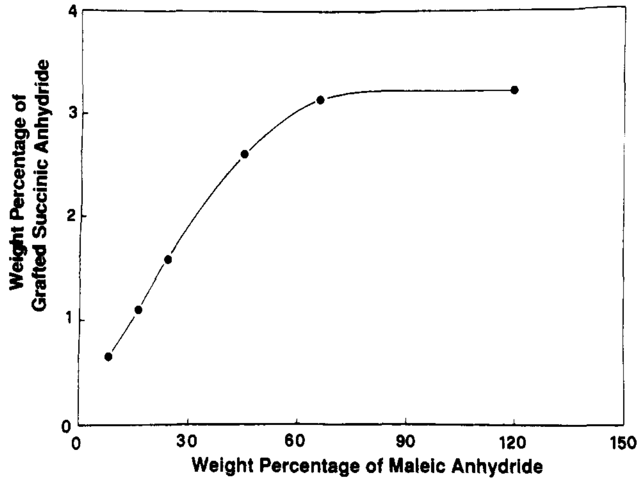
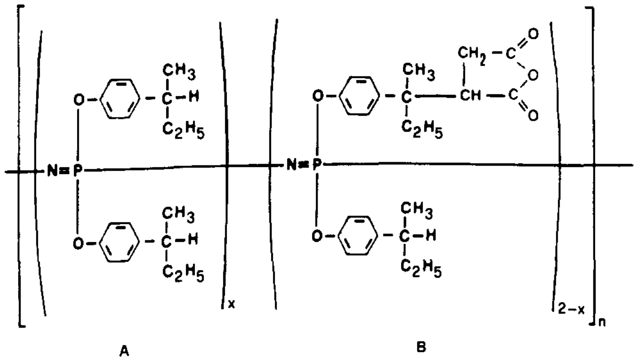


Figure 2. Influence of maleic anhydride concentration on the grafting reaction of SA onto PsBPP.

According to the IR and NMR spectroscopic data reported in Table I, the obtained modified polymer PsBPP-g-SA has the following structure:



in which homosubstituted monomeric units A and heterosubstituted phosphazene units B bearing SA moieties coexist in the same modified macromolecule.

In practice, the functionalization reaction of PsBPP with MA is carried out according to the procedure already described in the Experimental Section, also taking into consideration the influence on the overall grafting processes of several different experimental parameters.

First, the effect of the MA concentration on the grafting yield onto PsBPP was considered. Thus, experiments were performed in hot (139 °C) xylene solutions, treating 50 mg of PsBPP with variable amounts of MA, in the presence of 5 mg of benzoyl peroxide (BP) as the radical initiator, for 40 min. The polymer was recovered by precipitation in methanol and was then quickly washed and dried. The amount of SA actually grafted onto the polyphosphazene was determined by IR spectroscopy, according to the calibration plot reported in Figure 1. The corresponding data (see Figure 2) indicate that the percentage of grafted SA increases in the early steps of the process and reaches a plateau at 3% w/w for an excess of MA of roughly 60% w/w; after this point a further increase of MA in the reaction mixture does not influence any more the final content of SA grafted onto PsBPP.

The temperature effect was then examined: 50 mg of PsBPP dissolved in 1 mL of xylene, also containing 33 mg of MA and 5 mg of BP, was treated for 15 min at tem-

---

[38] *Handbook of Chemistry and Physics*; Weast, R. C., Selby, S. M., Eds.; CRC Press: Cleveland, OH, 1967; p F156.

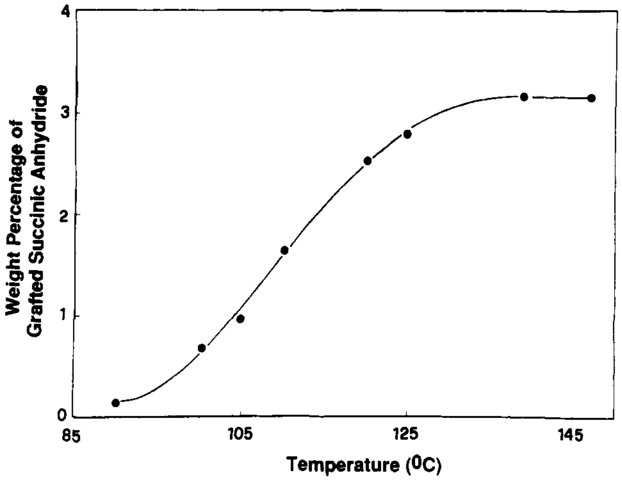


Figure 3. Influence of temperature on the grafting reaction of SA onto PsBPP.

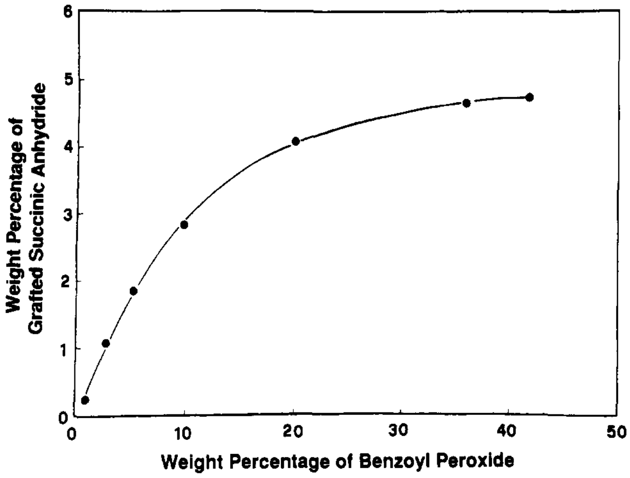


Figure 4. Influence of benzoyl peroxide concentration on the grafting reaction of SA onto PsBPP.

peratures varying between 95 and 139 °C. After precipitation and recovering, PsBPP-*g*-SA was analyzed by IR spectroscopy, and the percentage of SA grafted onto the phosphazene substrate was plotted vs the reaction temperature (see Figure 3). As can be seen from this picture, no grafting actually takes place below 90° C; if the temperature is increased from this value up to 139 °C, a steady increase of the percentage of grafted SA is observed until a plateau is reached at around 3% of this species inserted in the polyphosphazene matrix. This behavior may be ascribed to the lack of benzoyl peroxide breaking to produce radicals able to initiate the grafting process, which only starts to become significant at temperatures above 95–100 °C.[39]

The influence of benzoyl peroxide concentration on the grafting reaction of MA onto PsBPP was investigated by carrying out a series of experiments in Pyrex tubes containing 50 mg of PsBPP dissolved in 1 mL of xylene together with 33 mg of MA, at temperature of 125 °C, for 15 min, using different amounts of BP in each experiment. The corresponding results are reported in Figure 4. This picture shows that the amount of SA grafted onto PsBPP is strictly dependent on the percentage of BP used in the reaction and that roughly 5% of SA can be bound onto PsBPP at a BP concentration of 40% w/w, in comparison with that of the phosphazene polymer.

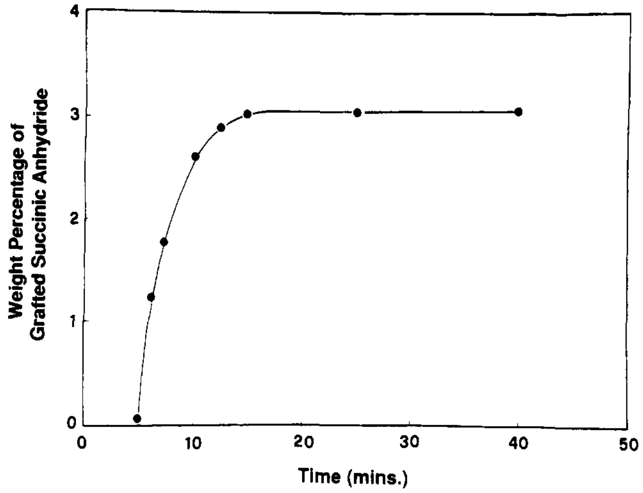


Figure 5. Influence of reaction time on the grafting reaction of SA onto PsBPP.

The last factor which was investigated concerning the reactivity of PsBPP with MA was reaction time. In this case, 50 mg of PsBPP dissolved in 1 mL of xylene together with 33 mg of MA and 5 mg of BP were heated at 139 °C for variable periods of time. The results found for the PsBPP-*g*-SA, recovered as described above, are reported in Figure 5, where it can be seen that, after an initial induction period (5 min), which is probably related to the time necessary for the Pyrex tube to equilibrate temperature with the oven, the grafting reaction starts steeply and reaches a plateau within 15 min. After this time, no further increase of the SA percentage grafted onto PsBPP could be observed.

From the above-mentioned results it can be concluded that all the investigated reaction parameters play a certain role in determining the final percentage of SA which is grafted onto PsBPP during the treatment of this polymer with MA. Moreover, from the analysis of the above reported data, it appears quite clearly that the optimization of the grafting reaction conditions is reached when the temperature is between 125 and 139 °C, the reaction time ranges around 15–20 min, benzoyl peroxide and MA percentages are kept roughly around 30–40% w/w in excess of the PsBPP polymer.

It should be pointed out that during the treatment of 50 mg of PsBPP dissolved in 1 mL of xylene with MA, in the presence of 5 mg of BP, at 125 °C, for 20 min, appreciable degradation of the polyphosphazene could be observed, as the weight average molecular weight (WM) of PsBPP-*g*-SA after the grafting process decreases to 9.4×10^5, starting from 2.3×10^6 of the pristine PsBPP.

It may be also observed that the grafting of SA moieties onto the polyphosphazene matrix modifies significantly the bulkiness of some side *sec*-butylphenoxy substituents in the PsBPP, which should result in an increase of the polyphosphazene chain rigidity. This fact is reflected by T_g value determinations carried out both on unmodified PsBPP and on several PsBPP-*g*-SA polymers at different percentages of SA functionalization. In fact, starting from the T_g value of −8.1 °C for the pure PsBPP (lit. −16 °C[9]), increasingly higher values of −7.6, −4.5, and 0 °C have been measured for PsBPP-*g*-SA polymers containing 1.31, 2.68, and 4.65% w/w, respectively, of grafted SA groups.

Adhesion Experiments. As reported in literature,[32,40] grafting MA onto polypropylene and ethylene–propylene

---

(39) Stannett, V.; Woodward, A. E.; Mesrobian, R. B. *J. Phys. Chem.* **1957**, *61*, 360.

(40) Schultz, J.; Lavielle, L.; Cave, A.; Comien, P. *J. Mater. Sci.* **1989**, *24*, 4363.

Table II

sample	P (N/m)	SA (% w/w)
1	73	0
2	444	0.05
3	567	0.1
4	654	0.3
5	2153	2.4
6[a]	3537	0.4

[a] This measurement has been obtained with a polypropylene sample containing 0.4% of SA residues, using the same experimental conditions adopted for PsBPP-*g*-SA copolymers.

copolymers influences not only the chemical reactivity of these materials but also the surface properties of the metal-polymer interfaces in the melt state.

For this reason, adhesion properties of PsBPP itself and PsBPP-*g*-SA polymers, containing variable amounts of grafted SA residues, were investigated on the surface of aluminum foils. The obtained results are reported in Table II. As can be seen from this table, adhesion strength increases with the increase of the SA content in the PsBPP-*g*-SA polymers, suggesting the presence of chemical reactions between melt-grafted PsBPP-*g*-SA and the aluminum surface.

According to the adhesion mechanism suggested for polyolefins grafted with MA,[40] the enhancement of the peel energy for PsBPP has to be attributed to chemical reactions occurring between the anhydride moieties in the melt polymers and the hydroxyl groups always present in the aluminum oxide layer covering the metal surface.[40-42]

It may be observed, moreover, that the highest adhesion strength for PsBPP-*g*-SA polymers was obtained when the SA content in this material was 2.4%; the obtained value of 2153 N/m is of the same order of magnitude as the value obtained for the PP-*g*-SA sample containing 0.4% grafted SA residues (3537 N/m in the reference experiment 6 in the Table II). This behavior has been ascribed to the very different bulk viscoelastic properties of PsBPP-*g*-SA rubber in comparison with the PP-*g*-SA, which possesses a pronounced crystallinity, probably due to the induction of a highly crystalline surface layer (e.g., transcrystalline).[42]

Acknowledgment. We are indebted to the "Progetto Finalizzato Chimica Fine e Secondaria II" of the Consiglio Nazionale delle Ricerche for financial support.

Registry No. Bp, 94-36-0; Al, 7429-90-5.

---

(41) Ulren, L.; Hjertberg, T. *J. Appl. Polym. Sci.* **1989**, *37*, 1269.
(42) Schonhorn, H. *Macromolecules* **1968**, *1*, 145.

Concentrated Emulsion Polymerization Pathway to Hydrophobic and Hydrophilic Microsponge Molecular Reservoirs

E. Ruckenstein* and L. Hong

Department of Chemical Engineering, State University of New York at Buffalo,
Buffalo, New York 14260

Received March 13, 1992. Revised Manuscript Received July 13, 1992

Porous particles of micrometer size have been prepared using the concentrated emulsion polymerization method. The dispersed phase with a volume fraction greater than 0.74, contained a monomer, or a polymer, a cross-linking agent, and inert liquids as porogens. The continuous phase consisted of an aqueous solution of a surfactant when the monomer of the dispersed phase was hydrophobic, and a surfactant solution in a hydrocarbon liquid when the dispersed phase was hydrophilic. Four kinds of porous materials have been achieved: (1) hydrophobic cross-linked (with divinylbenzene (DVB) as the cross-linking agent) polystyrene particles; (2) hydrophilic cross-linked polyacrylamide (with methylenebisacrylamide (MBAA) as the cross-linking agent) particles; (3) hydrophobic porous nutshells of cross-linked polystyrene surrounding a void filled with sparse poly(vinylbenzyl chloride) (poly (VBC)); (4) hydrophilic nutshells of cross-linked polyacrylamide encapsulating loosely entangled poly(ethylene oxide) (poly (EO)) coils. The nutshell structure was obtained by using a two-step procedure: First, a concentrated emulsion of oil in water (o/w) with a dispersed phase consisting of monomers (VBC and DVB) dissolved in a porogen was polymerized, or a concentrated emulsion of water in oil (w/o) in which the dispersed phase contained a polymer (poly(EO)) dissolved in water was prepared. In the second step, styrene/DVB was introduced into the o/w emulsion and an aqueous solution of acrylamide/MBAA into the w/o emulsion. The resulted systems were allowed to polymerize, thus generating polymer shells encapsulating either sparse poly(VBC) matrixes or loosely entangled poly(EO). The porous hydrophobic polymeric beads of the first kind have relatively small surface areas of 20-40 m^2/g, while those of the third kind have surface areas of about 300 m^2/g. The cross-linked particles of polyacrylamide of the second kind prepared with water as the porogen adsorb 68 mg of enzyme lipase per gram of polymer. The poly(VBC) encapsulated in the porous nutshell particles was functionalized with anchoring quaternary phosphonium cations. This functionalized substrate possesses a high adsorption capacity for cobalt carbonyl anions (2.78 mmol of Co/g of polymer) via ion pair formation as well as via physical adsorption.

Introduction

Porous polymer particles are used in many applications, such as chromatography, ion exchange, reactive polymer matrixes, and more recently in controlled release of drugs.[1] The synthesis of these macroreticular particles is, in general, based on the suspension polymerization of a dispersed phase that consists of a monomer, a cross-linking agent,

---

* To whom correspondence should be addressed.

(1) Eury, R.; Patel, R.; Longe, K.; Cheng, T.; Nacht, S. *Chemtech* **1992**, *Jan*, 42.