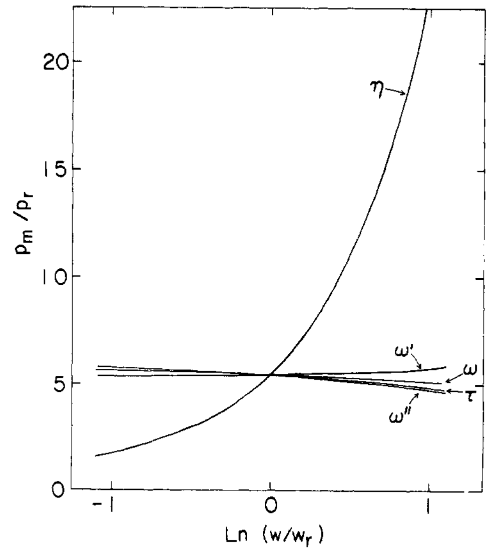

Figure 3. Values of p_m/p_r when the statistical weight denoted by w is varied about its reference value w_r. The assignment of w is shown for each curve.

should generally be greater than one for monosubstituted vinyl polymers.

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Organophosphazenes. 19. Copolymerization of 2-(α-Ethoxyvinyl)pentafluorocyclotriphosphazene with Styrene and Methyl Methacrylate[1]

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ABSTRACT: The novel phosphazene, 2-(α-ethoxyvinyl)pentafluorocyclotriphosphazene ($N_3P_3F_5C(OC_2H_5)=CH_2$) undergoes radical copolymerization with styrene and methyl methacrylate. The styrene system was examined in detail, with flame retardant copolymers having up to 43.7% phosphazene content being obtained. Reactivity ratios for the styrene–(α-ethoxyvinyl)phosphazene copolymerization have been calculated by several methods. An examination of the Alfrey–Price parameters for the phosphazene indicates that the major perturbation of the olefinic center is through the σ-electron-withdrawing effect of the phosphazene. The copolymer molecular weights decrease with increasing phosphazene content. The thermal decomposition of the copolymers is a two-step process, with the phosphazene being involved in the first step.

Introduction

Recent work in our laboratories has been devoted to the synthesis and reactions of organofunctional phosphazenes.[2] Of particular interest is the preparation of polymeric systems derived from organofunctional phosphazene monomers.[2-4] We originally demonstrated the feasibility of such an approach by reporting the copolymerization of 2-(α-methylvinyl)pentafluorocyclotriphosphazene, $N_3P_3F_5C(CH_3)_3=CH_2$, with styrene and vinyl benzene chloride.[3] These copolymers met our initial criteria of being hybrid organic–inorganic polymers, exhibiting significant flame retardant behavior[3] and having a functionalized surface due to the presence of the halophosphazene.[4] There are, however, problems with the inorganic monomer that are related to the polarity induced in the olefin by the highly electron-withdrawing[5-7] phosphazene substituent. The olefin polarity causes difficulties in the preparation of the monomer[8,9] and favors termination in copolymerization reactions.[3] We have recently reported the preparation of a new alkenylphosphazene monomer system derived from vinyl ethers in which it was proposed that the electron-donor effect of the alkoxy group toward the olefin would counterbalance the electron-withdrawing effect of the phosphazene.[9,10] This expectation was realized in the

Table I
Composition, Yield, and Molecular Weight Data[a] for Styrene (II)–(α-Ethoxyvinyl)pentafluorocyclotriphosphazene (I) Copolymers

run	feed ratio (I/II)	product ratio[b] (I/II)	reactn time, h	conversion, wt %	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
1	7.22	24.22	2	11.4	10.6 36.1[c]	70.7	6.67
2	5.78	20.64	2	12.0	9.8 31.0[c]	55.0	5.63
3	4.82	15.69	2	9.4	10.0	71.2	7.15
4	3.85	13.64	2	8.0	8.7	33.4	3.83
5	2.89	9.11	2	7.5	6.4	56.1	8.79
6	0.99	3.62	4	1.8			
7	2.94	5.78	18	61.3	6.9	15.0	2.18
8	2.02	4.20	18	55.4	3.2	7.8	2.48
9	2.00	3.94	18	52.7	2.3	6.6	2.91
10	1.00	2.80	18	35.0	1.6 5.9[d]	4.2	2.55
11	0.80	2.06	18	22.4	2.4	3.3	1.36
12	0.41	1.30	18	18.0	3.8	6.5	1.74
13	0.25		18	0.0			

[a] Molecular weights measured by gel permeation chromatography, except where indicated. [b] As determined from weight percent nitrogen.[3] [c] Membrane osmometry. [d] Vapor pressure osmometry.

synthesis of the monomer. This paper reports the copolymerization behavior of the 2-(α-ethoxyvinyl)pentafluorocyclotriphosphazene, $N_3P_3F_5C(OC_2H_5){=}CH_2$, monomer.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Ethyl Corp.) was converted to hexafluorocyclotriphosphazene,[11] which in turn was converted to (α-ethoxyvinyl)pentafluorocyclotriphosphazene[10] by previously reported procedures. Styrene (Aldrich) was dried over P_2O_5, distilled, and stored in a sealed, dark bottle under nitrogen at 0 °C. Prior to use, a small amount of styrene was added to methanol. If the solution remained clear, it was assumed that no spontaneous polymerization had occurred. Methyl methacrylate (Aldrich) was purified in a manner identical with that used for styrene. Azobis(isobutyronitrile), AIBN, (Aldrich) was recrystallized from ethanol/water. All other reagents and solvents were obtained from standard sources and used as received.

Measurements. Infrared spectra were obtained as KBr pellets with a Nicolet 6000 FT-IR spectrophotometer. Gel permeation chromatography was performed on a Waters AVC 202 high-pressure liquid chromatograph equipped with Waters 10^3 Å and 10^4 Å Microstyragel columns with toluene as the eluting solvent. The columns were calibrated with polystyrene standards (Waters). Thermal analysis were recorded on a Du Pont 900/950 thermal analyzer with the sample in He flow atmosphere and a 10 °C/min heating rate. Membrane osmometric data were obtained on a Wescan Model 230 recording membrane osmometer with toluene as the solvent. Data at four concentrations (1.02–3.36 g/L) were extrapolated to infinite dilution. Vapor pressure osmometry was performed by Schwartzkopf Microanalytical Laboratory. Elemental analyses were performed by Integral Microanalytical Laboratories. Reactivity ratios were calculated with both linear (Fineman–Ross[12] and Kelen–Tüdös[13]) methods with least-squares best fits of the data and the Mortimer–Tidwell nonlinear least-squares approach.[14]

Copolymerization of (α-Ethoxyvinyl)pentafluorocyclotriphosphazene and Styrene. Styrene and freshly distilled (25–30 °C; 0.02 mmHg) $N_3P_3F_5C(OC_2H_5){=}CH_2$ in various mole ratios were placed in a thick-walled reaction tube along with 2% AIBN. The reaction tube was sealed with a septum and flushed with nitrogen for 15 min through an exit needle. The tube was then placed in a constant-temperature bath (57 ± 1 °C) for 18 h. Several polymerizations to be used in reactivity ratio calculations were run limiting the percent conversion. The polymerization times for these reactions were thus decreased to between 2 and 4 h. At the end of this time period, the reaction was halted by opening the reaction vessel and adding 5–10 mL of methylene chloride. The solution was filtered to remove any insoluble material and then added dropwise to a stirred solution of 250 mL of methanol. The copolymer precipitates as a white powdery product. After filtration, the polymer was dissolved in methylene chloride, reprecipitated, and dried in vacuo. The composition yield and molecular weight data for these copolymers are given in Table I.

Copolymerization of (α-Ethoxyvinyl)pentafluorocyclotriphosphazene and Methyl Methacrylate. The methyl methacrylate (MMA) was purified in an identical manner with styrene. Reaction conditions and workup procedures utilized were identical with that described for the styrene copolymerizations. An equal molar mixture of MMA and $N_3P_3F_5C(OC_2H_5){=}CH_2$ was polymerized to 6.77% conversion and produced a copolymer that had a composition (MMA/$N_3P_3F_5C(OC_2H_5){=}CH_2$) of 3.15.

Attempted Homopolymerization of (α-Ethoxyvinyl)pentafluorocyclotriphosphazene. Numerous attempts were made at homopolymerization of $N_3P_3F_5C(OC_2H_5){=}CH_2$ using radical (AIBN, benzoyl peroxide), redox ($(NH_4)_2Fe(SO_4)_2\cdot 6H_2O/Na_4P_2O_7\cdot 10H_2O$[15]), anionic ($KHCO_3$, t-C_4H_9Li), and cationic [$BF_3\cdot O(C_2H_5)_2$, H_2SO_4] initiators. The radical systems appeared to give trace amounts of oligomers, while all other catalysts did not effect any polymerization.

Results and Discussion

As was the case with (α-methylvinyl)pentafluorocyclotriphosphazene,[3] homopolymerization of (α-ethoxyvinyl)pentafluorocyclotriphosphazene (I) was not observed. This may be ascribed to a combination of the reluctance of 1,1-disubstituted olefins to undergo homopolymerization and the strong electron-withdrawing nature of the $N_3P_3F_5$ moiety.[5,6] In principle, the electron-withdrawing substituent should favor anionic initiation; however, the anionic catalyst may be captured at the P(V) site rather than at the olefinic center.

Copolymerization reactions involving I proceed readily, and the system styrene–I was examined in detail. Infrared

$$N_3P_3F_5C(OC_2H_5){=}CH_2 + xC_6H_5C{=}CH_2 \xrightarrow[\Delta]{AIBN} [(C_6H_5CH{-}CH_2)(N_3P_3F_5C(OC_2H_5){-}CH_2)_y]_n$$

$$x = 0.41\text{–}7.22 \qquad y = 0.04\text{–}0.77$$

data show the retention of aromatic and phosphazene bonds and the absence of all olefinic absorptions in the copolymers. The compositional, conversion, and molecular weight data for the new copolymers are shown in Table I. It should be noted that reactions 1–6 were stopped at low conversions. This was necessary for certain of the calculations of reactivity ratios. The copolymers are white, powdery substances, which dissolve in methylene chloride, toluene, benzene, tetrahydrofuran, diethyl ether, and acetone. They are stable to air and dilute acid or base.

Table II
Reactivity Ratios for Styrene-(α-Ethoxyvinyl)pentafluorocyclotriphosphazene Copolymerization Reaction

method	r_1[a]	r_2[b]
Fineman–Ross	3.40	0.30
Kelen–Tüdös	3.56	0.28
Mortimer–Tidwell	3.04	0.19

[a] M_1 = styrene. [b] M_2 = $N_3P_3F_5C(OC_2H_5){=}CH_2$.

The copolymers were also found to be flame retardant in simple flame tests.

The styrene–I copolymers may be compared to the previously reported[3] styrene–$N_3P_3F_5C(CH_3){=}CH_2$ system. The maximum phosphazene incorporation in the (α-methylvinyl)phosphazene series was 36.7 mol %, which was achieved with a feed ratio (styrene/phosphazene) of 4:1. The maximum incorporation of I is 43.7 mol %, which was achieved with a 2.44:1 feed ratio. Feed ratios that are higher in I do not undergo polymerization. The higher incorporation of I compared to the α-methylvinyl analogue indicates a significant difference in the vinylphosphazene reactivity in these two systems and is consistent with our proposal of reduction of olefin polarity by a counterbalancing of the electron-withdrawing effect of the phosphazene with the donor effect of the alkoxy group.

In order to provide a more thorough examination of the reactivity of I, we have calculated the reactivity ratios (r_1 and r_2) for the styrene–I system. These data, calculated by three different methods, may be found in Table II. In comparing the three methods, it is observed that all give similar results with the results of both of the linearization methods falling within the 95% joint confidence limits of the Mortimer–Tidwell calculation. Since it is expected that the Mortimer–Tidwell approach will give the most reliable data,[14] those values of r_1 and r_2 were used to calculate the Alfrey–Price parameters,[16] with values of $Q = 0.18$ and $e = -0.06$ being obtained. It is apparent upon comparison of the reactivity ratios of styrene (M_1)–ethyl vinyl ether (M_2) ($r_1 = 80$, $r_2 = 0$)[17] to those of the styrene–I system that the olefinic center in I does not behave as a typical vinyl ether. The addition of a bulky group such as the phosphazene ring to the vinyl ether might be expected to offer some steric inhibition to copolymerization so the observed increase in activity indicates that the electronic structure of the vinyl ether is significantly perturbed by the $N_3P_3F_5$ moiety. Similar conclusions were drawn from the NMR data on I.[10] Some insight into the mechanism of modification of the olefin electronic structure can be gained from a comparison of the Q and e values for I to those for related monomers.[17] The Q value of I lies in the general range of those observed for vinyl ethers, thus indicating no major mesomeric interaction between the phosphazene and the olefin. The reluctance of the phosphazene unit to enter into significant conjugative interactions with unsaturated organic moieties has been previously noted.[6] The approximate nature of the Q, e data does not prohibit small amounts of mesomeric interactions occurring in I such as has been claimed in other organophosphazenes.[7,18] The e value for I is quite different from those typically found for vinyl ethers, and this difference may be ascribed to the reduction of the electron-rich nature of the vinyl ether by the strong σ-electron-withdrawing effect of the phosphazene moiety.

If the Q and e values for I are combined with the literature[17] values for methyl methacrylate (MMA), the reactivity ratios for the MMA–I copolymerization may be calculated. For an equimolar copolymerization of MMA and I, the copolymer composition calculated from the reactivity ratios and the copolymer equation is $(MMA)_{3.5}(I)_1$, which is in reasonable agreement (given the nature of the data) with the observed composition of $(MMA)_{3.15}(I)_1$.

Table III
TGA Data for Styrene-(α-Ethoxyvinyl)pentafluorocyclotriphosphazene Copolymers

wt % phosphazene in copolymer	weight loss range	% wt loss first step	T_{50}, °C
33.4	205–280	24.4	350
40.8	200–280	30.3	350
42.5	200–290	28.3	355
50.8	190–270	39.3	320
69.2	180–260	46.7	315

The reactivity ratios of the styrene–I system show that a styryl radical has a greater tendency to add to styrene than to I. Using a value of 165 L/(mol·s) for the styrene homopropagation rate constant (k_{11}),[19] we can estimate (from r_1) a value of k_{12} of 54.3 L/(mol·s), i.e., roughly a threefold preference for styrene homopropagation vs. cross propagation. The relucatnce of I to undergo homopolymerization suggests that the homopropagation rate constant of I, k_{22}, is diminishingly small. To get a value of r_2 of 0.19, the rate constant for the addition of the radical of I to styrene (k_{21}) must be large. The combination of large values of k_{11} and k_{21} leads to copolymers that are rich in styrene.

Molecular weight data for the styrene–I copolymers may be found in Table I. The membrane osmometry data is significantly higher than the gel permeation chromatography (GPC) data. If the GPC data is close to the true value, then the osmometric data would be artifically high due to diffusion of low molecular weight fragments across the membrane. Alternatively, polystyrene may not be a good GPC calibrant for the styrene–I copolymers. A low molecular weight polymer was selected for study by vapor-phase osmometry and it was found that the molecular weight was higher than the GPC value in roughly the same ratio as the membrane osmometry to GPC data. It appears that the GPC values are uniformly low and that the true values are closer to those obtained by the absolute methods. One possible explanation for the low GPC values would be electrostatic attraction between the phosphazene and phenyl rings, resulting in a reduction in size of the copolymer over the expected average dimensions of an unperturbed chain. The general trend in molecular weights is similar to that observed for the styrene–(α-methylvinyl)phosphazene copolymers, i.e., a reduction in molecular weight with increased phosphazene content. The high reactivity and low homopropagation rate of the phosphazene radical would result in increased occurrence of termination steps with increased amounts of phosphazene in the system.

The TGA data for thermal decomposition of the styrene–I copolymers are found in Table III. In each case, the decomposition is, at least, a two-step process, with a typical TGA scan shown in Figure 1. There is a correlation between the percent weight loss in the first step and the weight percent of I in the copolymer. Given this observation, it is reasonable to assume that the first stage of decompostion involves the (α-ethoxyvinyl)phosphazene region of the copolymer. There is also a lowering of the onset temperature for decomposition and the temperature required for 50% weight loss with increasing phosphazene content. These observations also suggest that the incorporation of I contributes to the destabilization of the copolymer to thermal decomposition. It is of interest to note the lower thermal stability of the (α-ethoxyvinyl)- com-

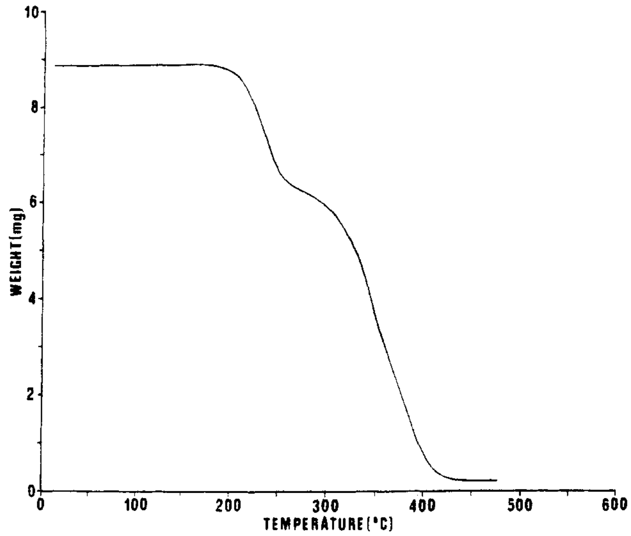

Figure 1. Typical TGA scan for styrene-(α-ethoxyvinyl)pentafluorocyclotriphosphazene copolymers.

pared to (α-methylvinyl)phosphazene[3] copolymers.

In summary, we have developed a new series of novel copolymers involving a vinylphosphazene and traditional organic monomers. Significant alterations of copolymerization behavior of vinylphosphazene monomers may be affected by the nature of the substituent on the olefinic center. The nature of the effect of the phosphazene on the vinyl ether center in I has been elucidated by a consideration of the Q and e values for this system.

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Registry No. $N_3P_3F_5C(OC_2H_5)=CH_2$, 80297-67-2; $(N_3P_3F_5(OC_2H_5)=CH_2)\cdot$(styrene) (copolymer), 80297-68-3; $(N_3P_3F_5C(OC_2H_5)=CH_2)\cdot$(MMA) (copolymer), 99798-90-0; styrene, 100-42-5.

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Photochemical Behavior of Poly(organophosphazenes). 4. Photosensitization Properties of Poly[bis(4-benzoylphenoxy)phosphazene]

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ABSTRACT: The reaction between poly[dichlorophosphazene] $(NPCl_2)_n$ and 4-hydroxybenzophenone leads to the formation of poly[bis(4-benzoylphenoxy)phosphazene] $[NP(OC_6H_4COC_6H_5)_2]_n$. This polymer proved to be an efficient triplet-state energy donor in heterogeneous-phase photosensitization experiments since the two benzophenone moieties supported at the phosphorus atoms of the phosphazene chain are able to transfer the absorbed energy to suitable acceptors, so inducing their photoreactions. The polymer may be recovered from the reaction mixture simply by filtration and reused for successive experiments.

Introduction

The possibility of anchoring metallic or metallorganic catalysts,[1] synthetic reagents,[2] enzymes,[3] etc. on polymeric substrates is a subject of current research. It has been found, in fact, that these molecules still maintain their catalytic activity when supported on polymeric matrices,[4] offering, on the other side, significant advantages in the separation and purification procedures of reaction products.[5]

In the last two decades, a great deal of work has been done also in supporting organic photosensitizers on insoluble polymeric substrates.

In 1973 Neckers and Blossey[6] reported the synthesis of polystyrene supporting Rose Bengal, a dye largely used in the photosensitized generation of singlet oxygen. Successively, two other molecules have been considered as possible polymer-supported photosensitizers, i.e., aceto-

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