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Organophosphazenes. 22. Copolymerization of ((α-Methylethenyl)phenyl)pentafluorocyclotriphosphazenes with Styrene and Methyl Methacrylate[1]

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ABSTRACT: Both 3- and 4-((1-methylethenyl)phenyl)pentafluorocyclotriphosphazene ($N_3P_3F_5C_6H_4C(CH_3)$=CH_2) undergo radical copolymerization with styrene and methyl methacrylate. Flame-retardant copolymers with up to 66% and 44% phosphazene content were obtained for the styrene and methyl methacrylate systems, respectively. Reactivity ratios and Alfrey–Price parameters for the styrene system show that the major perturbation produced by the phosphazene is a polar σ-electron-withdrawing effect. The methyl methacrylate system was found to exhibit significant penultimate effects in its reactivity behavior. The copolymers were characterized by using elemental analysis, gel permeation chromatography, membrane osmometry, TGA, and DSC.

Introduction

Considerably recent interest has been shown in the synthesis of polymers derived from organophosphazenes.[2-6] While some groups have concentrated on the ring-opening polymerization of cyclophosphazenes,[3] the reactions of poly(phosphazenes) with organometallic reagents,[2] or formation of poly(organophosphazenes) from silylated phosphoranimines,[5] work in our laboratory has been directed toward the synthesis of polymers containing pendant phosphazene residues. This method results in an organic polymer surrounded by a sheath of inorganic material, in contrast to most inorganic polymers, which have an inorganic backbone surrounded by organic material.[6] Our approach to the synthesis of these polymers has been by copolymerization of alkenylphosphazenes with organic olefins.[6-9] Certain complications in both monomer synthesis[10] and polymerization[7] have been ascribed to the strong electron-withdrawing effect exhibited by the phosphazene unit.[11] We have previously shown that one method for mediation of the electron-withdrawing effect of the phosphazene is by using olefins with strong electron-donating substituents.[11,12] An alternative approach involves the separation of the olefin from the phosphazene by an insulating function. We have recently reported the synthesis of α-methylethenylphosphazenes with a phenyl group between the phosphorus and olefinic centers, i.e. phosphazene derivatives of α-methylstyrene.[1,9] In this paper we report the addition copolymerization of these new organofunctional phosphazene monomers with styrene and methyl methacrylate.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Shin Nisso Kako) was converted to hexafluorocyclotriphosphazene, $N_3P_3F_6$,[13] and then to either 3- or 4-((1-methylethenyl)phenyl)pentafluorocyclotriphosphazene[1] by previously published procedures. Styrene and methyl methacrylate were distilled from calcium hydride and stored in dark bottles under a blanket of nitrogen at 0 °C. Prior to use, a small quantity of the monomer was added to an excess of methanol. If no turbidity was observed, it was assumed that no polymer was present. Azobis(isobutyrylnitrile) (AIBN) was recrystallized from ethanol and stored at 0 °C.

Measurements. Infrared spectra were obtained as KBr pellets on a Nicolet 6000 Series spectrophotometer. Gel permeation chromatography (GPC) was performed on a Waters A.V.C 202 high-pressure liquid chromatograph equipped with Waters 10^4- and 10^5-Å microstyragel columns. Membrane osmometry was accomplished via a Wescan Model 230 recording osmometer. Toluene solutions were employed for both GPC and osmometry measurements. Thermal analyses were carried out by using a Perkin-Elmer TGS-2 thermogravimetric system (TGA) or a DSC-4 differential scanning calorimeter (DSC) interfaced with a PETOS thermal analysis data station. Elemental analysis was performed by Robertson Laboratory, Inc. Copolymer polymer composition was determined from weight percent nitrogen.[7] Reactivity ratios for systems following the terminal model were calculated by using the Mortimer-Tidwell nonlinear least-squares approach,[14] and for systems following the penultimate model the methodology developed by Pittman[15] was employed.

Polymerization Reactions. Copolymerization reactions were carried out by one of two methods. **Method A.** Comonomers were placed in a thick walled tube, along with 2% AIBN (by wt.), and sealed with a rubber septum. The tube was then flushed with nitrogen. During this time, the tube was immersed in an ice bath

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Table I
Composition and Conversion Data for ((α-Methylethenyl)phenyl)pentafluorocyclotriphosphazene Copolymers Used for Reactivity Ratio Calculations

comonomers		M_1, mol %		
M_1	M_2	feed	polymer	% convn
Ia	STY	16.78	24.27	37.69
		15.61	23.84	47.08
		74.07	61.63	7.86
		71.86	58.90	8.55
		20.84	29.29	.07
		78.08	64.19	1.39
		76.63	61.63	2.77
		73.02	57.65	6.74
		27.06	31.91	9.61
		22.90	32.82	12.23
		23.37	32.36	13.82
		23.83	31.53	12.54
		34.43	43.39	23.94
		12.42	21.02	30.61
		12.12	15.03	32.08
Ib	STY	9.3	11.2	
		19.68	21.41	80.89
		29.09	30.21	68.02
		38.97	39.01	52.78
		48.41	45.13	49.70
		58.87	53.98	18.60
		68.33	58.21	12.68
		26.97	32.67	20.73
		23.03	26.65	19.10
		82.66	67.21	2.97
		81.96	66.72	3.03
Ia	MMA	14.61	24.94	5.49
		19.09	31.96	4.09
		20.1	36.6	
		24.64	43.03	3.76
		29.47	44.26	2.97
		10.22	17.99	11.42
		14.99	25.69	8.97
		20.41	32.50	7.77
		24.21	39.81	6.34
Ib	MMA	14.41	22.14	22.78
		18.42	27.32	11.70
		25.19	35.73	16.94
		30.61	41.83	12.55
		10.32	14.23	30.29
		14.76	21.24	20.17
		19.80	28.75	14.75
		25.62	36.75	13.89

to minimize the loss of either monomer. The tubes were then placed in an oil bath for a period of time and heated to 60 ± 2 °C. In a typical experiment 0.7553 g (2.176 mmol) of 4-((1-methylethenyl)phenyl)pentafluorocyclotriphosphazene (Ia), 1.1236 g (10.788 mmol) of styrene, and 0.0057 g of AIBN were allowed to react for 36 h. After purification, 0.7082 g (37.69% conversion) of a copolymer of the composition $(\text{styrene})_{3.12}(\text{Ia})_1$ (6.2% N) was obtained. Composition and conversion data for all copolymerization may be found in Table I.

Method B. Comonomers were placed in a thick walled tube along with 2% AIBN and subjected to several freeze–pump–thaw cycles. The tube was then evacuated, sealed, and placed in an oil bath for a period of time at 60 ± 2 °C. The results using method B were similar to those obtained by using method A except that higher molecular weights were observed when method B was employed (Table II).

In both methods, the polymerizations were terminated and the polymers isolated by precipitating the reaction mixtures into methanol. The polymers were filtered, washed with methanol, and dried. If further purification was required, the polymers were dissolved in methylene chloride and reprecipitated.

Results and Discussion

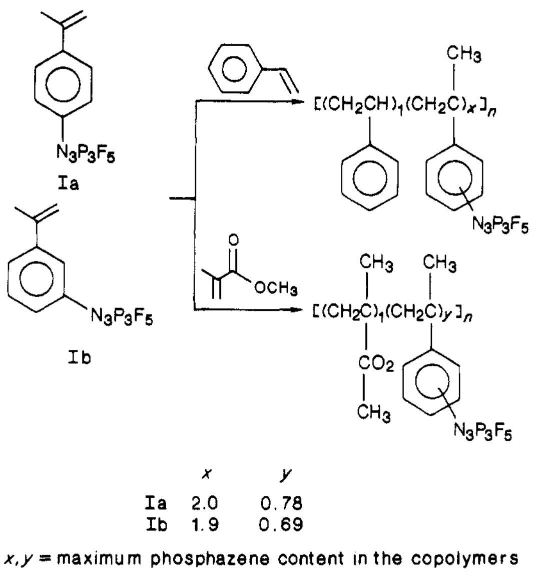
The organofunctional phosphazene monomers under investigation in this study, 3- and 4-((1-methylethenyl)phenyl)pentafluorocyclotriphosphazene (Ia,b), can be considered as α-methylstyrene derivatives with a pentafluorocyclotriphosphazene moiety in the para (Ia) or meta (Ib) position. Since α-methylstyrene derivatives do not undergo significant radical addition homopolymerization,[16] we have concentrated on copolymerization reactions with styrene (STY) and methyl methacrylate (MMA) as the comonomers (Scheme I). The copolymers that were produced were all white powders, soluble in a variety of common organic solvents. They were flame retardant in simple flame tests.

Table II
Selected Composition and Molecular Weight Data for ((α-Methylethenyl)phenyl)pentafluorocyclotriphosphazene Copolymers[a–c]

comonomers		M_1, mol %			
M_1	M_2	feed	polymer[d]	$10^{-3}\bar{M}_n$	$10^{-3}\bar{M}_w$
Ia	STY	34.4	43.4	19.0	32.3
		16.8	24.3	39.6	69.2
		16.8	24.3	113.0[e]	
		12.4	21.0	13.9	22.1
Ib	STY	58.9	54.0	6.5	7.9
		39.0	39.0	11.7	16.4
		29.1	30.2	13.1	22.6
		9.3[f]	11.2	75.3	254.0
		9.3[f]	11.2	100.0[e]	
Ia	MMA	24.6	43.0	8.3	10.8
		20.1	36.6	12.9	36.2
		14.6	24.9	14.5	57.4
Ib	MMA	25.2	35.7	14.8	20.7
		14.8	21.2	22.7	35.0
		10.3	14.2	24.5	51.0

[a] Molecular weights determined by GPC except where indicated. [b] Polymerization by method A except where noted. [c] Composition conversion data for all copolymerization reactions may be found in Table I. [d] As determined by weight percent nitrogen. [e] Membrane osmometry. [f] Polymerization by method B.

Scheme I



Selected composition and molecular weight data for the new copolymers may be found in Table II. As was observed in the copolymerization of other alkenylphosphazenes,[7,8] the molecular weight of the copolymers decreases with increasing phosphazene content. In cases where absolute molecular weight determination (by membrane osmometry) were carried out, the copolymer molecular weight is consistently higher than the values obtained by gel permeation chromatography (GPC). Since high molecular weight species were employed for osmometric determination, diffusion of low molecular weight fractions across the membrane is not a significant problem

Table III
Reactivity Data for Styrene-((α-Methylethenylphenyl)pentafluorocyclotriphosphazene Copolymers

	r_1[a]	r_2[b]	$Q(M_2)$	$e(M_2)$
Ia	0.41	0.28	0.72	0.72
Ib	0.58	0.28	0.63	0.58

[a] M_1 = styrene. [b] $M_2 = N_3P_3F_5C_6H_4C(CH_3){=}CH_2$.

so it is reasonable to assume that polystyrene is not a good calibrant for these copolymers. We have previously proposed that an electrostatic interaction between the phosphazene and neighboring organic functions is responsible for the lower molecular weight values obtained from GPC measurements.[8] A significant increase in molecular weight was observed when oxygen was rigorously excluded from the system by using freeze–thaw cycles, thus indicating a particular sensitivity of the phosphazene-based monomers to inhibition by oxygen.

The reactions of Ia or Ib with styrene lead to copolymers with a wide range of compositions (Table I). The maximum incorporation of the phosphazene into the polymers was 64 and 67%, respectively. This represents the highest incorporation of a phosphazene containing monomer into a copolymer to date. In previous copolymerizations with other phosphazene-containing monomers[7,8] the polarizing effect of the $N_3P_3F_5$ group limited the extent to which the phosphazene monomer entered into the reaction. In this case, the aromatic ring clearly moderates the polarizing effect of the phosphazene monomer. The amount of the phosphazene monomer incorporated into the copolymer is not affected by the isomer that is employed; i.e., similar feed ratios of Ia or Ib lead to polymers of similar composition regardless of which monomer was used. The reactivity ratios of Ia,b with styrene as the comonomer were calculated by using the Mortimer–Tidwell nonlinear least-squares approach[14] and may be found in Table III. An examination of the reactivity ratio data shows that both phosphazene monomers prefer to cross propagate. The steric crowding at I would tend to decrease the probability that another molecule of I would add to it. Electronically, one would expect the styryl radical to be more stable than I. If this is the case, then the addition of a styrene molecule to the growing chain end would be favored over the addition of a phosphazene monomer. Therefore, one would expect that the reactivity ratio for styrene would be greater than one. However, the opposite is true. There may be some electrostatic attraction between the electron-deficient aryl ring of I and styrene. This would lead to a tendency toward alternating copolymerization that is reflected in the low value for r_1xr_2. The values of r_1 for Ia and Ib lie within the intersection of the 95% joint confidence limits for their respective calculations; therefore, within the accuracy of this measurement, there is no difference between the reactivity of Ia and Ib in the copolymerization process. This observation is consistent with the spectroscopic studies of I that indicated minimal resonance interaction between the phosphazene and aryl rings.[1] Further insight into the electronic effect of the $N_3P_3F_5$ moiety on the α-methylstyrene unit can be obtained from the Alfrey–Price Q and e parameters[17] that were calculated from the reactivity ratios and are found in Table III. If one compares the Alfrey–Price parameters for p-nitrostyrene[18] (Q = 1.63; e = 0.39) with I, significant differences are noted. The nitro group represents a classic example of a conjugated electron-withdrawing substituent, and this is reflected in the large value of the Q (resonance) parameter compared to styrene (1.0). The fact that the Q values for I are less than that of styrene demonstrates the absence of significant mesomeric interaction between the phosphazene and aryl rings. The values for the e (polarity) parameter for I are even larger than that of nitrostyrene, indicating the high degree of polarity induced in the olefin by the nonmesomeric electron-withdrawing effect of the $N_3P_3F_5$ unit.

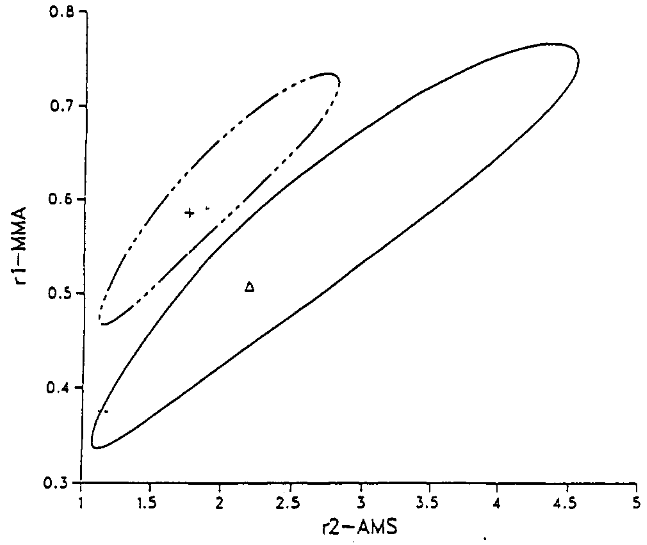


Figure 1. Calculated 95% joint confidence limit curves for methyl methacrylate-((α-methylethenyl)phenyl)pentafluorocyclotriphosphazene reactivity ratios (AMS = Ia or Ib): (Δ) Ia–MMA; (+) Ib–MMA.

Table IV
Penultimate Reactivity Parameters for ((α-Methylethenyl)phenyl)pentafluorocyclotriphosphazene Copolymers[a]

comonomers	r_1	r_1'	r_2	r_2'	multiple correltn coeff
MMA–Ia	0.70	0.23	0.38	2.90	0.976
MMA–Ib	1.23	0.32	0.0[b]	39.50	0.994
STY–Ia	0.63	0.18	0.63	0.095	0.992
STY–Ib	0.58	0.87	0.15	0.88	0.997

[a] M_1 = MMA or STY; M_2 = Ia or Ib. [b] Assumed to be zero from calculated value of –0.037

In contrast, the MMA copolymers show a decreased tendency for incorporation of Ia or Ib (Table I). The polymers with the highest phosphazene content contained only 44 and 42% phosphazene monomer, respectively. Attempts at increasing the phosphazene content by increasing the amount of Ia or Ib in the feed resulted in little or no polymer formation. The reactivity ratios for I with MMA were calculated from the available composition/conversion data. However, an examination of the 95% joint confidence limit curves (Figure 1) shows that the uncertainty in the calculated values of r_1(MMA) and especially r_2(I) are so large as to render the numbers meaningless. The most reasonable interpretation of this result is that the terminal model is not adequate to describe the mechanism for the copolymerization of I with MMA. Penultimate behavior, i.e. the effect of the next to last monomer unit on reactivity, is most commonly observed when the monomer contains bulky or polar substituents.[19] Since the phosphazene monomers fit both of these criteria, the data were reanalyzed by using a penultimate model[15] giving the results shown in Table IV. The reasonable (Ia/MMA) to excellent (Ib/MMA) multiple correlation coefficients indicate that the data are fit in these calculations. The significant parameter in each case is r_2 (k_{122}/k_{121}) which is large compared to r_2' (k_{222}/k_{221}), indicating that a penultimate effect is operative in

Table V
Thermal Analysis Data for ((α-Methylethenyl)phenyl)pentafluorocyclotriphosphazene Copolymers

comonomers	M_1[a] in polymer, mol %	T_{onset}, °C	% wt loss (1st step)	$T_{50\%}$, °C	T_g, °C
Ia-STY	43.39	286	36	392	112
	31.91	295	33	410	93
	24.27	310	22	421	93
	15.03	305	40	408	100
Ib-STY	58.21	315	27	339	79
	45.13	316	46	382	90
	30.21	297	37	395	88
	21.41	295	24	401	86
Ia-MMA	39.81	203	89	347	151
	32.50	199	85	349	146
	25.65	187	89	357	133
	17.99	198	88	356	131
Ib-MMA	41.83	192	83	357	97
	36.75	198	80	300	114
	28.75	194	86	359	109
	14.23	211	87	360	115

[a] M_1 = Ia or Ib.

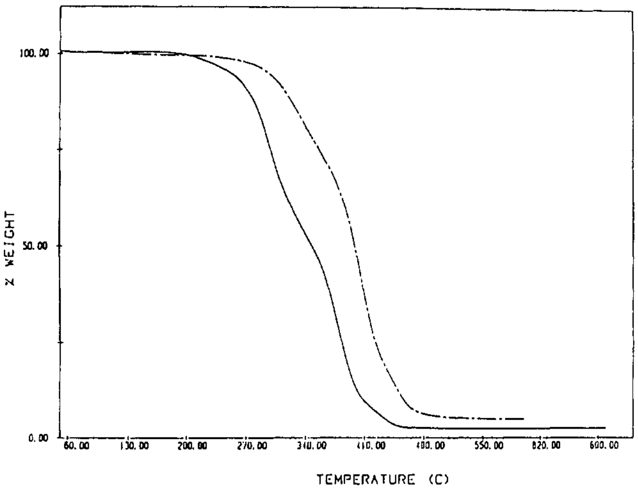


Figure 2. Typical TGA scans for styrene–((α-methylethenyl)-phenyl)pentafluorocyclotriphosphazene copolymers: (-—-) Ia–STY; (—) Ib–STY.

this system. The replacement of I with MMA in the penultimate position significantly increase the rate of cross reaction between a growing chain terminated with the phosphazene and a phosphazene monomer. This indicates an interaction between the phosphazene and MMA units in the chain that may decrease the electron-withdrawing ability of the phosphazene unit. The STY/I composition/conversion data were also analyzed by using the penultimate model (Table IV). The calculations suggest a small penultimate contribution to the overall mechanism. In each case (MMA and STY), the penultimate effect is more significant for Ib which may indicate that the meta disposition of the phosphazene moiety forces it closer to the penultimate monomer unit in the chain.

The TGA data for thermal decomposition of the STY copolymers are found in Table V. As with other alkenylphosphazene copolymers,[7,8] in each case the decomposition is a two-step process with the onset at roughly 300° (Figure 2). While it is tempting to partition the two stages to the two different monomer units, the correlation between phosphazene content and weight loss in the first step is only qualitative. A feature of particular interest is how the difference in structure between the two phosphazene monomers effects the stability of the copolymers. As shown in Figure 2, polymers containing Ia are more stable than those containing Ib. This suggests that the polymer undergoes cleavage to relieve steric strain. The bulky $N_3P_3F_5$ residue will crowd its neighbors to a greater extent in the 3-position than in the 4-position of the aryl unit, thus making polymers produced from Ib more amenable to thermal depolymerization. The phosphazene ring–polymer chain interactions proposed here are consistent with the increased importance of the penultimate effect in copolymers of Ib (vide ante). The MMA copolymers possess somewhat different thermal decomposition characteristics. The thermograms of these copolymers contain one weight loss step corresponding to the loss of about 80–90% of the material. The average onset temperature is 200 °C, and there appears to be little or no difference in the thermal stability of the copolymers produced by using Ia or Ib. Again, if the polymers fragment to relieve steric strain, this is not surprising. While the $N_3P_3F_5$ moiety will still cause greater crowding in the 3-position than in the 4-position, the flexibility of the carboxymethyl group of MMA should allow it to relieve the strain by pathways other than thermal scission.

Glass transition temperature (T_g) were determined by differential scanning calorimetry and appear in Table V. For reference, T_g values for poly(STY) and poly(MMA) are 100 and 114 °C, respectively. While there appears to be no correlation between the percent phosphazene in the polymer and the T_g, factors such as significant molecular weight differences between copolymers and the possibility of regions of blocks of MMA or STY may be important in determining the relative T_g values in these series. There is a difference in T_g depending on whether Ia or Ib was involved in the synthesis of the copolymer.

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Registry No. Ia, 105372-73-4; (Ia)(STY) (copolymer), 108416-14-4; (Ia)(MMA) (copolymer), 108416-15-5; Ib, 105372-74-5; (Ib)(STY) (copolymer), 108416-16-6; (Ib)(MMA) (copolymer), 108416-17-7; STY, 100-42-5; MMA, 80-62-6.

References and Notes

(1) Part 21: Shaw, J. C.; Allen, C. W. *Inorg. Chem.* **1986**, *25*, 4632.
(2) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.
(3) (a) Allcock, H. R.; Connolly, M. S. *Macromolecules* **1985**, *18*, 1330. (b) Allcock, H. R.; Lavin, K. D.; Riding, G. *Macromolecules* **1985**, *18*, 1340.
(4) (a) Allcock, H. R.; Chu, C. T.-W. *Macromolecules* **1979**, *12*, 551. (b) Allcock, H. R.; Evans, T. L.; Patterson, D. B. *Macromolecules* **1980**, *13*, 201.
(5) (a) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848. Neilson, R. H.; Wisian-Neilson, P. *J. Macromol. Sci., Chem.* **1981**, *A16*, 425.
(6) (a) Allen, C. W. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 77. (b) Allen, C. W. *J. Polym. Sci., Polym. Symp.* **1983**, *No. 70*, 79. (c) Allen, C. W. *ACS Symp. Ser.* **1988**, *No. 360*, 290.
(7) Dupont, J. G.; Allen, C. W. *Macromolecules* **1979**, *12*, 169.
(8) Allen, C. W.; Bright, R. P. *Macromolecules* **1986**, *19*, 571.
(9) Allen, C. W.; Shaw, J. C. *Phosphorus Sulfur* **1987**, *30*, 97.
(10) Allen, C. W.; Bright, R. P.; Ramachandran, K. *ACS Symp. Ser.* **1981**, *No. 171*, 321.
(11) (a) Allen, C. W. *J. Organomet. Chem.* **1977**, *125*, 215. (b) Allen, C. W.; Green, J. C. *Inorg. Chem.* **1978**, *17*, 3093.
(12) Allen, C. W.; Bright, R. P. *Inorg. Chem.* **1983**, *22*, 1291.
(13) Moeller, T.; John, K.; Tsang, F. *Chem. Ind.* (*London*) **1961**, 347.
(14) (a) Tidwell, P. W.; Mortimer, G. A. *J. Polym. Sci., Part A* **1965**, *3*, 369. (b) Tidwell, P. W.; Mortimer, G. A. *J. Macromol. Sci., Rev. Macromol. Chem.* **1970**, *4*, 281.
(15) Pittman, C. U., Jr.; Rounsefell, T. D. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 621. Pittman, C. U., Jr.; Rounsefell, T.

D. *Comput. Chem. Instrum.* **1977**, *6*, 145.
(16) The homopolymerization Ia was attempted with anionic (*n*-butyllithium), cationic (titanium tetrachloride), and radical (AIBN; benzoyl peroxide; benzoin methyl ether, *hν*) initiators. In each case, no polymer was obtained and the monomer was recovered.
(17) Alfrey, T., Jr.; Young, L. J. *Copolymerization*, 2nd ed.; Ham, G. E., Ed.; Wiley: New York, 1971.
(18) Young, L. J. Polymer Handbook, 2nd ed.; Brandrup, J., Immergut, E. H.; Eds.; Wiley: New York, 1975; Chapter II.
(19) Odian, G. *Principles of Polymerization*, 2nd ed.; Wiley: New York, 1981; p 478.

Polymerization of β-Monosubstituted-β-propiolactones Using Trialkylaluminum–Water Catalytic Systems and Polymer Characterization

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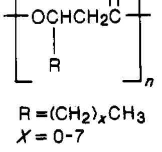
ABSTRACT: The catalysts ethylaluminoxane (EAO), methylaluminoxane (MAO), and a crude in situ catalyst preparation from the reaction of Et_3Al with water were used to synthesize poly([*R*,*S*]-benzyl malolactonate), PBML, and poly([*R*,*S*]-β-hydroxybutyrate), P([*R*,*S*]-HB). Studies of stereoregularity, crystallinity, and molecular weight were carried out on these homopolymers and their product fractions by 75.4-MHz ^{13}C nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), and gel-permeation chromatography (GPC), respectively. PBML and P([*R*,*S*]-HB) were fractionated into an acetone-soluble portion of comparatively lower molecular weight and low stereoregularity and an acetone-insoluble crystalline fraction with a higher molecular weight ($\bar{M}_w$ greater than 300 000 for PBML and P([*R*,*S*]-HB)) and with high degrees of stereoregularity (up to 88% isotactic diads for P([*R*,*S*]-HB)). The three catalysts were all capable of synthesizing an acetone-insoluble PBML and P([*R*,*S*]-HB) fraction of similarly high crystallinity. Measurements of the enthalpy of fusion (ΔH_m) by DSC for this fraction were usually between 6 and 8 cal/g for PBML and 14 and 16 cal/g for P([*R*,*S*]-HB), while their stereoregular isomers have ΔH_m values of 12.5 and 22 cal/g, respectively. The high peak melting temperatures observed by DSC for these fractions suggest the formation of crystalline regions which show essentially complete exclusion of the noncrystallizable monomer stereochemistry. Racemic benzyl malolactonate (BML) and β-butyrolactone (BL) monomers were copolymerized by using EAO and MAO catalysts. Analysis of these copolymers by ^1H and ^{13}C NMR allowed evaluation of the comonomer diad sequence distribution and showed that the copolymer composition was nearly identical with the monomer feed. The use of the in situ catalyst preparation to perform the above copolymerization resulted in lower yields and extreme sample heterogeneity.

Introduction

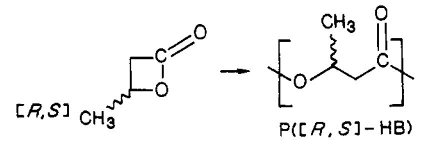
The class of β-monoalkyl-substituted poly(β-hydroxyalkanoates) (PHA) are found in a wide variety of bacterial microorganisms throughout nature[1] and function as carbon and energy storage materials.[2] Bacterial PHA commonly contains large amounts of ester units derived from β-hydroxybutyrate (HB), but units derived from β-hydroxyvalerate (HV) and even those with longer n-alkyl pendant groups are also found, as shown below.[1] These polymers are 100% isotactic because the chain chiral centers have only the *R* stereochemical configuration.[2,3]



PHA

The bacterial polyesters, when carefully isolated, can have viscosity molecular weight averages above 500 000 and a heterogeneity index of approximately 2.[4,5] The bacterial polyester containing primarily HB units is normally stored within the cell and subsequently degraded enzymatically to β-hydroxybutyric acid, which is a metabolite in the fatty acid β-oxidation cycle. This polymer is also biodegradable in environments such as soil, anaerobic sewage, and seawater.[6]

The polymerization of racemic β-butyrolactone (BL) to form poly([*R*,*S*]-β-hydroxybutyrate), P([*R*,*S*]-HB), as shown below, has previously been carried out by using the



BL P([*R*, *S*]-HB)

catalysts obtained by the reaction of Et_3Al or Et_2Zn and H_2O.[7-9] The aluminum-based catalyst produced a highly stereoregular, crystalline polymer fraction,[7-9] while the zinc catalyst produced only atactic, amorphous P([*R*,*S*]-HB). P([*R*,*S*]-HB) synthesized from the racemic β-lactone BL has, of course, a diastereomeric relationship to the optically pure polymer produced by bacteria from β-hydroxybutyric acid.

The aluminum-based catalyst most often used for the polymerization of β-substituted-β-propiolactones is that obtained directly from the reaction of Et_3Al and H_2O in toluene.[7,8] The use of additives, such as epichlorohydrin, in the formation of the catalyst has been investigated as well.[8] More recently, attention has been directed toward the catalyst ethylaluminoxane (EAO), which is claimed to be polymeric ($([-AlEt-O]_n-)$) in nature.[9] This catalyst is believed to be more stereoregulating, have better catalytic activity, and improved reproducibility for the polymerization of BL. EAO have also been used to polymerize a

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