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Polybenzyl Polymer from Reaction of Benzyl Salicylate and Phosphorus (V) Chloride: Chromatographic Purification and Degree of Polymerization from ^{1}H-NMR Spectrum

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ABSTRACT

A polybenzyl polymer which formed in the reaction of benzyl salicylate and phosphorus (V) chloride originates from the self-condensation of benzyl chloride catalyzed by the phenylphosphorodichloridate (I). A chromatographic procedure for purification of the polybenzyl polymer has been developed. Equations for calculating degree of polymerization from ^{1}H-NMR spectra of polybenzyl polymers are derived on the basis of the presence of CH_2Cl terminal groups. Generalized structural formulas which delineate the difference between linear and branched polybenzyl polymers are proposed. Relationships between the idealized polybenzyl polymers and maximum degrees of polymerization are suggested.

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INTRODUCTION

Continuing current interest [1, 2] in polybenzyl polymers prompts us to report: (1) our results on the formation of polybenzyl in the reaction of benzyl salicylate and phosphorus (V) chloride, (2) procedures for purification of the polymer, and (3) a method of determining its average degree of polymerization from the ^{1}H-NMR spectrum. These polymers are useful [2] intermediates for synthesis of surfactants, corrosion inhibitors, and bactericides.

EXPERIMENTAL

Reaction of Benzyl Salicylate and Phosphorus (V) Chloride

Purified benzyl salicylate (16.5 g, 0.0724 mole) was added dropwise over a period of 30 min to an equimolar quantity (15.0 g) of phosphorus (V) chloride in a distilling flask equipped with a magnetic stirrer and an absorption trap for hydrogen chloride. The mixture was stirred for an additional 15 min after addition was complete. An infrared spectrum of the reaction product was taken at this point. The reaction mixture (26.3 g) was distilled into a vacuum trap submerged in a Dry Ice/acetone bath protected from moisture by a phosphorus pentoxide drying tube. Benzyl chloride (4.20 g, 49%) was obtained at 123°C/6 Torr. Its identity and purity were checked by comparison of the IR spectrum and gas chromatographic retention time of an authentic sample. The residue (21.9 g) was distilled at $<$ 1 Torr to obtain 18.1 g (98.5%) of the phenylphosphorodichloridate (I). An IR spectrum (neat) was obtained on the polymeric residue.

Purification of Polybenzyl Polymer

The polymeric residue was dissolved in benzene (10 ml) and the solution washed three times each with 10% sodium carbonate and water, followed by drying over magnesium sulfate. After removal of benzene by distillation, a light brown polymeric residue remained which was also soluble in carbon tetrachloride and petroleum ether (30-60°C) and insoluble in ethanol.

The polymeric material was purified by absorption column chromatography [3] by using a 3/4 × 21 in. column of chromatographic absorbent silica gel (Matheson, Coleman, & Bell, 60-80 mesh) previously washed with carbon tetrachloride and petroleum ether. A carbon tetrachloride solution (3 ml) of the sample was placed on the column, and the chromatogram was developed and eluted with petroleum ether, the course of development being followed with UV light. The eluent was collected up to a point where fluorescent material reached the exit tube. A light yellow plastic substance remained after removal of solvent. On thin-layer chromatography (Eastman type K310R) of this material with carbon tetrachloride, a single spot (iodine vapor) with an R_f value of 0.38 was obtained. An immediate white precipitate of silver chloride formed when ethanolic silver nitrate was added to a small sample of an acetone solution of the purified polymer.

Polymerization of Benzyl Chloride in Presence of Aluminum Chloride

Redistilled benzyl chloride (15 ml) was added dropwise to a small amount of anhydrous aluminum chloride kept at 23°C. After a reaction time of about 1.5 hr, the reaction mixture was dissolved in benzene (10 ml) and the solution washed three times each with 10% hydrochloric acid and water. After the solution was dried with anhydrous magnesium sulfate and solvent removed by evaporation, a brown plastic material was obtained. A single spot with an R_f value of 0.38 was obtained in a thin-layer chromatogram with carbon tetrachloride developer.

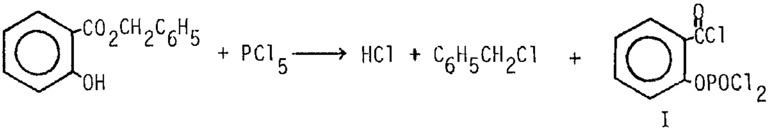
Spectra

IR spectra were obtained with a Perkin-Elmer grating model 337 instrument. Spectra were calibrated with bands of polystyrene.

^{1}H-NMR spectra were obtained with a Varian DP-60 spectrometer with the use of tetramethylsilane as internal standard. Chemical shifts were determined from side bands generated with a Hewlett-Packard wide-range oscillator (model 200 DCR). Side-band frequencies were determined with a Varian frequency counter (model V-4315).

RESULTS AND DISCUSSION

The reactions of alkyl salicylates and phosphorus (V) chloride were reported [4] as a new method of synthesis of alkyl chlorides from one to four carbons in high yields. When the reaction with benzyl salicylate was investigated in the present work, only a 49% yield of benzyl chloride was obtained although a 98.5% yield of the phenylphosphorodichloridate (I) was recovered [Eq. (1)]. An infrared



(1)

spectrum of the reaction mixture before distillation showed that only benzyl chloride and I were present, the reaction being conducted at ambient temperature. After distillation of benzyl chloride and I under reduced pressure, a polymeric residue remained. The IR spectrum of the polymer showed absorption bands not present in the spectrum of the original reaction mixture. The polymer was purified by chemical treatment and column chromatography. A test with alcoholic silver nitrate on the purified polymer showed the presence of reactive chlorine.

The IR spectrum of the polymer was similar to that of a polymer obtained from polymerization of benzyl chloride by use of aluminum chloride, except for an additional medium-intensity band in the spectrum of the former at 1263 cm^{-1}. The ^1H-NMR spectra for the two polymers were also similar, although the shapes of the absorption bands differed indicating differences in the nature of substitution of the polymers.

Degree of Polymerization from ^1H-NMR Spectra

Although some early investigators [1, 5] considered polybenzyl polymers to be linear polymers mainly substituted in the para position with lesser amounts of meta and ortho substitution, Haas et al. [6] were the first to furnish evidence that only highly branched polymers with short primary chains were formed as a result of multiple ring alkylation, a view that appears to be accepted by most current workers [1, 7].

Whether one uses a linear or branched structure or a mixture of the two, the ratio of CH_2Cl protons to the other CH_2 protons is the same for the same average degree of polymerization (n). This is more clearly evident in the generalized formulas (II-IV). Thus, structure II is a linear unsubstituted structure when x = 1, whereas

$$(C_6H_5CH_2)_x[C_6H_{5-x}CH_2]_{n-2}C_6H_4CH_2Cl$$

II

$(n_{max} = 7)$

$$(C_6H_5CH_2)_xC_6H_{5-x}CH_2[(C_6H_5CH_2)_yC_6H_{4-y}]_{n-3}CH_2C_6H_4CH_2Cl$$

III

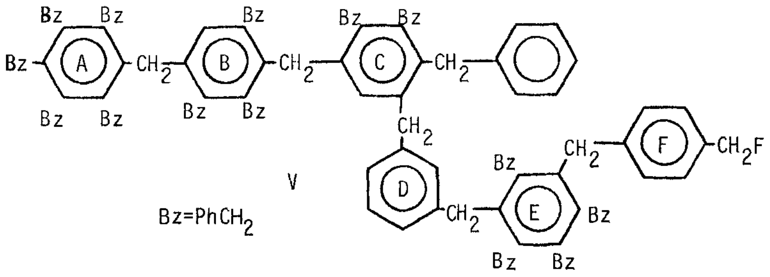
$(n_{max} = 12)$

$$(C_6H_5CH_2)_xC_6H_{5-x}CH_2[(C_6H_5CH_2)_yC_6H_{4-y}CH_2]C_6H_4CH_2Cl$$

IV

The unit in brackets can be substituted for one or more of the phenyl hydrogens.

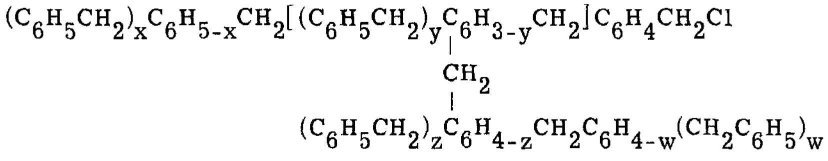
it becomes a polysubstituted structure for $x > 1$. For the idealized structure (II) fully substituted in one ring, the maximum degree of polymerization (n_{max}) is 7. In this generalized structure it is assumed that polysubstitution occurs preferentially in the alkyl-substituted ring rather than in the CH_2Cl-substituted ring because of deactivation of this ring to electrophilic substitution by the CH_2Cl group. Analogously, in the homologous structure III, $n_{max} = 12$. In the more generalized homolog, IV, the group in brackets can be substituted for one or more of the phenyl hydrogens leading to higher values for n. It should be emphasized that all of these structures (II-IV) have a linear structure based on a benzyl backbone polymer. This includes the type of structure (V) postulated by Haas et al. [6],



V

Bz=PhCH$_2$

in which the benzyl groups are pendant groups from a linear polybenzyl backbone (A-B-C-D-E-F). If substitution occurs on one or more of the phenyl groups in the bracket, a branched structure results, for example, VI, as a simple case.



$$\begin{array}{r} (C_6H_5CH_2)_xC_6H_{5-x}CH_2[(C_6H_5CH_2)_yC_6H_{3-y}CH_2]C_6H_4CH_2Cl \\ CH_2 \qquad\qquad\qquad\qquad\qquad\quad \\ (C_6H_5CH_2)_zC_6H_{4-z}CH_2C_6H_{4-w}(CH_2C_6H_5)_w \end{array}$$

VI

The fact that the protons of the polymer fall into three distinct groups which are clearly separated in the ^{1}H-NMR spectra, makes it possible to determine the average degree of polymerization (n). The chemical shifts for the two types of polymers are listed in Table 1 with the corresponding relative areas of the peaks. Equations to relate n to the relative areas are derived as follows.

If it is assumed that all polymer units terminate with a CH_2Cl group, then the relative areas of the CH_2Cl protons at 4.38 δ and the other CH_2 protons (3.78, 3.74 δ) can be used in calculating n. In a similar way, the ratio of CH_2Cl to aromatic protons (6.98, 6.96 δ) can be used or the ratio of CH_2Cl protons to the sum of other CH_2 + aromatic protons. The equations for these are given as 2-4, respectively. In these equations, n = average degree of polymerization, and A_{CH_2Cl}, $A_{CH_2Ar_2}$, and A_{ArH} are the relative areas of the peaks designated.

$$n - 1 = A_{CH_2Ar_2}/A_{CH_2Cl} \tag{2}$$

$$(4n + 1)/2 = A_{Ar-H}/A_{CH_2Cl} \tag{3}$$

$$(6n - 1)/2 = (A_{CH_2Ar_2} + A_{ArH})/A_{CH_2Cl} \tag{4}$$

The results of calculations of the average degree of polymerization based on Eqs. (2)-(4) are in Table 2. The values for polybenzyl from benzyl salicylate and benzyl chloride ($AlCl_3$) of 6 and 10-11, respectively, are in agreement for the three equations within experimental error. In comparison, Geller et al. [2] reported average degrees of condensation up to 4 for polybenzyl obtained from zinc chloride-catalyzed polycondensation of benzyl chloride under various conditions. They also correlated their data with refractive index and chlorine content although, it is not reported what solvent was used for the refractive index data.

As indicated, the values in the present work depend on the assumption that the CH_2Cl group is present in all of the polymer molecules.

TABLE 1. Chemical Shifts and Relative Areas of ^{1}H-NMR Peaks of Polybenzyl Polymers

Proton group	Chemical shift (δ)[a]		
	Benzyl chloride	Polybenzyl from benzyl salicylate	Polybenzyl from $AlCl_3$/benzyl chloride
$C\underline{H}_2Ar_2$	-	3.78	3.74
		(0.83)	(0.91)
$ArC\underline{H}_2Cl$	4.41	4.38	4.38
	(1.0)	(0.17)	(0.09)
$Ar\underline{H}$	7.25	6.98	6.96
	(2.52)	(2.09)	(2.05)

[a] Chemical shifts in δ units from tetramethylsilane in carbon tetrachloride solution; relative areas in parentheses.

TABLE 2. Average Degree of Polymerization (n) for Polybenzyl Polymers Calculated from ^{1}H-NMR Spectra

Equation	Degree of polymerization n	
	Polybenzyl from benzyl salicylate	Polybenzyl from $AlCl_3$/benzyl chloride
(1)	5.9	11
(2)	5.6	10
(3)	5.9	11

The possibility that some of the polymer chains might be terminated by anthracene groupings can be considered. Friedel and Crafts [8], in fact, originally studied the aluminum chloride-catalyzed self-condensation of benzyl chloride as a potential synthesis of dihydroanthracene. Montaudo et al. [9, 10] suggested termination by an anthracene unit on the basis of their IR and UV studies, and Finocchiaro and Passerini [11] pointed out that the degree of anthracene formation depended on the temperature of polymerization. Kuo and Lenz [1] reported that under reaction conditions where high degrees of ortho substitution were found, polymers with substituted anthracene units were qualitatively formed according to UV spectroscopic analysis. They formulated the cyclization reaction as a termination step occurring between two polymer chains to form a dihydroanthracene link which presumably was converted to anthracene structures by dehydrogenation under polymerization conditions.

As has been pointed out [12], dihydroanthracene units would not be distinguishable in UV or IR spectra from the other substituted phenyl groups in the polymer. ^{1}H-NMR spectra of both dihydroanthracene and anthracene have been reported. The spectrum [13] of dihydroanthracene shows sharp singlets at 2.87 and 7.18 δ for CH_2 and aromatic protons, respectively. The spectrum of anthracene shows a singlet for the 9,10 (peri) hydrogens at 8.31 δ with a more complex pattern for the 1,2 hydrogens in carbon disulfide [14, 15] and 8.36 in carbon tetrachloride [16]. The corresponding peaks obtained in the present work for a saturated solution of anthracene in carbon tetrachloride were 8.42 δ for the 9,10 hydrogens with complex splitting for the 1 and 2 hydrogens centered at about 8.01 and 7.44 δ. No absorption peaks for anthracene were present in the ^{1}H NMR spectra of the polybenzyl polymers prepared in the present work within the limits of observation. The peaks for dihydroanthracene would probably occur at about the same positions for aromatic and methylene groups observed. It should be pointed out that the 9 and 10 hydrogens in substituted anthracene would no longer be magnetically equivalent and the same would hold true for the methylene hydrogens of dihydroanthracene.

If anthracene units are present in the ^{1}H-NMR spectra of polybenzyl polymers as indicated by absorption peaks for 9,10 hydrogens at about 8.3-8.4 δ, a correction can be made in the equations, since CH_2Cl groups are being converted into absorption at this position. Another method to do this would be to obtain the amount of anthracene units from UV spectra and then use this information to modify the equations.

Kan et al. [17] reported that benzyl chloride undergoes polymerization to dimers and trimers by heating without catalysts. By using deuterium-labeled benzyl chloride and infrared analysis, these workers found that the reaction occurs as 40% ring-substitution and the rest in the side chain. The relative amounts of substitution in the ring were reported at 1.0, 0.26, and 0.18 for para, ortho, and meta, respectively. They suggested that the product from side chain substitution had structure VII.

$$C_6H_5CH_2CHClC_6H_5$$

VII

No evidence for any of the side chain product appeared in the NMR spectra of the present work or by any other workers since the report by Kan et al., and it would appear that this type of structure is not obtained in the product obtained in the catalyzed condensations. Since only dimers or trimers were formed from uncatalyzed thermal condensation whereas an average degree of polymerization close to 6 was obtained from the benzyl salicylate reaction, it appears that the phenylphosphorodichloridate (I) functions as a mild catalyst for the condensation. This may have some value in that by modifying the structure of this organic catalyst to obtain various degrees of catalytic activity, changes in the structure of the polymer could be effected.

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