Adhesion of the [Tetrakis(salicylidene)diaminobenzidine]zirconium Coordination Polymer to Silica and Alumina[1,2]

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The [tetrakis(salicylidene)-3,3'-diaminobenzidine]zirconium coordination polymer adheres very strongly to both silica and alumina surfaces. Hydrolyzed zirconium end groups appear to provide the strong adhesion required. This conclusion is based on adhesion studies with analogous oligomers with varied end-group composition. The studies show a correlation between the adhesion and the zirconium end-group concentrations. Furthermore, end-capped oligomers and polymers do not adhere to these surfaces. The alumina adhesion has been studied by sol-gel coatings on glass slides.

Introduction

Zirconium long-chain carboxylates,[4] branched zirconium alkoxy,[5] and zirconium pyrophosphate[6] groups have been coupled to silica, alumina, and/or aluminum (which is equivalent to alumina because the surface of aluminum is coated with alumina) using easily displaceable groups also coordinated to the zirconium(IV). However, *all* of the zirconium ligands of the previous studies were either monodentate or bidentate ligands, and such species with one negative charge are known to be quite labile.[7,8] More highly chelated ligands [such as the tetradentate Schiff base ligands in the zirconium coordination compounds and coordination polymers reported from our laboratory[9-11]] should provide appreciably more inert coupling between the surfaces and polymer matrices. A representation of the structure of a typical zirconium Schiff-base short-chain polymer (oligomer) used in this study is shown in Figure 1. The series of short-chain $[Zr(tsdb)]_n$ oligomers, where $tsdb^{4-}$ is the anion of *N,N',N'',N'''*-tetrakis-(salicylidene)-3,3'-diaminobenzidine, **1**, with different end-group ratios (cf. Table I) have been used to compare relationships between end groups and surface coupling. The relative concentrations of the $[Zr(tsdb)]_n$ oligomers remaining on the silica and alumina substrates after thorough washings were determined using the optical densities of the 400-nm charge-transfer absorption band[10] and the lengths and compositions of the oligomer chains.

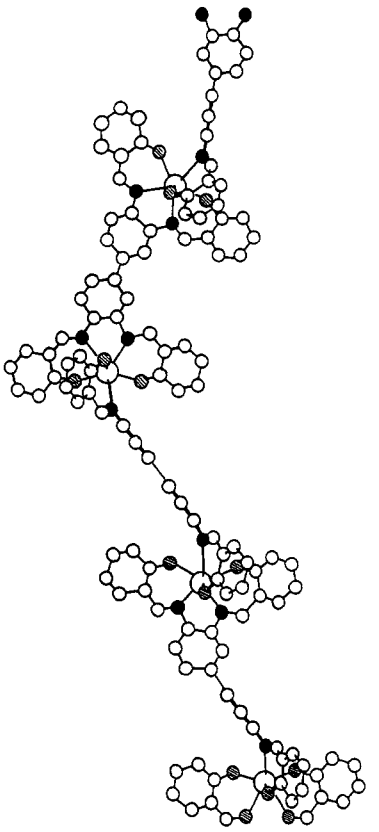

Figure 1. Structure of $[Zr(tsdb)]_n$ polymer[10] based on X-ray structure of monomeric model $[Zr(dsp)_2]$.[11] The large circles represent Zr, the small white circles represent C, the black circles represent N, and the striped circles represent O. For clarity, the H atoms and the portion of the eight-coordinate structure below the plane of the horizontal coordinating ligand are not shown.

Qualitative adhesion information had also been obtained by coating aluminum metal strips with the zirconium oligomers and studying the surfaces with near-UV reflectance spectrophotometry and with X-ray photoelectron spectroscopy (XPS).[2] And although our interest was in

(1) Preliminary reports on this work have been previously communicated: Wang, B.; Archer, R. D. *Polym. Mater. Sci. Engr.* **1988**, *59*, 120; **1989**, *60*, 710.
(2) Taken in part from: Wang, B. Ph.D. Dissertation, University of Massachusetts, Amherst, 1989.
(3) Current address: Dental Products Laboratory, 3M Center Bldg., St. Paul, MN 55144.
(4) Calvert, P. D.; Lalanandham, R. P.; Walton, D. R. M. *Adhesion Aspects of Polymeric Coatings*; Mittal, K. L., Ed.; Plenum Press: New York, 1983; p 457.
(5) Monte, S. J.; Sugerman, G. U.S. Patent No. 4,623,738, 1986.
(6) Monte, S. J.; Sugerman, G. U.S. Patent No. 4,634,785, 1987.
(7) Taube, H. *Chem. Rev.* **1952**, *50*, 69, specifically pp 83 and 97.
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(9) Archer, R. D.; Illingsworth, M. L.; Hardiman, C. J.; Rau, D. L. *Macromolecules* **1985**, *18*, 1371.
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(12) Brusasco, R.; Kershaw, R.; Saglio, J.; Dwight, K.; Wold, A. *Mater. Res. Bull.* **1986**, *21*, 301.
(13) Yoldas, B. E. *Am. Ceram. Soc. Bull.* **1975**, *54*, 289.
(14) Yoldas, B. E. *Appl. Opt.* **1980**, *19*, 1425.

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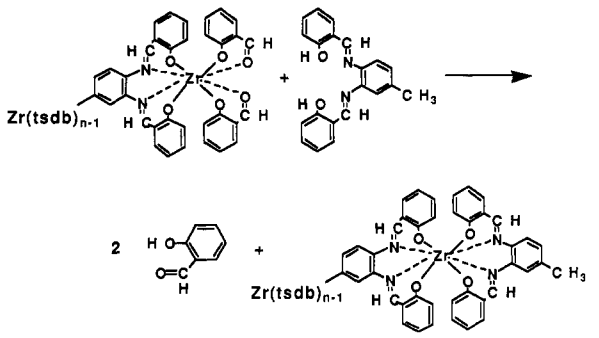
Table I. $[Zr(tsdb)]_n$ Oligomers for Surface Adhesion Studies

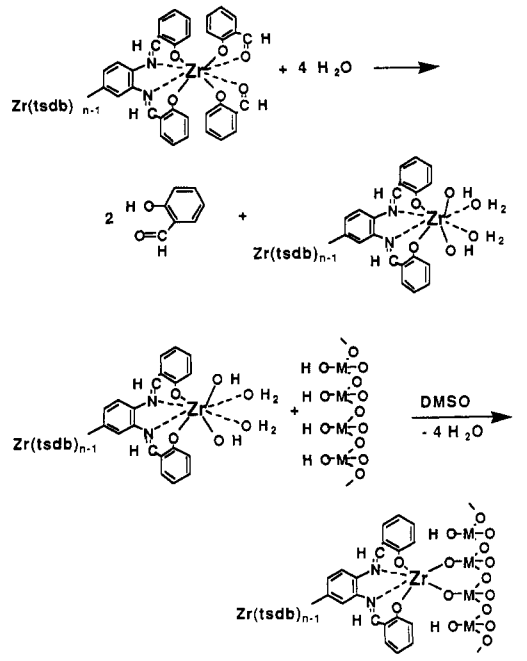
Zr(sal)$_4$:db	% Zr ends[a]	DP[a]	Zr/chain[b]
1.00:1.20	16	7.6	3.5
1.00:1.10	25	10.8	5.2
1.00:1.00	50	23.2	11.6
1.10:1.00	75	10.8	5.6
1.20:1.00	84	7.6	4.1

[a] Percent Zr end groups and average degree of polymerization (DP) based on extent of reaction (cf. ref 5). [b] Average Zr groups per chain based on DP and percentage of Zr end groups.

Scheme I



Scheme II



the adhesion of the zirconium oligomers to the usual alumina coatings on aluminum metal, transparent alumina substrates on glass plates have been prepared by a sol–gel process[12–14] in order to obtain more quantitative alumina adhesion results via UV–visible transmission spectra similar to those obtained for silica.

End-capped oligomers without hydrolyzable Zr end groups (Scheme I) were compared with the regular non-capped $[Zr(tsdb)]_n$ oligomers by the scribe-stripping test[15] in order to test our hypothesis that hydrolyzable Zr end groups were responsible for the observed adhesion (Scheme II).

(15) Tooke, W. J., Jr.; Montalvo, J. R. *J. Paint Technol.* **1966**, *38*, 18.
(16) Chiang, C.-H.; Ishida, H.; Koenig, J. L. *J. Colloid Interface Sci.* **1980**, *74*, 396.

Table II. Reaction Time vs Optical Density for $[Zr(tsdb)]_n$ Coatings on Silica and Alumina

	optical density[b]	
time[a]	silica {4.1×10^{-4} M $[Zr(tsdb)]_n$}	alumina {5.8×10^{-4} M $[Zr(tsdb)]_n$}
3	0.0043	0.0078
5		0.0100
7		0.0243
8	0.0130	
10		0.0288
12	0.0169	
20	0.0199	0.0297
40	0.0226	0.0314
80	0.0217	0.0282
160	0.0222	0.0294

[a] Minutes in contact with 60 °C DMSO solution of oligomer [DP = 23, 50% Zr end groups] before thorough washing. [b] Optical density at 400 nm.

Experimental Section

Zirconium Species. The zirconium oligomers were prepared by the condensation of tetrakis(salicylaldehydato)zirconium(IV) with 3,3′-diaminobenzidine as previously reported.[10] By modification of the mole ratios of the reactants, short-chain oligomers were prepared with different end-group compositions (see Table I). End-capped oligomers were prepared by the addition of *N,N′*-disalicylidene-3,4-diaminotoluene (dst), **2**, to freshly prepared oligomer samples prior to exposure to air as previously reported.[5]

Solvents. Reagent-grade acetone, dichloromethane, hydrogen peroxide, sulfuric acid, and nitric acid were used directly from freshly opened bottles. Dimethyl sulfoxide was dried with BaO followed by distillation over CaH_2.

Substrates. Microscope cover-glass plates, used as silica substrates, were degreased by a thorough scrubbing and rinsing with reagent-grade methylene chloride. After evaporation of the methylene chloride, the plates were suspended in a 1% solution of 30% aqueous H_2O_2 in concentrated H_2SO_4 for at least 2 h and were then thoroughly washed with distilled water and dried in vacuo overnight at 100 °C. When any spots or streaks still existed, the cleaning procedure was repeated.

Transparent alumina films on glass were prepared by the sol–gel method. The aluminum alkoxide sols were prepared by a modification of the procedures reported previously by Brusasco et al.[12] and by Yoldas.[13,14] This modified procedure allows thinner films than those obtained by Brusasco et al.[12] and avoids the balling-up problem observed by Yoldas.[14] Under argon, 13.5 g (ca. 13.9 mL) of aluminum *sec*-butoxide was transferred into a 200-mL round-bottom flask containing a Teflon stirring bar and fitted with a reflux condenser. Then 70 mL of distilled water was carefully added to the flask, and the contents of the flask were brought to boiling with stirring. After 30 min under reflux conditions, 0.8 mL of concentrated nitric acid (15 M) was added and refluxing was continued for an additional 30 min. After brief cooling, the reflux condenser was replaced with a distillation head, a condenser, and receiver. Distillation of *sec*-butyl alcohol from the sol was continued until the distillate reached a temperature of 100 °C, by which time all of the butyl alcohol had been removed. Next, 50 mL of hot water (about 80 °C) was added to the sol and a few drops of concentrated nitric acid was added to keep the pH of the sol at ca. 3.7. The sol was poured into a 200-mL beaker in a constant-temperature bath in order to keep the temperature at 80 °C during the coating process. Well-cleaned cover-glass plates (see above) were heated to 100 °C in an oven before they were dipped into the sol. As soon as the glass plates were coated with the alumina sol, the alumina-substrate covered plates were put into an oven at 400 °C for 4 h under air. The thickness of the alumina coatings prepared in this manner are about 10 000 Å (1 μm) as measured with an interferometer.

Surface Adhesion Studies. The experiments were conducted by dipping the substrates (the glass plates or sol–gel covered glass plates) into 8 mL of a hot (60 °C) dry DMSO solution of a $[Zr(tsdb)]_n$ oligomer in a 30-mL beaker for the appropriate time period, 3 h except for the first time-dependent studies shown in Table II. Then the substrates were taken and repeatedly

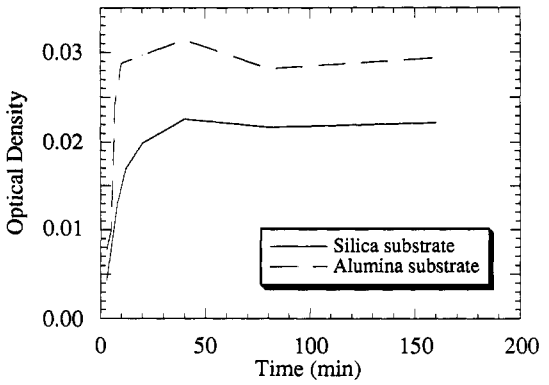


Figure 2. Reaction time vs oligomer adhesion for $[Zr(tsdb)]_n$ on silica and alumina.

washed with several 10-mL portions of DMSO until no more yellow color could be observed in the rinses. The substrates were then washed with 10 mL of acetone three times to remove any DMSO from the surface of the substrates. After air-drying for several hours, the relative concentrations of $[Zr(tsdb)]_n$ on the silica and alumina substrates were measured by transmission spectrophotometry. The relative amounts of the zirconium oligomer remaining on the surfaces were determined from the optical densities at 400 nm (where the zirconium centers have a charge-transfer transition) together with the average number of zirconium centers per chain. Whereas the absolute amount of an adhering zirconium oligomer chain cannot be obtained from such diffuse transmission spectra, the relative amounts are undoubtedly related to the optical densities corrected for the number of zirconium centers per chain.

Reflectance spectra were obtained for $[Zr(tsdb)]_n$ films on aluminum plates prepared in a similar manner. However, the scatter from one sample to another was too large to provide quantitative results.

The surface adhesion for DMSO solutions of $[Zr(tsdb)]_n$ (DP = 23) vs reaction time at 60 °C was studied on both silica and alumina substrates in order to ascertain the time required for equilibration between the substrates and the oligomer solutions. Then a series of five $[Zr(tsdb)]_n$ oligomers that have significantly different ratios of end groups (Table I) were investigated for surface adhesion on both silica and alumina at five concentration levels. For these studies, the substrates were equilibrated with the oligomer solutions for 3 h at 60 °C prior to the wash steps—the time is greatly in excess of the time required for equilibration.

The hot water resistance of the $[Zr(tsdb)]_n$ oligomer films on alumina and silica was determined by measuring the optical density at 400 nm vs time of immersion. The optical density is proportional to the amount of $[Zr(tsdb)]_n$ on the substrate. The silica and alumina substrates were coated with $[Zr(tsdb)]_n$ (DP = 23) as before and the washed and dried plates were then immersed in hot water (ca. 60 °C) for up to 100 h. The exact times are shown in Table V.

Scribe-Stripping Test.[15] The adhesion of regular $[Zr(tsdb)]_n$ and end-capped $[Zr(tsdb)]_n$ were compared using the scribe-stripping or scratch test. Solutions of 0.2 g of either regular or end-capped $[Zr(tsdb)]_n$ in 20 mL of DMSO were heated (60 °C bath) until the $[Zr(tsdb)]_n$ was dissolved. The silica and aluminum substrates were coated with the $[Zr(tsdb)]_n$ solutions by spin coating. After coating the substrates, the solutions were heated at about 100 °C until the solvent had evaporated completely. The films were scratched with a sharp razor blade, and the edges of the scratched surface were observed visually and photographed by optical microscopy.

Results and Discussion

The $[Zr(tsdb)]_n$ oligomers interact strongly with both silica and alumina. The adhesion reactions go rapidly at 60 °C and reach maximum surface adhesion coverage within 20 min (Table II and Figure 2), even with the longest chain oligomer used in this study. The remainder of the surface adhesion studies involved immersion of the substrates in the oligomer solutions at 60 °C for 3 h; thereby ensuring complete reaction. DMSO is a good scavenger for water and eliminates any reversal of the condensation reactions between the hydroxyl groups on the surfaces and hydroxo end groups on hydrolyzed oligomers.

The five $[Zr(tsdb)]_n$ oligomers shown in Table I, which include five different amine end group to Zr end-group ratios, were studied at five different concentrations to provide the optical density and relative oligomer chain data given in Tables III and IV for silica and alumina substrates, respectively. Plots of relative oligomer chain adhesion vs percentage of Zr end groups and solution concentrations are shown in Figures 3 and 4. The surface adhesion coverage correlates quite well both with the concentration of the $[Zr(tsdb)]_n$ solutions and with the percentage of Zr end groups. At the same solution concentration, a higher percentage of Zr end groups correlates with more oligomer chain adhesion.

The plots of relative oligomer chain concentration vs Zr end-group concentrations (Figures 5 and 6) show that the number of adhering chains tends to level off when reaching

Table III. Optical Densities for $[Zr(tsdb)]_n$ Coatings on Silica[a]

Zr end groups	concn of $[Zr(tsdb)]_n$ solution (M)					Zr/ chain
	4.6×10^{-4}	8.1×10^{-4}	1.16×10^{-3}	1.70×10^{-3}	2.09×10^{-3}	
16%	0.0030	0.0080	0.0150	0.0202	0.0221	3.5
	0.0009	**0.0023**	**0.0043**	**0.0058**	**0.0063**	
25%	0.0120	0.0233	0.0254	0.0331	0.0381	5.2
	0.0023	**0.0045**	**0.0049**	**0.0064**	**0.0073**	
50%	0.0321	0.0425	0.0550	0.0881	0.0901	11.6
	0.0028	**0.0037**	**0.0047**	**0.0076**	**0.0078**	
75%	0.0369	0.0454	0.0579	0.0810	0.0821	5.6
	0.0066	**0.0081**	**0.0103**	**0.0145**	**0.0147**	
84%	0.0297	0.0331	0.0450	0.0624	0.0661	4.1
	0.0072	**0.0080**	**0.0110**	**0.0152**	**0.0161**	

[a] Optical density (OD) at 400 nm for silica surfaces after 180 min in contact with 60 °C DMSO solution of oligomer and thorough washing. Numbers in bold face are the relative numbers of oligomer chains: OD/(Zr/chain).

Table IV. Optical Densities for $[Zr(tsdb)]_n$ Coatings on Alumina[a]

Zr end groups	concn of $[Zr(tsdb)]_n$ solution (M)					Zr/ chain
	4.6×10^{-4}	8.1×10^{-4}	1.16×10^{-3}	1.70×10^{-3}	2.09×10^{-3}	
16%	0.0005	0.0063	0.0108	0.0126	0.0135	3.5
	0.0001	**0.0018**	**0.0031**	**0.0036**	**0.0039**	
25%	0.0056	0.0146	0.0181	0.0290	0.0311	5.2
	0.0011	**0.0028**	**0.0035**	**0.0056**	**0.0060**	
50%	0.0289	0.0404	0.0553	0.0890	0.0911	11.6
	0.0025	**0.0035**	**0.0048**	**0.0077**	**0.0079**	
75%	0.0352	0.0485	0.0658	0.0685	0.0684	5.6
	0.0063	**0.0087**	**0.0118**	**0.0122**	**0.0122**	
84%	0.0310	0.0441	0.0512	0.0520	0.0574	4.1
	0.0076	**0.0108**	**0.0125**	**0.0127**	**0.0140**	

[a] Optical density (OD) at 400 nm for alumina surfaces after 180 min in contact with 60 °C DMSO solution of oligomer and thorough washing. Numbers in bold face are the relative numbers of oligomer chains: OD/(Zr/chain).

Table V. Water Resistance at 60 °C for $[Zr(tsdb)]_n$ on Silica and Alumina

time (h)	$[Zr(tsdb)]_n$-coated silica		$[Zr(tsdb)]_n$-coated Al_2O_3	
	OD[a]	retained (%)	OD[a]	retained (%)
0	0.0524	100	0.0298	100
2	0.0482	92	0.0289	97
24	0.0441	84	0.0280	94
48	0.0411	78	0.0277	93
100	0.0406	77	0.0272	91

[a] Optical density at 400 nm for $[Zr(tsdb)]_n$ with DP = 23 and 50% Zr end groups.

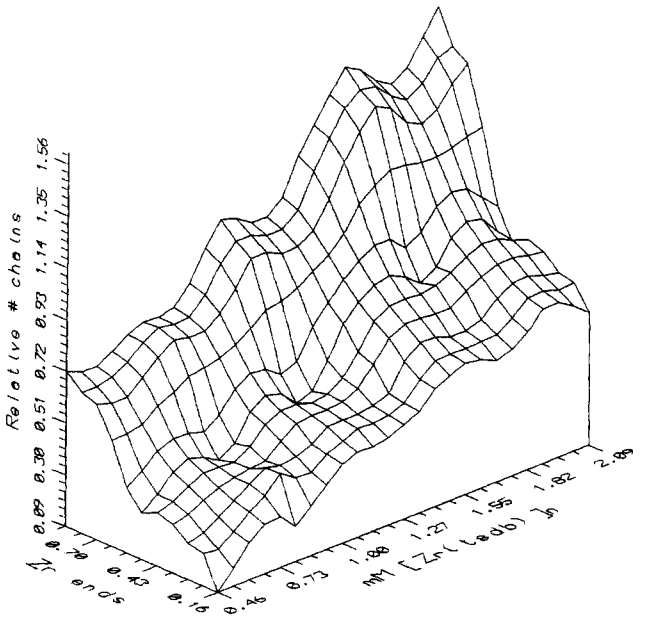


Figure 3. Oligomer chains on silica vs percent Zr end groups and DMSO solution concentrations of $[Zr(tsdb)]_n$.

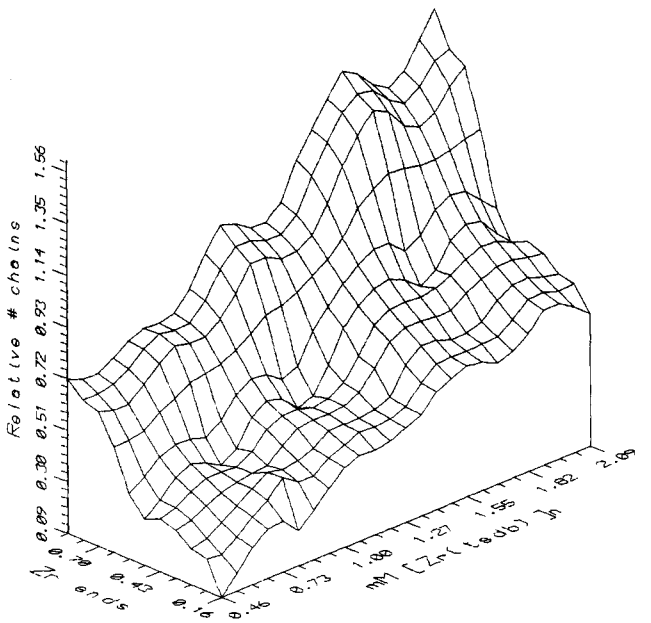


Figure 4. Oligomer chains on alumina vs percent Zr end groups and DMSO solution concentrations of $[Zr(tsdb)]_n$.

the highest Zr end groups concentrations, possibly reaching a saturation. Also, for equivalent Zr end-group concentrations, the longest chains (those with 50% Zr end groups—represented as triangles in the plots) have the fewest chains adhering to the surfaces—apparently because they tend to bend over and take up more space on the surfaces. This decrease is also evident in the troughs that exist at the 50% Zr end group region of the surfaces shown in Figures 3 and 4.

The amine end group would be expected to have hydrogen-bond interactions with the surface hydroxides, but amines attached to the surface can be at least partially removed during the vigorous solvent washes. Chiang et al.[16] have found amine interactions with silica surfaces by FTIR., specifically an aminosilane coupling of the amine end of APS ((γ-aminopropyl)triethoxysilane) on silica.

The strength of the $[Zr(tsdb)]_n$ adhesion has been shown through scribe-stripping tests. The scribed edge is very

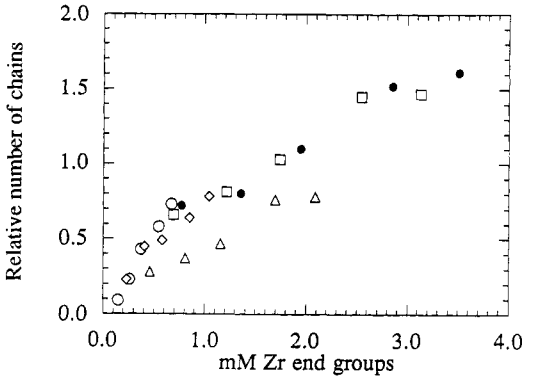


Figure 5. Oligomer chains on silica vs Zr end-group concentrations for DMSO solutions of $[Zr(tsdb)]_n$. ○ = 16% Zr end groups; ◇ = 25% Zr end groups; △ = 50% Zr end groups; □ = 75% Zr end groups; ● = 84% Zr end groups.

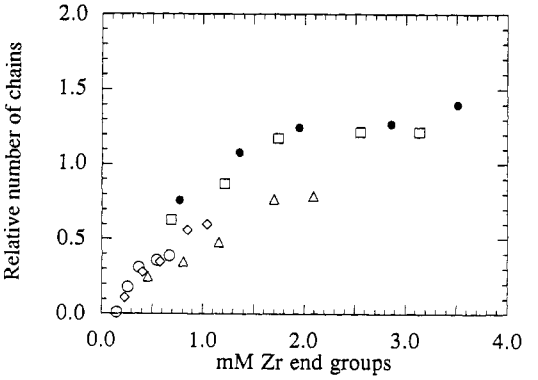


Figure 6. Oligomer chains on alumina vs Zr end-group concentrations for DMSO solutions of $[Zr(tsdb)]_n$. ○ = 16% Zr end groups; ◇ = 25% Zr end groups; △ = 50% Zr end groups; □ = 75% Zr end groups; ● = 84% Zr end groups.

straight and clean when a 0.5-μm film of the $[Zr(tsdb)]_n$ oligomer, which had been spin-coated on a glass plate, has been scratched. A clean straight edge indicates good adhesion to the surface. This strong adhesion does not exist if the zirconium end groups of $[Zr(tsdb)]_n$ are capped with dst^{2-} prior to spin-coating the oligomer on the silica surface or if the silica surface is silanized prior to the spin-coating. The end-capped oligomer films on silica and films made from the regular oligomers placed on silanized glass both show irregular chipped edges when subjected to the scribe-stripping test, and no oligomer could be observed on the silica surfaces after the surface is washed in these latter two cases. Similar surface adhesion studies by scribe-stripping $[Zr(tsdb)]_n$ films spin-coated on sol–gel alumina have shown that a strong interaction also occurs between $[Zrtsdb]_n$ and alumina. Again this adhesion is not apparent if the zirconium end groups of $[Zr(tsdb)]_n$ are capped with dst^{2-} prior to spin-coating the oligomer on the alumina surface.

The oligomer adhesion was also checked with XPS using the zirconium $3d_{5/2}$ and $3d_{3/2}$ peaks near 190 eV (Figure 9). Measurements taken at concentrations too low to ascertain for certain from the visible spectra that the oligomer was still on the surface still show the zirconium peaks. However, the end-capped polymers show no detectable zirconium peaks; therefore, the zirconium peaks are due to adhering zirconium oligomer chains. Separate studies[17] have shown that the Schiff base without zirco-

(17) Tong, W., recent unpublished results.

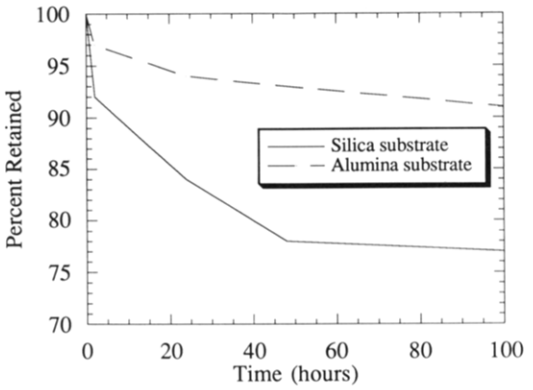


Figure 7. Water resistance (60 °C) of the polymer-coated silica and alumina surfaces vs time.

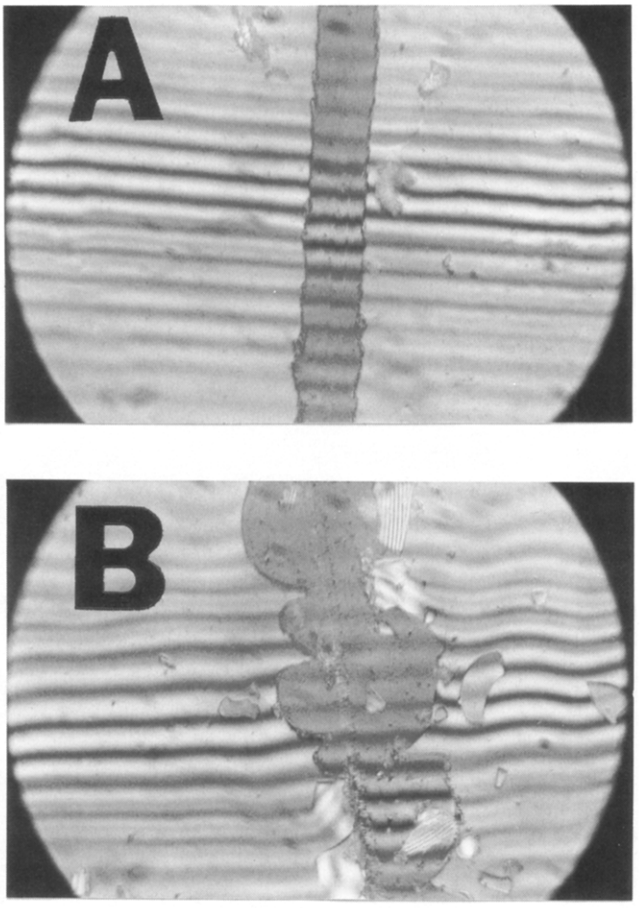


Figure 8. Scribe-stripping tests for regular (top) and end-capped (bottom) $[Zr(tsdb)]_n$ polymer on silica. Results on alumina are virtually identical.

nium coordinated to it does not show comparable adhesion to the hydroxylated surfaces either; thus our adhesion scheme appears to be correct.

Excellent water resistance for organozirconates on silica has been reported by Calvert et al.,[4] based on the measurement of weight loss. The $[Zr(tsdb)]_n$ oligomers on alumina and silica also show excellent hot water resistance (see Figure 7). The greater loss of the oligomer from silica relative to alumina under extended hot water treatment is either due to more amine adhesion in the case of silica (which can be hydrolyzed at the higher temperatures) or more hydrolytically unstable bonds between silica and the zirconium oligomer. Alumina is less acidic than silica, and any amine group adhesion may be so weak that it is largely lost in the DMSO washes at

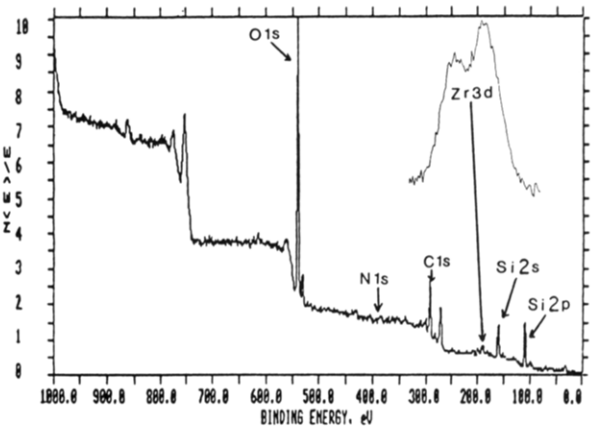


Figure 9. XPS peaks for $[Zr(tsdb)]_n$ on silica after thorough washing with DMSO. Inset shows Zr peaks that are missing when zirconium end groups are capped prior to reaction with silica.

room temperature prior to the hot water treatment. This lower acidity may also help explain the lower coverage of the oligomer on alumina than on silica when identical conditions are used. Gettings et al.[18] have shown that surfaces treated by aminosilanes exhibit adhesion failure when exposed to moisture. In the present study, relatively little polymer degradation is noted, even for the low-coverage samples used in the water resistance experiments. Obviously, the chelate effect keeps the polymer from dissociating and the hydrophobic tetradentate ligand protects the silica and alumina surfaces from extensive hydrolysis.

Whereas the preceding results paint a fairly clear picture of the adhesion of $[Zr(tsdb)]_n$ to silica and alumina, a calculation of the number of oligomers in solution relative to the available surface area indicates that only a small fraction (less than 1%) of the oligomers actually adhere to the surface. [That is, even for the most dilute solutions used, 4.6×10^{-4} M, the 8 mL of solution used to soak each cover glass contains about 3.7 μmol of oligomer. The maximum surface coverage for these oligomers cannot be much greater than 3.3 μmol/m^2 (or 10 000 cm^2) based on an appropriate Schiff base ligand/zirconium footprint size of about 50 Å^2.[20] However, the total surface area in each of these experiments is not over 25 cm^2 (including the cover glass and the inside of the small beaker holding the solution). Therefore, the most dilute solutions used have enough oligomer to coat of the order of 100 plates under the experimental conditions used. Naturally those with more zirconium end groups have enough for several hundred plates.] When more concentrated solutions were used, higher coverage was observed (Tables III and IV); thus less than full coverage was obtained in the dilute solutions that already have a many-fold excess of reagent. That this less than full coverage in the dilute solutions is not a kinetics problem is shown quite conclusively by the results in Table II. That is, even though the coverage levels off after about 20 min of immersion, the results in Table III and IV are based on 180-min immersions. Apparently less than one percent of the zirconium end groups are hydrolyzed to hydroxides. This also explains why the zirconium end groups do not seem to interact with each other in these dilute solutions. Also, similar oligomers that are deliberately more extensively hydrolyzed exhibit more extensive surface adhesion.[17]

(18) Gettings, M.; Baker, F. S.; Kinloch, A. J. *J. Appl. Polym. Sci.* **1977**, *12*, 2375.

Thus we conclude that the zirconium oligomers adhere very strongly to both silica and alumina through hydrolyzed zirconium end groups. These results have led us to use such oligomers to prepare block copolymers with β-butyrolactone and stearoyl chloride.[19] Such copolymers provide increased adhesion for polyesters and polyenes, respectively, to both silica and alumina.

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(19) Archer, R. D.; Wang, B. *Polym. Mater. Sci. Eng.* **1989**, *61*, 101.

(20) The footprint size is based on the length of the Schiff base end group (about 15 Å) and the minimum width of a flat aromatic system (about 3.3 Å). Thus: (1 molecule/50 $Å^2$)(10^{20} $Å^2/m^2$)(1 mol/6.0 × 10^{23} molecules)(10^6 μmol/mol) = 3.3 μmol.