Synthesis and Characterization of Phosphorus-Containing Polystyrene

Oana Petreus,[1] Ecaterina Avram,[1] Gabriela Lisa,[2] Diana Serbezeanu[1]

[1]*"Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda. Alley, 700487 Iasi, Romania*
[2]*Technical University "Gh. Asachi," Faculty of Industrial Chemistry, B-dul D. Mangeron 71, Iasi 700050, Romania*

ABSTRACT: Chemical modification of a chloromethylated polystyrene (CMPSt) was performed by the reaction of the chlorometyl group with the P—H bond of 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide. A kinetic study on the phosphorylation reaction of CMPSt with different chlorine contents and/or different molecular weighs was reported. The obtained polymers bearing phosphorus containing cyclic bulky groups were characterized by analytical methods, FTIR and ^{1}H NMR spectroscopy. Their thermal behavior and flammability were also studied. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2084–2092, 2010

Key words: polystyrene; chemical modification; chloromethylated polystyrene; phosphorus bulky reactant

INTRODUCTION

The chemical modification of the reactive groups present on polymers is a useful way to prepare new polymers bearing specialized functional groups for various applications. Such a modification can be easily achieved by the reaction of different chemicals with a reactive pendant group, such as chloromethyl, present on the polymer.[1] The chloromethyl groups have a very high chemical activity, and can induce further organic reactions. Various functional groups can be introduced into the molecular chains of polystyrene by the transformation reaction of the chloromethyl groups.

Consequently, CMPSt appears as a precursor of many functional macromolecules, more precisely, when CMPSt is used as a starting material, various functional polymers can be synthesized through macromolecular reactions. For example, graft copolymers, dendritic copolymers, and high-branched star copolymers can be synthesized, with CMPSt as a macromolecular initiator of atom transfer radical polymerization (ATRP)[2–5]; ion exchange resins, chelate resins, and adsorption resin with special functional groups can be prepared[6–8]; catalysts and ligand supported on polymer used in organic synthesis can be produced,[9] functional microbeads of polymer can be produced by CMPSt post-crosslinking to be further used in the separation of biomacromolecules and in chromatography, as a stationary phase[10–12]; polymer surfactants and compatibilizers for polymer blends can be synthesized,[13] and so on. Obviously, CMPSt will have wide applications in many scientific and technical fields.

Incorporation of phosphorus compounds on chloromethylated copolymer styrene-divinylbenzene was used for the separation and recovery of palladium from different solutions.[14] The same copolymer was functionalized with alkyl-phosphonate groups and incorporated into meso-macroporous silica. The material was used as an active and selective catalyst in the epoxidation of cyclohexene with hydrogen peroxide.[15]

As known, polystyrene is one of the most flammable aromatic polymers. Incorporation of flame retardant additives in polystyrene affects its mechanic properties, chemical stability, and induces a rapid ageing the compositions. When the phosphorus atoms became part of the polymeric chain for improving the flame retardancy properties of the polystyrene, the material does not posses the desirable physical properties any more and, usually, the degree of polymerization is low. Flame retardant noncrosslinked polystyrene was synthesized from chloromethylated polystyrene and alkaline salt of dialkyl phosphates.[16] No information is available on the thermostability and flame retard properties of chlorometylated polystyrene chemically modified with aromatic phosphorus containing products.

In this study, chloromethylated polystyrenes with different substitution degrees and different molar weights were reacted with an aromatic phosphorus compound possessing a reactive P—H group. Kinetic data of this reaction were correlated with the substitution degree of the starting material, and with its

Correspondence to: O. Petreus (opetreus@yahoo.com).

molar weight. The new polystyrenes containing phosphorus in a side bulky structure were characterized by FTIR and ^{1}H NMR spectroscopy, to prove their structure. Glass transition and thermal stability were determined and compared with the initial chloromethylated polystyrene. The flammability properties were determined, too.

EXPERIMENTAL

Materials

Polystyrene (PSt) samples with a the number-average molecular weight of 1.70, 4.10, and 8.20 $\times$ 10^4 were prepared by suspension polymerization, on changing the monomer to initiator ratio. The subsequent chloromethylation reaction was carried out as previously described.[17] 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide from Chemos GmbH, Germany, was dried for 2 h at 170°C in vacuum before use.

Chloroform, methyl alcohol, N-methyl pyrolidone (NMP), and dimethyl acetamide (DMAc) were reagents at room temperature grade, used without further purification.

Measurements

Elemental analyses for phosphorus were performed by the molybdenum blue method[18]; the chlorine content was determined by the modified Schöninger method.[19]

FTIR spectra were recorded on a Vertex 7 Spectrometer with KBr pellets and ^{1}H NMR spectra, on a Bruker Avance DRX 400, by using a solution in CDCl$_3$.

To determine the kinetic constants and the reaction degrees, the following method was used: the amount of HCl evolved in time from the reaction between DOPO and CMPSt was capped and analytically measured, then correlated with the number of reacted functional groups. The reaction rate constants were determined according to Eq. (1):

$$\frac{1}{(a - x)} = kt \tag{1}$$

a = molar concentration of reactants (CMPSt + DOPO), x = concentration of reacted functional groups, t = time of the reaction (min), and k = rate constant.

The inherent viscosities (η_{inh}) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in a NMP solution, at 25°C, at a concentration of 0.5 g dL^{-1} (K 0.01049, No I).

Thermo gravimetric (TGA) and differential thermo gravimetric (DTG) analyses were performed under nitrogen flow (20 cm^3 min^{-1}) at a heating rate of 10°C min^{-1} from 25 to 700°C, with a Mettler Toledo model TGA/SDTA 851. The initial mass of the samples was of 3–5 mg. The initial decomposition temperature (IDT) is the temperature at which the sample achieves a 5% weight loss, the temperature of the 10% weight loss (T_{10}) being also recorded.

The glass transition temperature (T_g) of polymers was determined on a Mettler Differential Scanning Calorimeter DSC 12 E, at a heating rate of 10°C min^{-1}, under nitrogen. Heat flow cursive temperature scan from the second run were plotted and used for reporting the glass transition temperature. The mild-point of the inflection curve resulting from the typical second heating was assigned as the glass transition temperature of the respective polymers.

Flammability tests were performed using the modified Underwriters Labs. UL-94. Test specimens were considered sheets of glass fibber Z 6040 with sizes: 127 mm length, 12.7 mm width, and 0.4 mm thickness; these sheets were impregnated with 20 wt. pct. phosphorus-modified polystyrene. Polystyrene, chloromethylated polystyrene, and phosphorus-modified polystyrene were dissolved in chloroform and uniformly spread on the glass sheets, followed by drying at room temperature for 24 h and in a air oven at 120°C. Five test specimens of each material were treated for two 10-second ignitions by a 9.5 mm bunsen burner flame applied to the bottom of the vertically mounted sample. The oxygen index (LOI) was calculated using Davies and Horrocks[20] empiric equation and limited oxygen index (LOI) was determined using a Limiting Oxygen Index Chamber 340AJH0038:

$$OI = 0.032[P\%] + 0.187$$

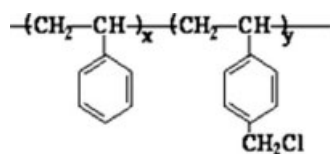### The chloromethylation reaction of polystyrene

The chloromethylation reaction of polystyrene (PSt) was performed by a described elsewhere.[21] The fraction of repetitive units was determined by accepting the statistical structure of the polymer (Scheme 1):

For this structure, the average molecular weight (M_m) can be calculated [Eq. (2)]:

$$M_m = xM_{St} + yM_{CMSt} \tag{2}$$

M_{St} = molecular weight of the styrene units; M_{CMSt} = molecular weight of chloromethylated styrene units.

For the determination of the functionalization degree (FD) of a polymer and statistical modeling of the functionalized repeating unit, it is necessary to determine an element E in the functional group. In this work, chlorine was determined in the initial

Scheme 1 Statistical structure of chloromethylated polystyrene.

polymer [Eq. (3)]:

$$Cl\% = \frac{yA_{Cl}}{M_m} \times 100 \qquad (3)$$

A_{Cl} = atomic mass of element Cl from the function group.

The fraction of functionalized styrene units can be calculated with Eq. (4), while the functionalization degree (FD) can be calculated using Eq. (5):

$$y = \frac{\%Cl \cdot M_{CMSt}}{100 \cdot A_{Cl} - Cl\%(M_{CMSt} - M_{St})} \qquad (4)$$

$$x = 1 - y$$

$$FD = \frac{y}{M_m} \qquad (5)$$

Three samples of chloromethylated polystyrene with different molecular weights and the same chlorine content, and two samples of chloromethylated polystyrene with the same molecular weight and different chlorine contents were selected for the synthesis of phosphorus-functionalized polystyrene.

Phosphorus-modified polystyrene

A CMPSt and DOPO mixture in 13% excess (the rates of components were calculated as a function of the substitution degree of CMPSt) was heated at 165–170°C under nitrogen for 6 h. After cooling, the resulted solid was dissolved in chloroform, precipitated in anhydrous methanol and dried under vacuum at 120°C for 48 h. For the lower molecular weight samples, purification can be performed by refluxing in hot toluene, dissolution in DMAc, and precipitation in methanol. The white powder is twice redissolved and precipitated, as above, for eliminating the excess DOPO. The characteristics of starting materials and of phosphorus-modified polystyrene (PPSt) are given in Table I.

The reaction of chloromethylated polystyrene and DOPO was carried out on the phosphorus-modified polystyrene according to Scheme 2.

The same method could be applied to calculate the functionalization degree of phosphorus-modified polystyrene. The phosphorus and chlorine content in the final product showed be also determined. The fraction of repetitive units was determined by

TABLE I
Characteristics of Chloromethylated Polystyrenes and of Phosphorus-Modified Polystyrenes

Sample[a]	Cl (%)	P (%)	FD[b]	M_m[c]	$\eta\%$[d]
17	13	–	0.46	126	
P 17	0.35	6.7	0.216	208	97
41	12.9	–	0.46	126	
P 41	0.4	6.8	0.219	214	98
82_1	12.7	–	0.45	126	
P 82_1	0.35	6.7	0.216	208	97
82_2	16.9	–	0.65	135.5	
P 82_2	0.6	8.2	0.260	227	93.7

[a] 17 is chloromethylated polystyrene with molecular weight 17,000; P 17 is phosphorus-modified sample 17; 41 is chloromethylated polystyrene with molecular weight 41,000; P 41 is phosphorus-modified sample 41; 82_1 is chloromethylated polystyrene with molecular weight 82,000 and FD = 0.45; P 82_1 is phosphorus-modified sample 82_1; 82_2 is chloromethylated polystyrene with molecular weight 82,000 and FD = 0.65; P 82_2 is phosphorus-modified sample 82_2.
[b] Molar substitution degree.
[c] Average molecular weight of the structural unit.
[d] Reaction yield.

accepting the new statistical structure of polymer PPSt (Scheme 2).

Where: x = fraction of styrene units; y = fraction of remaining units bearing chloromethyl groups; z = fraction of units bearing phosphorus pendant groups.

For this structure, the average molecular weight (M_{mP}) can be calculated [Eq. (6)]:
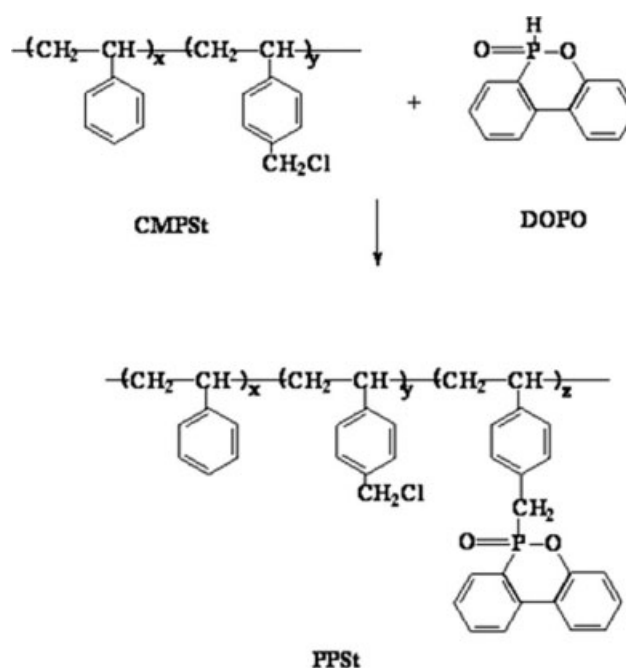
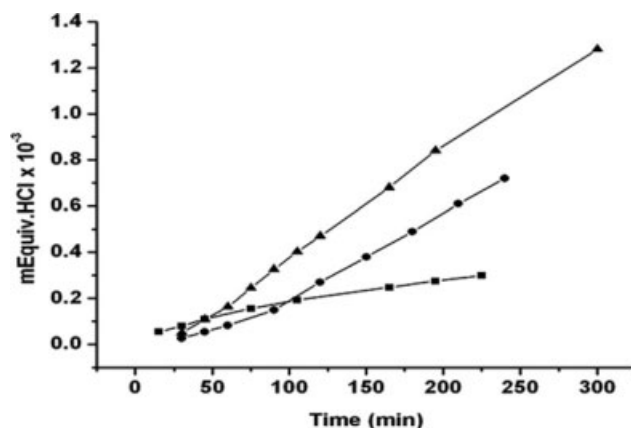**Scheme 2** The reaction of chloromethylated polystyrene and DOPO.

Figure 1 Evolution of HCl cursive time during the reaction of CMPSts (with different molecular weights and the same FD) with DOPO. (-■-) mol. weight = 17,000 and FD = 0.46 (-●-) mol. weight = 41,000 and FD = 0.46 (-▲-) mol. weight = 82,000 and FD = 0.46.

$$M_{mP} = xM_{St} + yM_{CMSt} + zM_{PPSt} \qquad (6)$$

$$Cl\% = \frac{yA_{Cl}}{M_{mP}} \times 100 \quad \text{and} \quad P\% = \frac{zA_P}{M_{mP}} \times 100$$

A_{Cl} = atomic mass of element Cl; A_P = atomic mass of element P.

The fraction of styrene units (x) remains; $y + z = (1 - x)$.

The degree of substitution with DOPO groups could be calculated from Eq. (7):

$$y = \frac{Cl\%.M_{mP}}{A_{Cl} \times 100} \quad \text{and} \quad z = \frac{P\%.M_{mP}}{A_P \times 100} \qquad (7)$$

$$(y + z) \text{being known} = (1 - x) \qquad (8)$$

M_{mP} could be calculated from eqs. (7) and (8). The fraction of remaining units, bearing chloromethyl groups: $y = 1 - x - z$ and the functionalization degree of the final product can be calculated using Eq. (9):

$$F_{PD} = \frac{z}{M_{mP}} (Mmol/g) \qquad (9)$$

The yield of the reaction between CMPSt and DOPO was calculated using Eq. (10).

$$\eta = \frac{z}{y + z} \times 100 \text{ (molar percent)} \qquad (10)$$

RESULTS AND DISCUSSION

Synthesis

Phosphorus-modified polystyrene was prepared by the reaction of chloromethylated polystyrene with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (Scheme 2). The substitution of chlorine with the bulky cyclic phosphorus compound was carried out at elevated temperature, using a large excess of phosphorus reactant. The reactive P—H group interacts with the —CH$_2$Cl group of chloromethylated polystyrene. The occurrence of HCl released from the reaction proved the substitution, and could also offer kinetic data on the process. HCl was capped and analytically measured cursive time, using CMPSt with different molecular weights and the same substitution degree. The data presented in Figure 1 suggest that a high content of functional chloromethylated groups hindered the reaction with the bulky phosphorus reactant.

If the same number of functional groups is distributed to a chain with higher molecular weight, the reaction rate is gradually enhanced.

If the reaction involves two samples of chloromethylated polystyrene with the same molecular weight and different substitution degrees (Fig. 2), the aspect of the evolution HCl curves will be different.

A higher content of chloromethylated groups seems to enhance the reaction rate with the phosphorus reactant for CMPSt with similar molecular weights, which contradicts the date presented in Figure 1. However, it is known[20] that chloromethylated polystyrene with high molecular weight and a higher substitution degree has a larger polydispersity. Consequently, in the case of curve P 82$_2$, it is possible to have a small density of the reactive chloromethyl groups on each chain segment contained in a large polydisperse mass.

Table II presents the reaction rate constants determined according to Eq. (1).
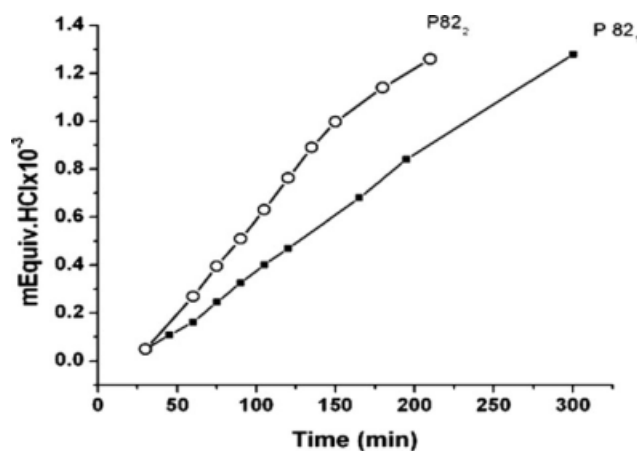

Figure 2 Evolution of HCl cursive time of the reaction of CMPSt (with the same molecular weight and the different FDs) with DOPO (-■-) mol. weight = 82,000 and FD = 0.216; (-○-) mol. weight = 82,000 and FD = 0.260.

TABLE II
Reaction Rate Constants for Phosphorus-Modified Polystyrenes

Sample	FD	k (L mol^{-1} min^{-1} 10^{-3})
P 17	0.216	1.15
P 41	0.219	3.38
P 82$_1$	0.216	4.65
P 82$_2$	0.260	7.02

Chemical structure and general characterization

The structure of phosphorus-modified polystyrene was identified by FTIR and ^{1}H NMR spectroscopy. Figure 3(a) presents the FTIR spectra of phosphorus-modified polystyrene P 41 versus the phosphorus reactant DOPO, over the 2000–4000 cm^{-1} range. The figure also evidences the disappearance of the absorption band for P—H at 2436 cm^{-1} for phosphorus-modified polystyrene spectrum (P 41). Figure 3(b) plots the FTIR spectra of P 41 the comparatively with **41** over the 1700–600 cm^{-1}. Some difficulties in their correct estimation were related to the superposition of absorption bands over the range 1000–1300 cm^{-1}. However it is evident that the absorption bands for C—Cl bond at 691 and 700 cm^{-1} were replaced by a strong absorption band for aliphatic-phosphorus group, placed at 925 cm^{-1}. The absorption band from the 1266 cm^{-1} range associated to —CH$_2$Cl in CMPSt was split in three bands in the P 41 spectrum, one of these bands belonging to P=O absorption at 1250 cm^{-1}. A strong absorption band at 750 cm^{-1} is attributed to the CH$_2$—P vibration [Fig. 3(a,b)].

Furthermore, substitution of chlorine from the —CH$_2$Cl group of the chloromethylated polystyrene with DOPO was evidenced by ^{1}H NMR (Fig. 4).

The characteristic peaks associated to the protons of the —CH$_2$Cl group situated at 4.56 ppm in the CMPSt spectrum disappeared in the P 41 one. The characteristic peak associated to the protons of the —CH$_2$—DOPO group was moved to 2.7–3.2 ppm. The peak associated to the aromatic protons (a) situated at 7.07–7.12 ppm could be repositioned while those associated to the aromatic protons (b) situated at 6.52–6.53 ppm were moved to 6.49–6.8 ppm. A large number of peaks associated to the aromatic protons, and belonging to the DOPO structure, was identified between 7.35–8.21 ppm. The large multiplet associated to the CH—CH$_2$ protons was shifted from 1.48–1.51 ppm in CMPSt to 0.85–2.2 ppm in P 41.

Phosphorus-modified polystyrene was soluble in the same polar solvents as CMPSt (NMP, DMAc, DMF, chloroform, dioxane) (Table III), solubility decreases with the increase of the substitution degree.

The inherent viscosity of phosphorus-modified polystyrene appeared over the 0.19–0.34 dL g^{-1} range (Table IV). The values for chloromethylated polystyrenes with the same substitution degree and different molar weights enhanced with molar weight. When the substitution degree is higher, at the same molar weight, a decrease in inherent viscosity could be observed. Inherent viscosity for phosphorus-modified polystyrene, is either similar or enhanced for different molecular weights. An exception is represented by sample P 82$_2$, probably due to its larger polydispersity.

Thermal properties

The glass transition temperatures (T_g) of DOPO-modified polystyrene, evaluated from the DSC curves, compared with CMPSt, and the starting polystyrene were presented in Table V. DSC measurements showed no evidence of either crystallization or melting either the polystyrene or the modified one, which is a proof of an amorphous morphology.

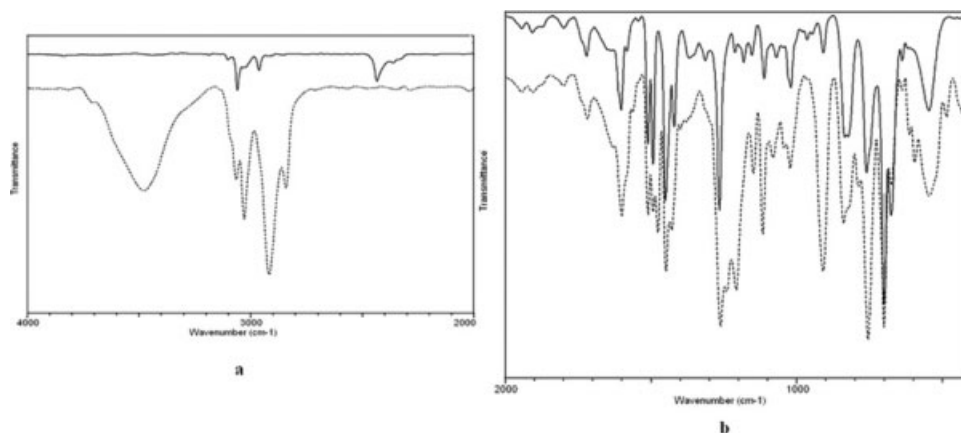**Figure 3** (a) FTIR spectra of phosphorus-modified polystyrene P 41(…) versus the phosphorus reactant DOPO(—), over the 2000–4000 cm^{-1} range. (b) FTIR spectra of 41(—) versus phosphorus-modified polystyrene P 41(…) over the 400–2000 cm^{-1} range.
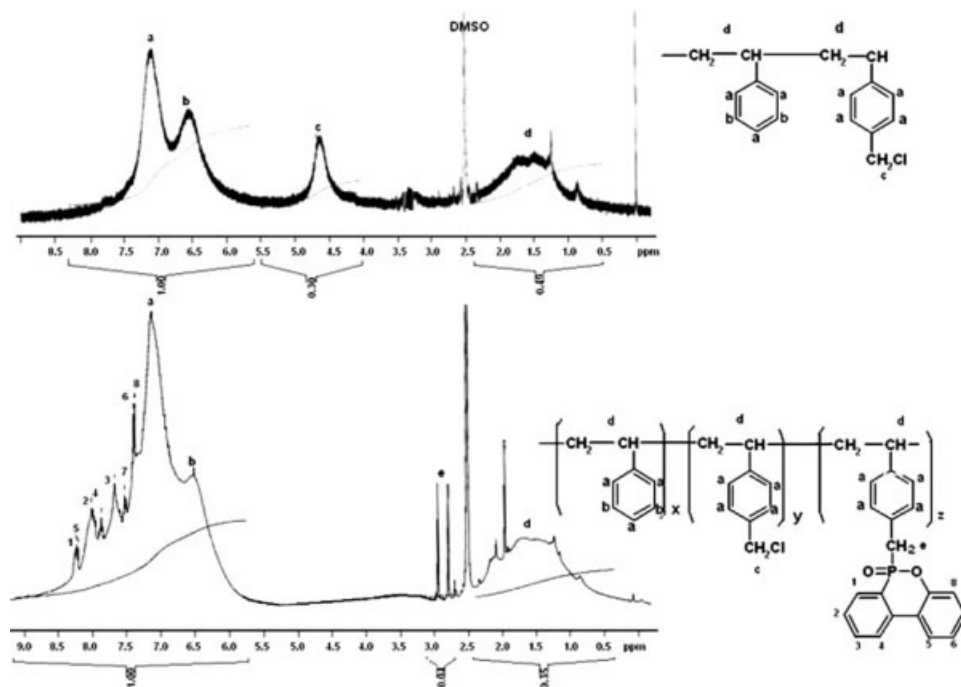
Figure 4 ^{1}H NMR spectra for chloromethylated polystyrene and phosphorus-modified (in DMSO-d_6).

When polystyrene was chloromethylated, an increase of T_g could be observed; also a higher increase of T_g chlorine substitution by a bulky cyclic radical produces. The increase is higher for higher substituted DOPO polystyrene. At the same time, phosphorus-modified polystyrene exhibited good solubility and higher T_g. This indicated that the DOPO bulky cyclic group produced a decrease in the interchain attraction existing in the initial CMPSt. Also skeletal rigidity this group imparts.

The thermal stability of polymers was evaluated by dynamic thermogravimetric analysis in nitrogen, at a heating rate of $10°C$ min^{-1}. Thermogravimetric analysis is widely applied for evaluating the thermal stability of polymers, as it requires only a small sample and only a few hours work. Figure 5 plot the TG and differential weight loss DTG curves of the samples, at a heating rate of $10°C$ min^{-1}.

The most important thermogravimetric characteristics of the polymers, obtained from the thermogram, are listed in Table VI.

All samples of phosphorus-modified polystyrene exhibited good thermal stability, and no weight loss up $280°C$. The mass loss is 69–87%. The rate of the decomposition for 82 P was relatively faster in steps I and II, becoming lower at finish. It is interesting that the $M_{residue}$ is much higher for chloromethylated samples than for phosphorus containing ones. When molecular weight of polymers enhanced, the differences between phosphorus-modified samples and parent ones decreased, being near equal to 82–82P pairs. Using as thermal stability criteria, the onset temperature of polymer decomposition and the thermal stability series was established as:

$$17 < 41 < 82$$
$$P\ 82_1 < P\ 41 < P\ 17$$

The surveys were extended to the kinetic processing of the thermogravimetric data. The Freemann-Caroll[22] method based on Eq. (11), led to the kinetic

TABLE III
Solubility of CMPSt and the Phosphorus-Modified Polystyrenes with Different Substitution Degrees

Polymer	NMP	DMAc	DMF	CHCl$_3$	Dioxane	Acetone	Methyl alcohol	Toluene
CMPSt	+	+	+	+	+	−	−	−
P 17	+	+	+	+	+	−	−	+
P 41	+	+	+	+	+	−	−	±
P 82$_1$	+	+	+	+	+	−	−	−
P 82$_2$	±	+	+	+	±	−	−	−

NMP, N-methylpyrrolidone; DMAc, dimethylacetamide; DMF, dimethylformamide; +, soluble; ±, partially soluble; −, insoluble.

TABLE IV
Inherent Viscosity for CMPSt and Related DOPO-Modified Polystyrene

Sample	17	41	82_1	82_2
FD	0.46	0.46	0.46	0.65
η_{inh} (dL g^{-1})	0.19	0.24	0.31	0.27
Sample	P 17	P 41	P 82_1	P 82_2
FD	0.216	0.219	0.216	0.260
η_{inh} (dL g^{-1})	0.19	0.40	0.34	0.24

characteristics shown in Table VII:

$$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)} = n - \frac{E_a}{R} \times \frac{\Delta\left(\frac{1}{T}\right)}{\Delta \ln(1-\alpha)} \quad (11)$$

By plotting the graph of $\Delta \ln (d\alpha/dT)/\Delta \ln (1 - \alpha)$ as a function of $\Delta (1/T)/\Delta \ln (1 - \alpha)$ from the line slope, the activation energy E can be calculated; also, from origin interception, the reaction order n may be obtained. The pre-exponential factor is computed with Eq. (12):

$$\frac{d\alpha}{dT} = \frac{1}{a} A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (12)$$

The fractional values of the reaction order can be explained by a possible radical mechanism of the thermal degradation of polymers.

Flammability properties

The results of the flammability test are given in Table VIII.

TABLE V
Glass Transition Temperatures (T_g) of DOPO-Modified Polystyrene, Evaluated from the DSC Curves, versus CMPSt and Initial Polystyrene

Sample	Average molecular weight of structural unit	Cl (%)	P (%)	T_g (°C)
Polystyrene	104[a]	0	0	92
	104[b]	0	0	96
	104[c]	0	0	96
CMPSt				
17	126	13	0	134
41	126	12.99	0	152
82_1	126	12.7	0	158
Phosphorus-modified polystyrene				
P 17	208	0.35	6.7	154
P 41	214	0.40	6.8	175
P 82_1	216	0.35	6.7	174

[a] Polystyrene with molecular weight 17,000.
[b] Polystyrene with molecular weight 41,000.
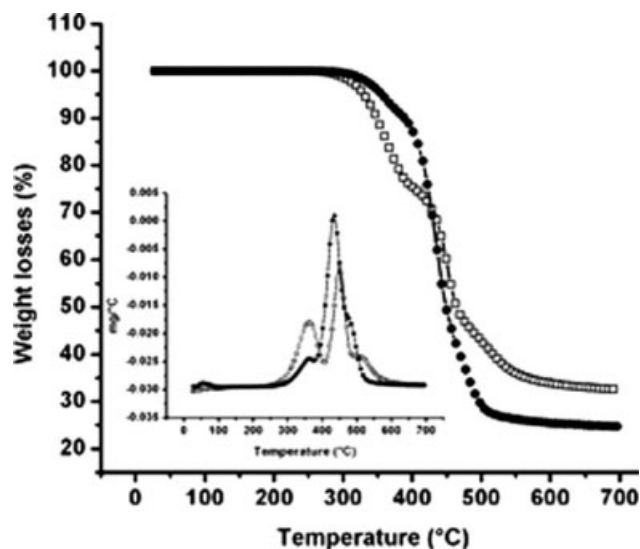[c] Polystyrene with molecular weight 82,000.

Figure 5 TG and DTG curves of samples 82_1 (-□-) and **P** 82_1(-●-) at a heating rate of 10°C min^{-1}.

PSt and CMPSt samples entire burn, while PSt-DOPO one presents self-extinguishing behavior. Both CMPSt and PSt-DOPO samples produce no dripping flammable particles. Oxygen index for CMPSt could be not calculated using empiric equation of Horrocks but experimental LOI value showed a little enhanced value in comparison with PSt. The highest value is obtained for DOPO-modified sample. A good correspondence was obtained between calculated and experimental values for oxygen index. PSt-DOPO sample performs a $V - 0$ behavior using Underwriters Labs. UL-94 test.

Underivatized polystyrene rapidly burns, producing some burning droplets and very small residue; the chlorometylated polystyrene behavior was similar, only the burning residue was slightly enhanced. Phosphorus-modified polystyrene shows an excellent flame resistance and an intumescent and significant char structure, the combusted zone being reduced (Fig. 6). The enhanced carbonaceous char resulted after burning the PSt-DOPO sample could be related to the role of phosphorus in its thermo-oxidative behavior.

CONCLUSIONS

Chemical modification of chloromethylated polystyrene was performed by reaction of the chloromethyl group with the P—H bond of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide. A kinetic study on the phosphorylation of CMPSt with different chlorine contents reveals that a lower content of chloromethylated groups accelerates the reaction, for samples with the same molecular weight. Analytical methods, FTIR and NMR spectra support the structure of the new polymers bearing phosphorus

TABLE VI
Thermogravimetric Characteristics of the Polymers

Sample	Stage of thermal degradation	T_{Onset} (°C)[a]	T_{Peak} (°C)[b]	T_{Endset} (°C)[c]	W (%)[d]	M_{Resid} (%)[e]
17	I	217	232	247	7.00	28.35
	II	323	356	385	6.52	
	III	418	447	461	36.99	
	IV	462	522	553	21.24	
17P	I	355	431	513	87.71	13.29
	II	–	–	–	–	
	III	–	–	–	–	
41	I	230	244	315	4.01	27.23
	II	315	349	373	11.93	
	III	422	446	461	37.77	
	IV	461	520	549	19.06	
41P	I	289	312	325	2.37	18.01
	II	383	435	455	64.63	
	III	455	491	513	14.99	
	IV	–	–	–	–	
82	I	267	323	351	12.73	24.64
	II	416	442	463	45.68	
	III	463	525	551	16.95	
	IV	–	–	–	–	
82P	I	323	370	407	10.74	24.21
	II	407	434	452	44.85	
	III	452	480	503	20.20	
	IV	–	–	–	–	

[a] The onset temperatures of polymer decomposition.
[b] Thermal degradation peak temperatures of samples decomposition.
[c] Thermal degradation end set temperature in every stage.
[d] Mass loss in every stage.
[e] Weight loss of the samples in the end of a decomposition.

TABLE VII
Kinetic Characteristics of the Samples

Sample	Stage of thermal degradation	$\ln A$[a]	E_a[b] (KJ/mol)	n[c]
17	I	16.28 ± 3.82	84.90 ± 15.54	2.40 ± 0.180
	II	33.54 ± 0.46	48.87 ± 2.22	0.42 ± 0.003
	III	80.29 ± 0.55	505.24 ± 3.20	1.72 ± 0.014
	IV	14.15 ± 0.43	128.39 ± 2.77	0.91 ± 0.016
17 P	I	31.56 ± 0.18	212.33 ± 0.98	1.09 ± 0.008
41	I	9.35 ± 0.18	79.99 ± 0.90	0.82 ± 0.016
	II	64.33 ± 0.56	409.71 ± 3.24	1.37 ± 0.016
	III	4.21 ± 0.49	65.01 ± 3.06	0.43 ± 0.021
41 P	I	28.33 ± 2.36	161.92 ± 11.22	1.58 ± 0.097
	II	34.30 ± 0.28	229.71 ± 1.56	0.76 ± 0.010
	III	21.88 ± 0.71	169.65 ± 4.39	1.03 ± 0.021
82	I	20.71 ± 0.18	136.09 ± 0.88	1.41 ± 0.012
	II	55.17 ± 0.54	358.48 ± 3.14	1.22 ± 0.016
	III	1.40 ± 0.75	44.87 ± 4.83	0.30 ± 0.002
82 P	I	21.63 ± 0.57	141.31 ± 2.85	1.38 ± 0.035
	II	43.55 ± 0.25	282.77 ± 1.42	1.14 ± 0.007
	III	27.65 ± 0.69	202.52 ± 4.25	1.24 ± 0.019

[a] Pre-exponential factor.
[b] Apparent activation energy.
[c] Reaction order.

TABLE VIII
Flammability Test Determinations

Sample	Weight (%)	Weight loss (%)	Burning residue (%)	Incandescent burning time (s)	Self extinguishing time (sec.)	Dripping	Oxygen index a	Oxygen index b	Test UL-94
PSt	20	99.6	0.4	>10	>25	Yes	18	19	−
CMPSt	20	96.7	3.3	>10	>25	No	−	26	−
PSt-DOPO	20	74.9	25.1	3	5	No	40	41.8	$V-0$

[a] Oxygen index calculated by Horrocks and Davies equations.
[b] Oxygen index experimental determined using a Limiting Oxygen Index Chamber 340AJH0038.

containing cyclic bulky groups. The thermal stability of such phosphorus-containing polystyrenes is higher than that of the chloromethylated parent polystyrenes. Phosphorus-modified polystyrene shows excellent flame resistance and an intumescent and significant char structure, the combusted zone being reduced.
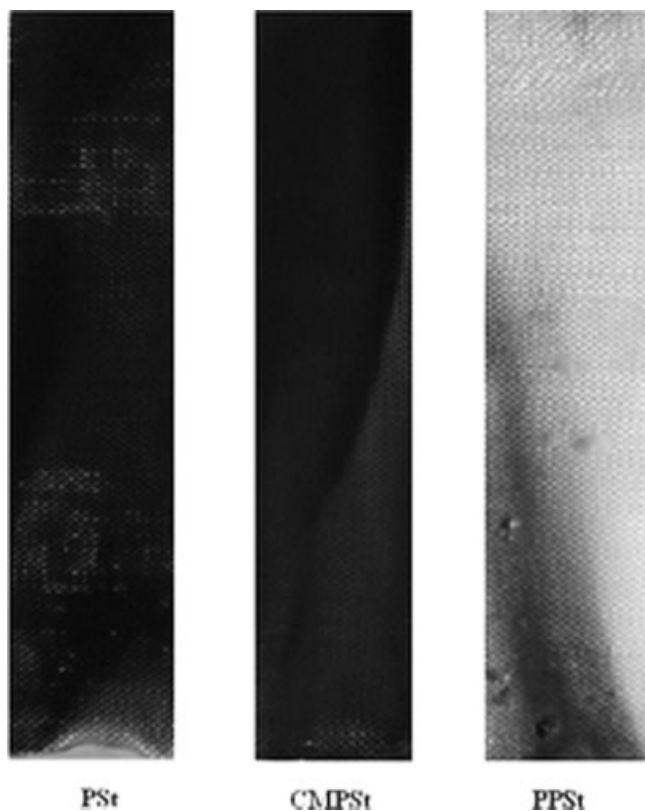

Figure 6 Effect of the flame contact on phosphorus-modified polystyrene, PPSt, CMPSt, and unmodified PSt.

References

1. Wu, C. S.; Liu, Y. L.; Chiu, Y. S. J Appl Polym Sci 2002, 85, 2254.
2. Stoeckel, N.; Wieland, P. C.; Nuyken, O. Polym Bull 2002, 49, 243.
3. Liu, B.; Hu, C. Chin J Acta Polym Sin 2002, 1, 47.
4. Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. Macromolecules 1996, 29, 1079.
5. Weimer, M. W.; Fréchet, M. J.; Gitsov, I. J Polym Sci Part A: Polym Chem 1998, 36, 955.
6. Hafez, M. A. H.; Kenawy, I. M. M.; Akl, M. A.; Lashein, R. R. Talanta 2001, 53, 749.
7. Druta, I.; Avram, E.; Cozan, V. Eur Polym J 2000, 36, 221.
8. Ji, N. C.; Qui, R. J.; Wang, C. H.; Sun, C. M.; Tang, Q. H. Chinese Chem Lett 2005, 16, 1193.
9. Gao, B.; Liu, Q.; Jiang, L. Chem Eng Process 2008, 47, 852.
10. Masuda, T.; Nishimura, Y.; Tonegawa, M.; Kitahara, K.; Arai, S.; Yamashita, J.; Takai, N. J Chromatogr A 1999, 845, 401.
11. Theodorakis, M. C.; Whitlock, T. W.; Tran, K. J Nucl Med 1982, 23, 693.
12. Unsal, E.; Bahar, T.; Tuncel, M.; Tuncel, A. J Chromatogr A 2000, 898, 167.
13. Fu, H. K.; Huang, C. F.; Huang, J. M.; Chang, F. C. Polymer 2008, 49, 1305.
14. Marques, G.; Bourdelande, J. L.; Valiente, M. React Funct Polym 1999, 41, 77.
15. Popa, A.; Parvulescu, V.; Tablet, C.; Ilia, G.; Iliescu, S.; Pascariu, A. Polym Bull 20008, 60, 149.
16. Mango, L. A., III. U.S. Pat. 3,993,635 (2004).
17. Avram, E.; Luca, C.; Petrovan, S.; Mihailescu, C. Polym Plast Technol Eng 1996, 35, 757.
18. Merz, W. Microchim Acta 1959, 47, 456.
19. Haslan, J.; Hamilton, B.; Squirell, D. C. M. Annalyst 1960, 85, 556.
20. Davies, D.; Horrocks, A. R. J Appl Polym Sci 1986, 31, 1655.
21. Avram, E. Polym-Plast Technol Eng 2001, 40, 275.
22. Freeman, E. S.; Carroll, B. J Phys Chem 1958, 62, 314.