Macromolecules **1989,** *22,* 75–79

to obtain some of the ^{13}C NMR spectra is described in the literature.[7] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or on a Carlo Erba Strumentazione CHN Elemental Analyzer 1106. The size-exclusion chromatography measurements were performed on a Waters Associates GPC II instrument with a Nelson Analytical data handling system by using 500-, 10^4-, 10^5-Å μ Styragel columns. The SEC operating conditions consisted of a mobile phase of THF containing 0.1% $(n\text{-Bu})_4N^+Br^-$, a flow rate of 1.5 mL/min, a temperature of 30 °C, and a sample size of 0.05 mL of 0.1% solution. IR spectra were recorded as thin films on a Perkin-Elmer 283 infrared spectrometer. Differential scanning calorimetry (DSC) measurements were made on a Du Pont Model 910 instrument under nitrogen against an aluminum reference from 0 or −140 °C to 150 °C.

Synthesis. In a typical procedure, a three-necked round-bottom flask equipped with a magnetic stirrer, nitrogen inlet, and a septum was charged with 2.0 g (14.6 mmol) of $[Ph(Me)PN]_n$ and ca. 20 mL of dry THF. The solution was cooled to −78 °C and then *n*-BuLi (3.0 mL/2.5M) was added slowly via syringe. After the mixture was stirred for 1 h at −78 °C, a solution of benzaldehyde (0.80 mL, 7.9 mmol) in 20 mL of THF was added and the mixture was allowed to warm slowly to room temperature. After the reaction mixture was stirred at room temperature for at least 1 h, ca. 2 mL of a saturated solution of ammonium chloride was added to quench the alkoxide ion. This mixture was poured into H_2O and THF was removed on a rotary evaporator. The precipitated polymer was recovered from the water and was purified by dissolving in THF and reprecipitating into hexanes, a process that was repeated two times. The ferrocene derivatives were further purified by Soxhlet extraction with hexanes and ethanol. All polymers were dried overnight in a vacuum oven at 50 °C. The yields of the purified polymers were in excess of 82% based on the degree of substitution determined by integration of the ^{1}H NMR spectra. Analytical and SEC molecular weight data are listed in Table I and NMR spectroscopic data are given in Table II. The IR spectra of **1**–**7** exhibited a strong OH stretching vibration between 3280 and 3350 cm^{-1}.

Acknowledgment. We thank the United States Army Research Office for generous financial support of this project, Dr. John Banewicz for performing some of the elemental analyses, and Mary Alice Schaefer for assistance in the thermal analyses.

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An Ionically Cross-Linkable Polyphosphazene: Poly[bis(carboxylatophenoxy)phosphazene] and Its Hydrogels and Membranes[1]

Harry R. Allcock* and Sukky Kwon

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received February 12, 1988

ABSTRACT: Hexachlorocyclotriphosphazene and poly(dichlorophosphazene) react with the sodium salt of ethyl *p*-hydroxybenzoate to give small molecule cyclic and high polymeric phosphazenes with aryloxy ester side groups. The structures and physical properties of both classes of compounds were investigated by ^{31}P NMR, ^{1}H NMR, and infrared spectroscopies and by thermal analysis. Reaction of these compounds with potassium *tert*-butoxide brought about complete hydrolysis of the ester groups to yield aqueous media-soluble, carboxylic acid bearing cyclic and high polymeric phosphazenes. The carboxylic acid bearing high polymer formed ionic cross-links when treated in aqueous media with salts of di- or trivalent cations, such as calcium chloride, copper bromide, copper sulfate, or aluminum acetate, to yield hydrogels and membranes. Aluminum ions proved to be more efficient cross-linking reagents than the divalent cations. The cross-linked gels were stable in neutral or strongly acidic aqueous media, but the cross-linking process was reversed in basic aqueous solutions of excess monovalent cations.

Introduction

The design and synthesis of new macromolecules for the preparation of membranes is one of the major challenges of modern polymer chemistry. At present a variety of polymeric membranes are used in applications as diverse as gas separations, microfiltration, hyperfiltration, hemodialysis, electrodialysis, controlled drug delivery, and genetic engineering.[8–15] The need for new membrane materials in biomedical engineering is particularly acute.

The synthetic polymers that are currently used as membranes can be divided into two categories: (1) neutral polymers such as polyethylene, poly(methyl methacrylate),[12] poly(organosiloxanes), and cellulose[13] and (2) ionic polymers such as poly(acrylic acid),[14] sulfonated polystyrene,[14] and perfluorinated ionomers.[15] The consideration of a polymer for incorporation into membranes

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Scheme I

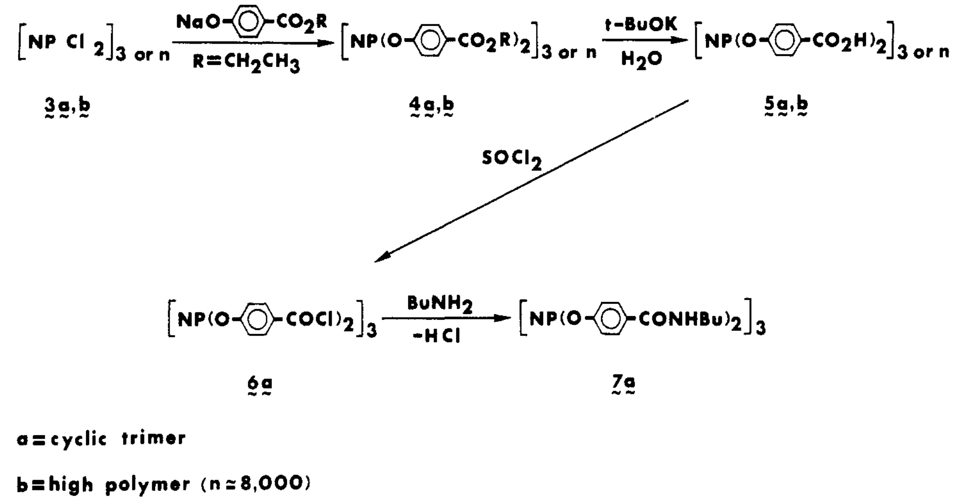


Table I

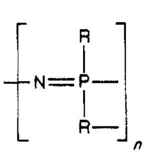
Characterization Data for Trimers and High Polymers

compd		analysis[a]				^{31}P NMR,[b] ppm	^{1}H NMR, ppm	IR, cm^{-1}
		% C	% H	% N	% Cl			
4a	calcd	57.4	4.79	3.73		singlet at +7.7	two doublets at 7.1–8.0	1710 (C=O)
	found	57.36	4.84	3.78	0.02		quartet at 4.3	1250 (P=N/P—O)
							triplet at 1.4	
5a	calcd	52.66	3.13	4.39		singlet at +9.0	two doublets at 6.9–7.7	2500–3500 (OH)
	found	52.80	3.21	4.31				1670 (C=O)
								1240 (P=N/P—O)
4b	calcd	57.53	4.79	3.73		singlet at −20.3	two doublets at 6.9–7.7	1710 (C=O)
	found	57.25	4.94	3.66	0.03		quartet at 4.2	1260 (P=N/C—O)
							triplet at 1.3	
5b	calcd	52.60	3.13	4.38		singlet at −19.4	two doublets at 7.0–7.8	2500–3500 (OH)
	found	52.68	3.17	4.35				1680 (C=O)
								1250 (P=N/P—O)

[a] Analytical data were obtained by Galbraith Labs., Knoxville, TN. [b] All samples were proton decoupled. Chemical shift positions were relative to aqueous 85% H_3PO_4. A D_2O capillary lock was used.

involves a subtle balancing of properties such as hydrophilicity, molecular weight, crystallinity, polarity, mechanical strength, and the solvation-type affinity between specific polymers and small molecule solutes or gas molecules. In these terms, the tailoring of sophisticated membrane systems is still in its infancy.

In previous studies, we have shown how the macromolecular substitutive synthesis of poly(organophosphazenes) (1) allows the properties of these polymers to be varied over a wide range by the incorporation of different substituent groups (R).[16,17]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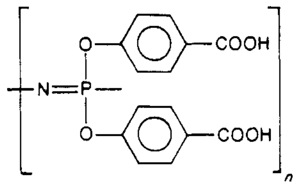


2

These property changes can be orchestrated with great subtlety both by varying the R group in single-substituent polymers and by the use of two or more cosubstituent groups attached to the same chain. In this way individual polymers may be hydrophobic, amphiphilic, or hydrophilic; water-stable or water-erodable; crystalline or amorphous; or bioinert or bioactive. In recent publications,[5-7] we have developed methods for the radiation cross-linking of specific polyphosphazenes in order to optimize their behavior as membranes or hydrogels.

In this paper we discuss an alternative method for the formation of cross-links, particularly cross-links that can be broken readily by a change of pH in aqueous media. The approach involved the development of a new method for the synthesis of phosphazenes with carboxylic acid units in the para positions of aryloxy groups attached to a phosphazene chain (2). This polymer is soluble in basic aqueous media. Like poly(acrylic acid),[18] polymer 2 cross-links in the presence of di- or trivalent cations, and this process has been used to form hydrogels and membranes that can be resolubilized by exchange of cations.

Results and Discussion

Model Reactions with Cyclic Trimers. The synthesis route chosen for the introduction of carboxylic acid containing side groups involved the reaction of the sodium salt of ethyl *p*-hydroxybenzoate with poly(dichlorophosphazene), $(NPCl_2)_n$, followed by hydrolysis of the ester function to the carboxylic acid. Previous experience indicated that the reaction conditions chosen for both steps would be critical and that the exploration of such conditions could be best carried out first at the small molecule level rather than with the high polymer.[19] Hence, preliminary studies were performed with the use of the phosphazene cyclic trimer, $(NPCl_2)_3$, as a model for the high polymer.

The overall reaction is shown in Scheme I. Thus, at the cyclic trimer level, hexachlorocyclotriphosphazene (**3a**) was allowed to react with the sodium salt of ethyl *p*-hydroxybenzoate to form the ester-type aryloxyphosphazene, **4a**. The structure of this compound was confirmed by elemental analysis (see Table I) and by NMR and infrared spectroscopy. For example, the ^{31}P NMR spectrum showed a singlet at +7.7 ppm, and the ^{1}H NMR spectrum consisted of two doublets at +7.1 to +8.0 ppm (aromatic protons), a quartet at +4.3 ppm (methylene protons), and a triplet at +1.4 ppm (methyl protons). The infrared spectrum contained a C=O stretch at 1710 cm^{-1} and a P=N/P—O combination band at 1250 cm^{-1}.

Hydrolysis of **4a** to the carboxylic acid was attempted by several methods, including acidic hydrolysis with hydrochloric acid in tetrahydrofuran or with *p*-toluenesulfonic acid or basic hydrolysis with sodium hydroxide. These attempts failed to give the hexacarboxylic acid derivative without decomposition of the skeleton. However, the use of potassium *tert*-butoxide[20] brought about a clean hydrolysis of **4a** to **5a**. The structure of **5a** was verified by elemental analysis, NMR, and infrared techniques (see Table I) and by derivatization of the carboxylic acid units.

Thus, compound **5a** was treated with thionyl chloride to form the acid chloride (**6a**), and this reacted with *n*-butylamine in the presence of triethylamine to give the *n*-butylamido derivative, **7a**. The structure proof for this compound was based on the following data. First, the conversion of **4a** to **5a** and **6a** was accompanied by a disappearance of the infrared OH stretching bands but a retention of the skeletal P=N/P—O band at 1250 cm^{-1}. The ^{31}P NMR spectrum of **7a** in methylene chloride consisted of a singlet at +8.45 ppm. The ^{1}H NMR spectrum included two doublets at +7.0 to +8.45 ppm (aromatic protons), a quartet at +3.3 ppm (NH-CH_2), a multiplet at +1.3 to +1.8 ppm ($NHCH_2CH_2CH_2CH_3$), and a triplet at +0.9 ppm (CH_3). The survival of the phosphazene ring throughout these side-group transformations was considered to be favorable evidence that the same reactions might be feasible at the high polymeric level.

High Polymer Reactions. Poly(dichlorophosphazene) (**3b**) was allowed to react with the sodium salt of ethyl *p*-hydroxybenzoate to form the (aryloxy)phosphazene ester, **4b**. Polymer **4b** is a microcrystalline, flexible, film-forming material with a glass transition temperature of +7.5 °C and a T_m of 127.4 °C. The molecular weight of **4b** was estimated by gel permeation chromatography to be in the region of 3×10^6. In solid-state properties and in appearance, polymer **4b** is similar to poly(diphenoxyphosphazene), $[NP(OC_6H_5)_2]_n$.[21,22]

Hydrolysis of **4b** to the carboxylic acid derivative, **5b**, was accomplished with potassium *tert*-butoxide with the use of reaction conditions similar to those established for the cyclic trimer. Polymer **5b** was isolated as a white powder that was insoluble in acidic or neutral aqueous media but soluble in aqueous base. The structures of polymers **4b** and **5b** were deduced from a combination of microanalysis, ^{31}P NMR, and infrared data (see Table I). For example, after the hydrolysis, the ^{31}P NMR spectrum of **5b** consisted of a clean singlet at −19.4 ppm. The ^{1}H NMR spectrum of **5b** showed that the quartet at 4.3 ppm and the triplet at 1.4 ppm (C_2H_5 groups) had disappeared, but the aromatic protons at 6.8–7.7 ppm remained. Conversion of the ester (**4b**) to the carboxylic acid (**5b**) brought about a slight lowering in the T_g to −4.7 °C.

Cross-Linking of Polymer 5b. Unlike the water-soluble polymers studied previously in which methylamino,[5] methoxyethoxyethoxy,[7] or protected glyceryl[6] side groups were attached to a phosphazene ring, polymer **5b** did not cross-link when exposed to γ radiation. This difference is ascribed to the availability of aliphatic carbon–hydrogen bonds in the first three polymers and their absence in **5b**. Attempts to cross-link **5b** by chemical condensation of the carboxylic acid groups with di- or trifunctional reagents, such as diamines or glycerol, were impeded by experimental difficulties.[23]

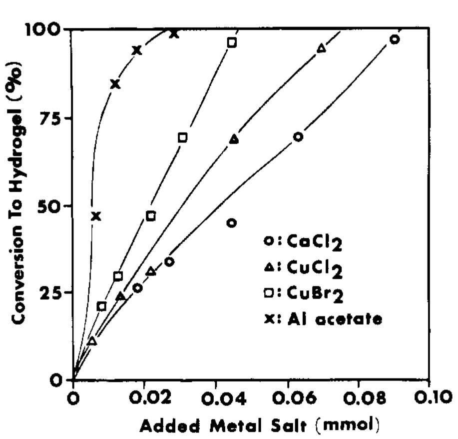
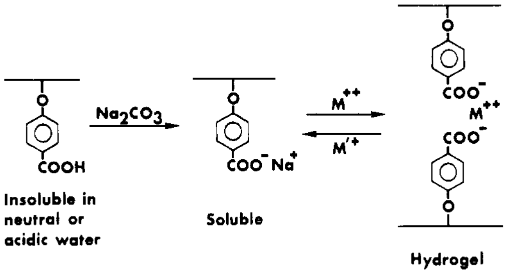


Figure 1. Fraction of ionically cross-linked polymer (hydrogel) formed by the interaction between $[NP(OC_6H_4COOH)_2]_n$ (**5b**) and metal salts in water. The percentage conversion to cross-linked polymer was estimated from the weight of recovered, un-cross-linked polymer.

Scheme II



However, it was found that polymer **5b** underwent facile cross-linking in aqueous media when treated with salts of di- or trivalent cations, such as calcium, copper, or aluminum. The amount of water-swelled, cross-linked polymer formed increased as the concentration of calcium chloride, copper chloride, copper sulfate, or aluminum acetate was increased. Figure 1 illustrates the relative effectiveness of the different salts in bringing about total gelation of the system. The markedly greater effectiveness of aluminum ion can be attributed to its trivalent character. In these experiments, Cu^{2+} appeared to be a more effective cross-linking agent than Ca^{2+}, perhaps because cupric ion has a higher preference for octahedral coordination than does the Ca^{2+} ion or because of the greater Lewis acidity of Cu^{2+} that results from its smaller radius. Thus, the cross-linking process can be understood in terms of "salt bridges" between the chains, as shown in Scheme II. The hydrogels and membranes formed by this process were soft, highly swollen materials. An aluminum ion cross-linked example was found to contain 9.5 g of water for every 1 g of polymer.

The cross-linking process could also be effected by immersion of solid films of polymer **5b** into aqueous solutions of, for example, copper sulfate. Instead of dissolving, the polymer film swelled as water penetrated the matrix, but the swelling was limited by the diffusion of cupric ions into the polymer.

Ionically cross-linked gels formed by both processes were stable in acidic and neutral media. However, treatment with basic solutions of monovalent cations resulted in cleavage of the ionic cross-links and dissolution of the polymer. This occurred at pH 7.5 for systems cross-linked by Ca^{2+} or Cu^{2+} ions, but the Al^{3+} cross-linked systems required base strengths in excess of pH 9 before the polymer dissolved. Treatment of the Ca^{2+}, Cu^{2+}, and Al^{3+} cross-linked polymers with excess aqueous potassium chloride at pH 7.5 also resulted in cleavage of the ionic cross-links.

Experimental Section

Equipment. The ^{31}P NMR spectra were obtained in the Fourier transform mode with a JEOL FX90Q NMR spectrometer. The ^{1}H NMR spectra were obtained with the same spectrometer operated at 90 MHz. Infrared spectra were recorded by means of a Perkin-Elmer 580 spectrometer. Gel permeation chromatography was carried out with the use of a Hewlett-Packard HP1090 liquid chromatograph with an HP1037A refractive index detector, an HP3329A integrator, and an HP9121 disk drive. The system was controlled by a Hewlett-Packard HP83B computer. A polarizing optical microscope was used to check for crystallinity. Glass transition temperatures (T_g) were recorded with the use a Perkin-Elmer DSC 7 instrument with a PE7500 computer.

Materials. Tetrahydrofuran (VWR), dioxane (VWR), and diethyl ether (VWR) were freshly distilled under nitrogen from sodium benzophenone ketyl. Hexachlorocyclotriphosphazene (mp 110–113 °C) was obtained from a tetramer–trimer mixture (Ethyl Corp.), which was purified by two fractional vacuum sublimations at 60 °C/0.5 Torr, two recrystallizations from hexane, and two further vacuum sublimations. Poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C.[22] Ethyl *p*-hydroxybenzoate (Aldrich) was purified by recrystallization from methylene chloride and hexane. Triethylamine (Aldrich) and *n*-butylamine (Sigma) were purified by vacuum distillation in the presence of calcium hydride, and the distilled amines were stored over molecular sieves before use. Potassium *tert*-butoxide (Aldrich), *p*-toluenesulfonic acid (Aldrich), hydrochloric acid (Fisher), thionyl chloride (Aldrich), copper sulfate (Sigma), glycerol (Aldrich), sodium spheres (Aldrich), sodium hydroxide (Fisher), dimethyl sulfoxide (Aldrich), calcium chloride (Aldrich), copper chloride (Aldrich), copper bromide (Sigma), and aluminum acetate (Aldrich) were used as received.

Preparation of Compound 4a. Sodium spheres (1.99 g, 0.084 mol) were added to 150 mL of dry dioxane. To the suspension was added ethyl *p*-hydroxybenzoate (18.7 g, 0.112 mol) dissolved in dry dioxane (30 mL), and the mixture was stirred at reflux for 10 h. To this sodium salt solution was slowly added compound **3a** (2.5 g, 7.2 mmol), followed by the addition of tetra-*n*-butylammonium bromide (0.4 g) to assist complete substitution. The reaction mixture was then stirred at reflux for 72 h. The ^{31}P NMR spectrum of the solution showed a singlet at +7.7 ppm. The solution was filtered through a 1-in. layer of silica gel, and the solvent was removed by evaporation. The compound was purified by column chromatography with an eluent mixture of methylene chloride and THF (9:1). After drying under vacuum, a bright yellow solid (**4a**) (82%), mp 78–80 °C, was obtained.

Preparation of Compound 5a. Potassium *tert*-butoxide (4.43 g, 0.043 mol) was suspended in 100 mL of dry ether. This mixture was cooled to 0 °C, and 0.2 mL (0.11 mol) of water was added via syringe. After 5 min of stirring at 0 °C, compound **4a** (0.5 g, 0144 mmol) was added. The ice bath was removed, and the mixture was allowed to react at room temperature. Thin-layer chromatography tests showed that the starting compound had disappeared completely after 20 h. A large excess of ice water was then added, and the aqueous layer was separated. The isolated aqueous solution was acidified with hydrochloric acid. After three ether extractions, water was removed by evaporation, and the final product was dried overnight under vacuum. A white solid (**5a**) was obtained (yield 62%). This compound did not melt below 275 °C.

Preparation of Compound 6a. Thionyl chloride (10 mL) was added to compound **5a** (22 mg, 0.21 mmol). The mixture was heated to reflux and the powder dissolved completely after 1 h. After an additional 1 h, the solution was cooled and the excess thionyl chloride was removed by vacuum drying. The product dissolved in dry THF, was filtered under nitrogen, and was dried overnight under vacuum.

Preparation of Compound 7a. Compound **6a** (100 mg, 0.1 mmol) was dissolved in dry THF (20 mL). To the solution was added an excess of *n*-butylamine (5 mL, 0.068 mol), followed by triethylamine (1 mL) as a hydrochloride acceptor. The mixture was stirred at room temperature for 24 h. The residual amines were removed by evaporation under vacuum to yield **7a**, mp 194–197 °C.

Preparation of Polymer 4b. Poly(dichlorophosphazene) (**3b**) (4 g, 0.0345 mol) was dissolved in dry dioxane (200 mL). The solution was added slowly to the sodium salt of ethyl *p*-hydroxybenzoate (29.8 g, 0.1794 mol). Tetra-*n*-butylammonium bromide (0.5 g) was added as a phase-transfer catalyst. The reaction mixture was stirred at reflux for 48 h. A ^{31}P NMR spectrum contained a singlet at −20.3 ppm. The solution was allowed to cool, and the polymer was isolated by precipitation into water. The polymer was purified by further reprecipitations from THF into water (3 times) and into hexane (twice). The yield was 85%.

Preparation of Polymer 5b. Polymer **4b** (0.5 g, 1.33 mmol) was dissolved in dry THF (20 mL). The solution was added slowly to a mixture of potassium *tert*-butoxide (4 g, 0.04 mol) and 0.2 mL (0.011 mol) of water in dry THF (100 mL). For the first 5 min the mixture was cooled to 0 °C; it was then stirred at room temperature for 40 h. A large excess of ice water (300 mL) was added, and the solution was concentrated by evaporation. The solution was dialyzed through a cellulose tube against deionized water. After dialysis for 72 h, the polymer was isolated by acidification of the solution with hydrochloric acid. The beige-colored polymer was obtained after centrifugation and vacuum drying (yield 85%).

Ionic Cross-Linking Reactions with Polymer 5b. Polymer **5b** (20 mg, 0.063 mmol) was dissolved in 0.2 mL of sodium carbonate solution (6 mg). To separate polymer solutions were added various concentrations of four different metal salts (CaCl$_2$, CuCl$_2$, CuBr$_2$, and aluminum acetate) in aqueous solutions (0.006–0.09 mmol). The solutions were stirred for 1 min to produce the cross-linked gels. The soluble portion was collected and precipitated by acidification with hydrochloric acid. The un-cross-linked polymer was then isolated by centrifugation, washing, and drying under vacuum. The weight of the cross-linked portion was estimated from the weight of the unreacted polymer. The water swellability of the gels was calculated by weighing the fully swelled gel followed by drying under vacuum for 36 h and reweighing the dry gel.

Cross-Linking of Polymer Films. Polymer **5b** (100 mg, 0.31 mmol) was dissolved in dimethyl sulfoxide (5 mL). The solvent was removed slowly by evaporation in a dry casting chamber in order to form a uniform and thin film. The dried polymer was then immersed in a solution of copper sulfate (5 g) in 100 mL of water and allowed to swell to the maximum allowed by this cross-linking process. The film was removed from the copper sulfate solution and dried overnight under vacuum.

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Registry No. **3a**, 940-71-6; **4a**, 84942-83-6; **5a**, 69322-61-8; **7a**, 116374-59-5; $4\text{-NaOC}_6\text{H}_4\text{CO}_2\text{CH}_2\text{CH}_3$, 35285-68-8; CaCl$_2$, 10043-52-4; CuCl$_2$, 7447-39-4; CuBr$_2$, 7789-45-9; Al acetate, 139-12-8.

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(23) The difficulty encountered in the isolation of covalently cross-linked systems after treatment with diamines is due to the limited choice of suitable solvents and the fact that, in solvents such as dimethyl sulfoxide, salt formation precedes covalent coupling. Condensation cross-linking with diols or triols in the presence of dicyclohexylcarbodiimide is difficult to accomplish because of the persistent presence of traces of water in the reactants.

Novel Melt-Processable Poly[(acyloxy)aloxane] as Alumina Precursor

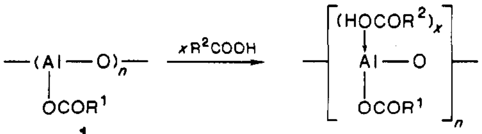
Yoshiharu Kimura,* Masaya Furukawa, Hideki Yamane, and Toshio Kitao

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Kyoto 606, Japan. *Received January 6, 1988*

ABSTRACT: A poly[(acyloxy)aloxane] with both *n*-dodecanoic acid (DA) and 3-ethoxypropanoic acid (EPA) ligands was prepared by the sequential reaction of triethylaluminum (TEA) with DA, water, and EPA, respectively. The hydrolytic polymerization of the first-stage product, diethyl(dodecanoato)aluminum, yielded a less soluble cross-linked oligomer of poly[(dodecanoyloxy)aloxane] (PDA). Further reaction with EPA afforded soluble thermoplastics of poly[(acyloxy)aloxane] with DA and EPA mixed ligands. The viscosity of the polymers was found to be dependent on the EPA to TEA ratio when the DA to TEA ratio was kept at unity. The maximum inherent viscosity, 0.58 dL/g, was observed at an EPA to TEA ratio of 0.8. The structure of these polymers was confirmed by ^{27}Al NMR, as well as other spectroscopic techniques and elemental analyses. The hexacoordination states of the aloxane, characteristic of the polymers, were due to the chelation of both the carboxylate and carboxyl groups of DA and EPA. Even for the products with less than 1.0 molar ratio of EPA per repeat unit, the ethoxy group of EPA also participates in the coordination. Since the polymers melted at ca. 200 °C, they could be melt–spun into thin fibers with a ram extruder having an orifice of 0.5 mm in diameter. Both spinnability and the quality of the filaments obtained were found to be best for the polymer with an EPA to TEA ratio of 0.8, whose molecular weight was higher than that of the other polymer samples. The as-spun fibers of this polymer were annealed at 160 °C in a flow of air and then pyrolyzed in a flow of nitrogen from 160 to 700 °C. Above 700 °C the flow was changed to air again, and the fiber was sintered up to 1400 °C. In the course of this multistep pyrolysis the fiber was subjected not only to shrinkage but also to the phase transition of alumina. Hence, the physical properties and the morphology of the fiber were greatly dependent on the pyrolysis temperature. The highest strength and modulus of the sintered fiber were 520 MPa and 48 GPa, respectively. These values ought to increase upon suppression of the abrupt phase transitions. On the bases of these data, poly[(acyloxy)aloxane] with DA and EPA mixed ligands was proven to be versatile as a melt-processable preceramic polymer for alumina.

Introduction

Poly[(acyloxy)aloxane] **1** consists of an Al–O backbone and carboxylate side group. The aluminum can be "properly coordinated" by an appropriate amount of carboxylic acid (eq 1), with the hexacoordination state of the aloxane unit as accomplished in **2**.[1,2] This poly[(acyloxy)aloxane] with carboxy ligands, **2**, becomes more soluble, higher in molecular weight, and better in solution processability than the original polymer **1**. With **2** as a preceramic polymer, the preparation of high-performance alumina fiber has been demonstrated.[1] However, **2** was not melt-processable like other alumina preceramic polymers reported so far,[3] and much effort was necessary in making the precursor fiber with good quality. In this paper we report a novel poly[(acyloxy)aloxane] **2c** with melt-processability and for which a high efficiency in spinning is obtained.



$$-\underset{\underset{\textstyle OCOR^1}{|}}{(Al}-O)_n- \xrightarrow{x R^2COOH} -\left[\begin{matrix}(HOCOR^2)_x\\ \downarrow\\ Al-O\\ |\\ OCOR^1\end{matrix}\right]_n- \qquad (1)$$

1

2a, $R^1 = R^2 = CH_2CH_2OEt$
2b, $R^1 = R^2 = (CH_2)_{10}CH_3$
3c, $R^1 = (CH_2)_{10}CH_3$, $R^2 = CH_2CH_2OEt$

The principle of molecular design for such melt-processable poly[(acyloxy)aloxane] can be explained with the aid of the two derivatives of the series discussed below. One derivative is poly[(3-ethoxypropanoyl)oxy)aloxane], **2a**, having the 3-ethoxypropanoic acid (EPA) ligand to monomer ratio of 0.5,[1] and the other derivative is poly[(*n*-dodecanoyloxy)aloxane], **2b**, having one *n*-dodecanoic acid (DA) per repeat unit.[4] The former is characterized by a good dry-spinnability of its solution, and the latter, having a longer alkyl chain, is characterized by a thermoplastic property despite its poor spinnability. As both characteristics can be attributed to their own ligands, a

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