Synthesis, Characterization, and Block Copolymerization of a Bifunctional Zirconium Coordination Complex: Bis[2,2′-[[4-[[[(3-isocyanato-4-methylphenyl)amino]carbonyl]amino]-1,2-phenylene]bis(nitrilomethylidyne)]bis[phenolato](2–)(*N*,*N*′,*O*,*O*′)]zirconium(IV)

Wenyan Tong and Ronald D. Archer*

Department of Chemistry, University of Massachusetts,
Amherst, Massachusetts 01003

Received February 19, 1992

Introduction

Our laboratory has been interested in the zirconium coordination chemistry of Schiff-base ligands for many years.[1] One of our goals has been to introduce d^0 zirconium(IV) ions into organic polymers in order to produce homogeneous inorganic-organic hybrid polymers. However, the isolation of reactive metal coordination compounds which can serve as monomers for alternating inorganic–organic copolymers has proven difficult because the reactive end groups tend to undergo reactions which prevent pure reactive monomers from being obtained.

However, taking advantage of the unequal activity of the two NCO functionalities of tolyl–2,4-diisocyanate (TDI) at room temperature and TDI's ability to deactivate traces of water through the formation of a byproduct that does not interfere with the synthesis and isolation of the desired product, a pure coordination compound that is reactive with amines and alcohols is possible. The desired metal-coordination product, bis[2,2′-[[4-[[[(3-isocyanato-4-methylphenyl)amino]carbonyl]amino]-1,2-phenylene]bis(nitrilomethylidyne)]bis[phenolato](2–)(*N*,*N*′,*O*,*O*′)]zirconium(IV) (note the components benzene, nitrilo, urea, isocyanato, and phenol, hence bnuip), Zr(bnuip)$_2$, has reactive isocyanate groups at both ends of the molecule.

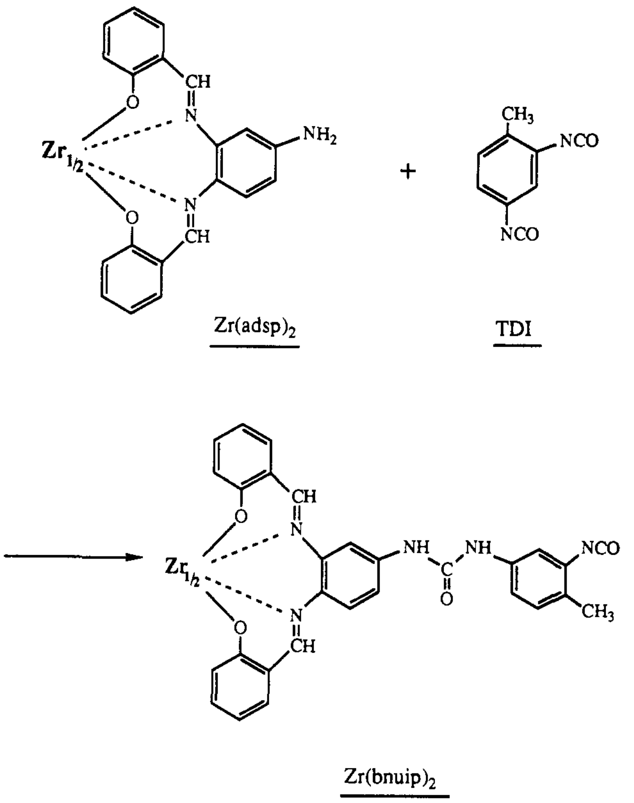
Zr(bnuip)$_2$ has been obtained through the addition reaction between bis(4-amino-*N*,*N*′-disalicylidene-1,2-phenylenediaminato)zirconium(IV),[2] Zr(adsp)$_2$, and TDI, as shown in Scheme I.

Zr(bnuip)$_2$ is an eight-coordinate Schiff-base chelate complex. Because of the two isocyanate groups, it should be very reactive with organic compounds which have active hydrogen, e.g., amines and alcohols. Thus, Zr(bnuip)$_2$ is a new precursor for preparing linear metal-containing polymers, especially for preparing zirconium-containing polyurethanes and polyureas. Zr(bnuip)$_2$ can react with bifunctional oligomers and polymers which have active hydrogen on their end groups and form linear zirconium-containing block copolymers. A copolymer of Zr(bnuip)$_2$ and poly(tetrahydrofuran), PTHF, has been prepared in this manner (see Scheme II). An orange-red, transparent plastic film was obtained by casting this copolymer solution onto a nonstick surface.

Experimental Section

Syntheses. Zr(bnuip)$_2$. The reaction and filtration of the product were carried out under dry nitrogen or argon to maintain anhydrous conditions. Freshly opened bottles of HPLC grade tetrahydrofuran (THF), anhydrous diethyl ether, and TDI (98%+, HPLC, Fluka) were used without further purification. All glassware was dried (ca. 150 °C) prior to use. Zr(adsp)$_2$ was prepared following a previously reported procedure.[2] The purity of the Zr(adsp)$_2$ was confirmed by elemental analysis, proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, and thin-layer chromatography (TLC) with results analogous to those previously reported.[2]

Scheme I



A 500-mL round-bottom flask was charged with 100 mL of a 0.11 M TDI solution in THF (11 mmol). Then 60 mL of a saturated 0.011 M Zr(adsp)$_2$ solution in THF (0.66 mmol) was very slowly added to the above solution under constant stirring at room temperature. The addition of Zr(adsp)$_2$ took about 4 h. The reaction solution was allowed to stir for an additional 5 h. The solution was reduced to half-volume by rotary evaporation, and diethyl ether was added (reaction solution:ether = 2:3 by volume) to precipitate the product. The yellow moisture-sensitive product was obtained by filtering, washing thoroughly with ether, and drying in vacuo at 54 °C for 4 h; yield, 77%. Anal. Calcd for ZrC$_{58}$H$_{42}$N$_{10}$O$_8$: C, 63.43; H, 3.85; N, 12.76. Found: C, 63.28; H, 3.72; N, 12.82.

In a separate experiment, fractional precipitation led to the isolation of a more-soluble byproduct, which was isolated as needlelike pale-yellow crystals. The product was characterized by NMR spectroscopy as *N*,*N*′-bis(3-isocyanato-4-methylphenyl)urea.

Copolymer of PTHF and Zr(bnuip)$_2$. THF was purified over LiAlH$_4$, by heating under reflux overnight and finally distilled fractionally. PTHF (Polyscience, MW = 1000) was dried under boiling toluene, using the toluene–water azeotrope and a trap-type distillation adapter. After no more water could be removed, the rest of the toluene was distilled from the PTHF in vacuo. Anhydrous diethyl ether and di-*n*-butyltin dilaurate (Strem Chemicals) were used without further purification. The reactions were kept anhydrous under prepurified nitrogen gas.

First, 1.016 g of Zr(bnuip)$_2$ (0.925 mmol) and 1.109 g of PTHF (1.109 mmol to provide a 1:1.2 mol ratio of NCO:OH end groups) were added to 100 mL of THF. Then four drops of dibutyltin dilaurate (ca. 0.15 mmol, equivalent to about 8 mol % of NCO end groups) was added. This clear orange reaction solution was heated for 16 h under reflux with stirring. An orange-red viscous solution was obtained after concentrating the solution to about 10 mL. Approximately 100 mL of anhydrous diethyl ether was added to the viscous solution, and a sticky precipitate formed. After decanting the ether solution, another 100 mL of ether was added. The orange precipitate was stirred in the ether solution and isolated by filtration. The orange product was washed several times with ether and dried overnight in vacuo at room temperature.

A cast film of the copolymer was prepared by pouring a concentrated orange-red THF solution of the copolymer (1.5 g in 30 mL THF) into

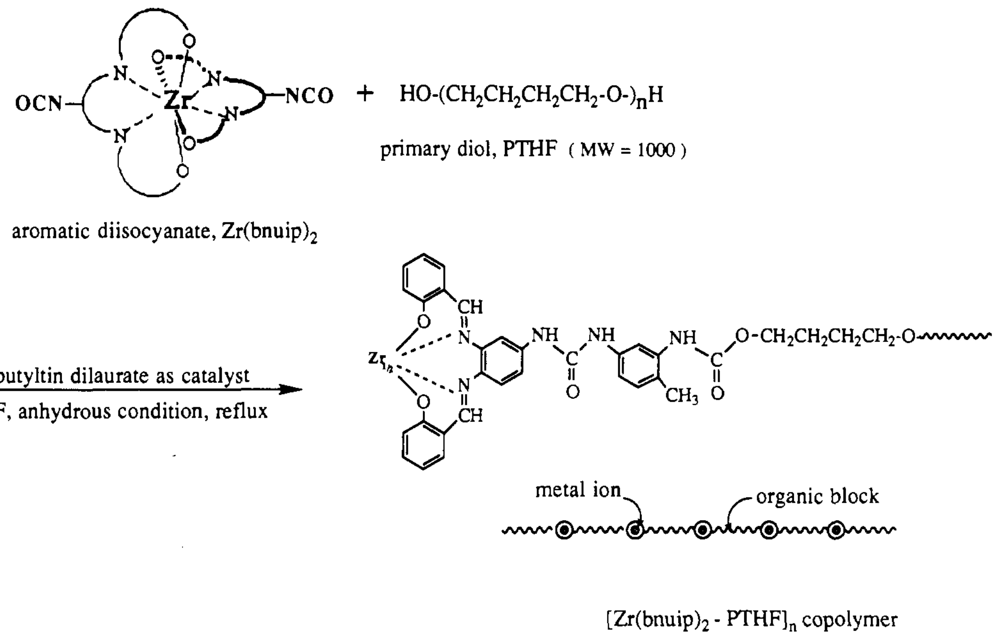
---

[1] (a) Archer, R. D.; Day, R. O.; Illingsworth, M. L. *Inorg. Chem.* **1979**, *18*, 2908. (b) Archer, R. D.; Illingsworth, M. L.; Rau, D. N.; Hardiman, C. J. *Macromolecules* **1985**, *18*, 1371. (c) Wang, B.; Archer, R. D. *Inorg. Chem.* **1990**, *29*, 39.

[2] Illingsworth, M. L.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 4312.

0020-1669/92/1331-3332$03.00/0

Scheme II



a flat-bottom vessel which had been pretreated with $(CH_3)_3SiCl$ to deactivate the glass surface. After solvent evaporation in vacuo at room temperature, an orange-red transparent filmed formed. A smooth flexible film about 0.5 mm thick was peeled from the vessel. It turned hard after being dried completely in air at room temperature.

Characterization. The infrared spectra were recorded on a Perkin-Elmer Model 1310 spectrometer for $Zr(bnuip)_2$ and on a Mattsen Cygnus 100 FTIR spectrometer for the copolymer. The infrared samples were prepared as KBr mulls. Proton NMR spectra were measured with a Varian Model XL200 spectrometer in DMSO-d_6, in $CDCl_3$, and/or in THF-d_8, as appropriate. Ultraviolet–visible spectra were obtained with a Perkin-Elmer Lambda Array Model 8640 spectrophotometer using *N*-methylpyrrolidone (NMP) and dimethylformamide (DMF) solutions.

Gel permeation chromatography was conducted with a Waters Model 6000-A pump, Model R401 differential refractometer, and 10^3-Å Ultrastyragel column, using chloroform as the solvent, and calibrated with polystyrene standards. The viscosity measurements were conducted with an Ubbelohde-type viscometer in $CHCl_3$ at 30.0 °C at concentrations from 0.1 to 0.4 g/dL. The thermal analyses were conducted with Perkin-Elmer TGS-2 and DSC-4 thermal analyzers under nitrogen gas with scan rates of 20 °C/min, except as noted. Both systems include Perkin-Elmer thermal analysis data stations and System 4 microprocessors.

Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory.

Results and Discussion

Syntheses. $Zr(bnuip)_2$. A new zirconium Schiff-base complex with two NCO functional groups was obtained through the addition reaction of $Zr(adsp)_2$ with excess TDI in tetrahydrofuran.

The reactions of diisocyanates are usually more complicated kinetically than those of monoisocyanates. In TDI, the isocyanate group in the 2-position is initially less reactive than the one in the 4-position because of a strong deactivation of the 2-position by the methyl group. After the 4-NCO group has reacted with an amine group (and becomes a urea group –NH–CO–NH–), the 2-NCO is even less reactive than it was initially.[3] Therefore, in addition to these two isocyanate groups having quite different activation energies for the addition reaction with the amine groups of $Zr(adsp)_2$, the probability of any disubstitution is minimal. The different activation energies of the two –NCO groups in TDI should ensure selectivity with amines such as $Zr(adsp)_2$ at low temperatures. Furthermore, the primary amine groups of $Zr(adsp)_2$ are aromatic amines, which generally react quite slowly with isocyanates below room temperature. According to the proton NMR results, the addition reaction at room temperature only occurs at a single –NCO group, that must be the one in the 4-position on the basis of relative reactivities. The –NCO in the 2-position appears to be free from addition. Above room temperature, both positions become reactive.

Excess TDI was used in the reaction system to immobilize the traces of water (<0.01%) which exist in the solvent (THF). The more reactive NCO groups (4-position) on the excess TDI are hydrolyzed rather than the less active NCO groups of the product, $Zr(bnuip)_2$. This partially hydrolyzed TDI reacts further with another TDI molecule producing the observed very-pale-yellow byproduct that has a ^1H NMR spectrum (one singlet at 8.2 ppm for the NH proton, one singlet at 2.3 ppm for the two methyl protons and two peaks at 7.3–7.6 ppm for the aromatic protons in acetone-d_6 with relative intensities of 2:6:6, respectively) consistent with *N*,*N*′-bis(3-isocyanato-4-methylphenyl)urea, that is known to be formed by the hydrolysis of TDI.[4] (The hydrolysis reactions are shown in Scheme III.) This byproduct has sufficient solubility in THF not to coprecipitate with the desired product. Because TDI is miscible with diethyl ether, the rest of the TDI can be completely removed from the product by washing with ether.

Copolymer of PTHF and $Zr(bnuip)_2$. In general, the reaction conditions greatly affect the copolymerization. For this copolymer, the ratio of NCO:OH end groups, the solvent, the presence or absence of catalysts, reaction time, reaction temperature, concentration of the reactants, and mixing speed can all affect the yield and/or copolymer characteristics.

Whereas theoretically an NCO:OH mole ratio of exactly 1:1 would be required to obtain maximum molecular weights, most urethane formulations have NCO:OH ratios of 1:1 to 1.1:1 to provide for branching and cross-linking, which occurs at the NCO group.[5] In order to obtain a soluble product for easy handling and characterization, we used a 1:1.2 NCO:OH ratio and a short-chain PTHF (MW = 1000). This deficiency in NCO groups minimizes side reactions and provides short-chain polymers for easy characterization.

Anhydrous conditions were used in order to avoid the reaction between water and isocyanates, which forms CO_2 and amines,

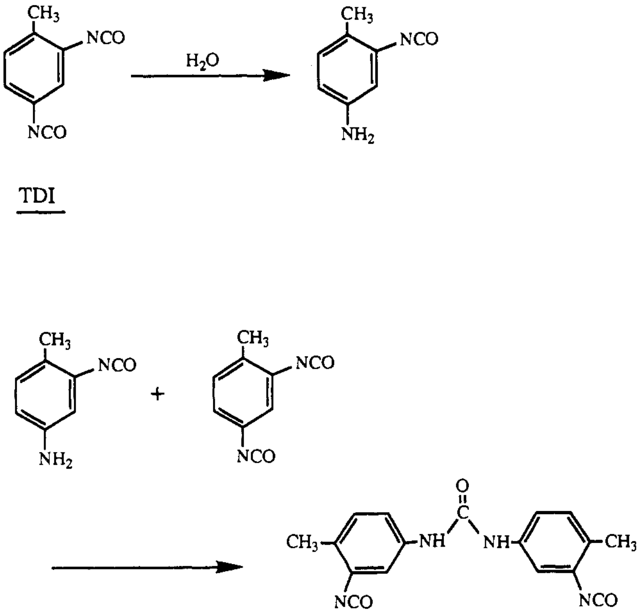
---

(3) Saunders, J. H.; Frisch, K. C. *Polyurethanes: Chemistry and Technology, I. Chemistry*: John Wiley: New York, 1962; p 150.

(4) Pelley, R. L. U.S. Pat. No. 2,757,184, July 31, 1956.

(5) Doyle, E. N. *The Development and Use of Polyurethane Products*; McGraw-Hill: New York, 1971.

Scheme III



which undergo further reaction with other isocyanate groups to give disubstituted ureas.

Although it is known that solvents with increased dielectric constants and solvents that can form H bonds decrease the NCO/OH reaction rate, solvents with low dielectric constants, such as toluene, provide insufficient solubility for $Zr(bnuip)_2$. THF is a suitable solvent for both $Zr(bnuip)_2$ and poly(THF). Also, the reflux temperature of THF (bp 66 °C) is low enough to minimize side reactions, such as the reaction of the isocyanate group with other hydrogen donors such as urea or urethane. This side reaction becomes significant above 100 °C.

An 8 mol % solution of di-*n*-butyltin dilaurate was used as a catalyst to provide suitable reaction rates in THF. The organotin compounds are more powerful catalysts for the NCO/OH reaction than trialkylamines but are poor catalysts for the NCO/H_2O side reaction.[6] Even so, a 16-h reaction time was used to ensure complete reaction. Any unreacted PTHF and the catalyst are both soluble in diethyl ether and were removed by the ether washes.

Characterization. $Zr(bnuip)_2$. The infrared, the proton nuclear magnetic resonance, and the ultraviolet–visible spectral results are shown in Table I.

In the infrared spectrum of $Zr(bnuip)_2$, an extremely intensive absorption arising from the asymmetric stretching vibration mode of NCO was observed in the expected region, 2260 cm^{-1}. In general, disubstituted ureas show an absorption band around 1650 cm^{-1} due to C=O stretching.[7] The new band in $Zr(bnuip)_2$ at 1660 cm^{-1} (compared with $Zr(adsp)_2$) was assigned to the stretching vibration of the C=O (urea type) double bond. A medium-intensity absorption due to a N—H (urea type) stretching vibration occurs at 3380 cm^{-1}.

To eliminate the reaction between $Zr(bnuip)_2$ and DMSO, THF-d_8 was used as the solvent for ^1H NMR measurements. For comparison, ^1H NMR spectra of $Zr(adsp)_2$ (prepared in our laboratory) were also taken in DMSO-d_6, $CDCl_3$, and THF-d_8. The results for $Zr(adsp)_2$ in DMSO-d_6 are in agreement with those of ref 2.

Table I. Spectral Data for Zirconium Schiff-Base Chelates

$Zr(adsp)_2$	$Zr(bnuip)_2$	assgnt
	Infrared (cm^{-1})[a]	
1612 (s)	1590 (s)	C=N
1315 (ms)	1300 (ms)	Ar—O(Zr)
3369 (mw), 3438 (mw)		N–H (amine)
	3380 (m)	N–H (urea)
	2260 (vs)	N=C=O
	1660 (m)	C=O (urea)
	^1H NMR (δ, ppm)[b]	
	2.25 (6) (s)	methyl H
		aromatic H[c]
5.93 (4) (m), 6.30 (4) (m), 6.83 (4) (m), 7.08 (4) (m)	5.95 (4) (m), 6.35 (4) (m), 6.88 (4) (m)	ring I
6.6–6.7 (4) (m), 7.2 (2) (d)		ring II
	7.0–7.2 (8) (m)	ring III and I
	7.4–7.6 (8) (m)	ring III and II
8.37 (2) (s), 8.43 (2) (s)	8.51 (4) (s)	aldimine H
4.82 (4) (s)	4.75 (0.3) (s)	amine H
	7.98 (2) (s), 8.12 (2) (s)	urea H
	Ultraviolet–Visible (nm)[d]	
ca. 440 (23, sh)[e]	ca. 440 (23, sh)[e]	
[ca. 430 sh][e]	[ca. 430 sh][e]	
381 (26.2, 53 000)	379 (26.4, 76 000)	n–π* transition
[376]	[377]	
310 (32.3, sh)		
[308]	[301, sh][f]	
292 (34.2, 33 000)	≤274 (36.5, 110 000)[g]	
[275][g]	[274][g]	

[a] Abbreviations: s = strong, v = very, m = medium, w = weak. [b] In THF-d_8. δ downfield from tetramethylsilane. The relative peak integration values are given in parentheses. Abbreviations: s = singlet, d = doublet, m = multiplet. [c] Rings: ring I, phenol ring connected to Zr through one oxygen atom; ring II, diamine ring connected to Zr through two nitrogen atoms; ring III, toluene ring with NCO group on it. [d] In NMP solution. The energies (in 10^3 cm^{-1} units) and the molar extinction coefficients (M^{-1} cm^{-1}) are listed in parentheses; sh = shoulder. The wavelengths of the absorption bands in DMF solution are given in brackets. [e] Estimated value (assuming Gaussian curve). [f] This shoulder is ill-defined in NMP solution. [g] Imprecise due to solvent absorption.

The proton NMR spectrum of $Zr(bnuip)_2$ is somewhat complicated; however, only one type of methyl proton at 2.25 ppm and two types of urea proton at 7.98 and 8.12 ppm were observed (Table I). This indicates that the addition reaction between $Zr(bnuip)_2$ and TDI occurs only at one type of NCO, obviously at the 4-position (based on reactivity differences). Because of the carbonyl functionality within the urea group, the urea group is more electron withdrawing than the amine group. Thus, the aromatic protons on ring II (see the footnotes in Table I) are more deshielded when the urea group replaces the amino group. The spectrum of $Zr(bnuip)_2$, as expected, shows this trend relative to $Zr(adsp)_2$. The protons on ring I are not noticeably affected by this replacement because of the distance between ring I and the urea group.

Also, another interesting observation is worth mentioning. A very weak signal at 4.75 ppm, apparently arising from amine protons, is observed in $Zr(bnuip)_2$ and integrates as 0.3 proton per molecule. It seems that the isocyanate groups in $Zr(bnuip)_2$ can be partially hydrolyzed to amine groups by traces of water in the THF-d_8 solvent at room temperature during the time of the ^1H NMR measurements. But this hydrolysis is not very fast because a small water peak is still observed in the spectrum. In other words, at room temperature, the NCO groups in $Zr(bnuip)_2$ can react with water in the absence of certain catalysts, but the reaction is quite slow.

The peak which belongs to the aldimine has very different patterns in $Zr(bnuip)_2$ and $Zr(adsp)_2$. (See Table II.) In H_2-ndsp, the two aldimines are different chemically because of the 4-nitro group on the diamine ring. But this difference is too small to be observed in the ^1H NMR spectrum, and only a singlet was observed (at 200 MHz). However, in $Zr(adsp)_2$ the quadridentate ligand $adsp^{2-}$ is no longer planar. It is slightly distorted in order to fit the Zr^{IV} ion size and to obtain the least electron replusion between the two perpendicular ligands.[1a,2] This dis-

---

(6) See Ref 3, p 230.
(7) Rao, C. N. R. *Chemical Applications of Infrared Spectroscopy*; Academic Press: New York, 1963; p 264–5.

Table II. Aldimine ^{1}H NMR Data in Different Solvents

compd	solvent	δ (ppm)	$\Delta\delta$ (ppm)
Zr(adsp)$_2$	DMSO-d_6	8.469, 8.517	0.048
		8.5 (doublet)[a]	very small[a]
	CDCl$_3$	8.388, 8.426	0.038[c]
	THF-d_8	8.373, 8.435	0.062
Zr(bnuip)$_2$	THF-d_8	8.514 (singlet)	
H$_2$ndsp[b]	DMSO-d_6	8.3 (singlet)[a]	

[a] Reference 2. [b] 4-Nitro-*N*,*N'*-disalicylidene-1,2-phenylenediamine. [c] The $\Delta\delta$ value is the same on both 200- and 80-MHz instruments, which indicates two independent chemical shifts.

tortion alters the electron current in the aromatic rings, which appears to enhance the difference between the two aldimine protons. It is probably the reason we only found one singlet for the aldimine protons in H$_2$ndsp, but two very close singlets for them in Zr(adsp)$_2$. The latter one looks like a "doublet", but the "coupling constant" changes in different solvents and has an identical $\Delta\delta$ (in ppm) at both 80 and 200 MHz.

After Zr(adsp)$_2$ is converted to Zr(bnuip)$_2$ (the amino group in Zr(adsp)$_2$ is replaced with an aryl-substituted urea), only a single peak is observed for the aldimine protons in the ^{1}H NMR spectrum. The flexible unsaturated aryl-substituted urea group freely rotates and apparently deshields the two NH groups unequally (0.08 and 0.14 ppm) and provides the single peak.

The electron absorption spectrum of Zr(bnuip)$_2$ in NMP solution shows a peak at about 379 nm, which is tentatively assigned to an n–π^* transition of the Schiff-base ligand.[8] As noted in ref 8, a band in this region is observed for the ligand itself in solvents of appropriate polarity. Therefore, we feel that the extra transition (the shoulder at about 440 nm) is more likely to be the ligand-to-metal charge-transfer transition, although in reality they may be mixed. For Zr(adsp)$_2$, a shoulder is also observed at the same place.

Copolymer of PTHF and Zr(bnuip)$_2$. The FTIR spectrum of the [Zr(bnuip)$_2$–PTHF]$_n$ copolymer shows many absorption bands including the bands due to the ether linkage (at about 1120 and 1000 cm^{-1}) and methylene vibrations (C–H stretching at about 3000 cm^{-1}), all of which occur at about the same energy as in pure PTHF.[9] Fresh samples show a very weak 1000-cm^{-1} signal, whereas samples aged for a few days at room temperature in air exhibit an appreciably stronger 1000-cm^{-1} infrared band, but still somewhat weaker than in the pure crystalline PTHF. The absorption at 1000 cm^{-1} is a characteristic band of crystalline PTHF,[9] and the intensity of that band should be proportional to the degree of crystallinity of the PTHF derivatives. The lower crystallinity is typical for copolymers.

Also, in the infrared spectrum of [Zr(bnuip)$_2$–PTHF]$_n$, a new band due to the urethane-type carbonyl vibration was observed at 1720 cm^{-1}. Many characteristic bands for Zr(bnuip)$_2$ were still there. It is interesting to note that the intensity of the absorption due to the urea-type carbonyl vibration is a little lower than the one due to the urethane-type carbonyl vibration. This difference results from the lower symmetry in a urethane group.

The intrinsic viscosity of [Zr(bnuip)$_2$–PTHF]$_n$ in CHCl$_3$ at 30 °C is about 0.10 dL/g. The relationship between intrinsic viscosity and molecular weight for PTHF usually cannot be applied to copolymers containing PTHF units. The viscosity may be lower than, higher than, or similar to that of PTHF depending on the nature of the copolymeric units, its interaction with the solvent, and the sequence distribution of the units which comprise the copolymers.[9]

The gel permeation chromatographic results show that the weight average molecular weight (M_w) is 10 300 based on polystyrene calibration and a M_w:M_n ratio of 1.8, where M_n is the measured number average molecular weight. The molecular weight distributions are broad, consistent with previous observations for polyurethanes derived from PTHF glycols of nearly uniform molecular weight.[9] The molecular weight results indicate an average degree of polymerization (DP) of about 10 (or n = 5 because these are copolymers). This is consistent with the NCO:OH load ratio of 5:6, for which a DP = 11 is expected.

The [Zr(bnuip)$_2$–PTHF]$_n$ copolymer is very soluble in many organic solvents. A smooth transparent orange-red film can be cast from either the THF solution or from a chloroform solution. The film can be easily peeled from the deactivated glass surface when only partially dried. When the film dries further, it becomes less flexible, and after thorough drying, the film has no flexibility at all and turns into a hard plastic film.

The DSC results for [Zr(bnuip)$_2$–PTHF]$_n$ at 30 °C/min scan rate under nitrogen show an exothermic peak at 149 °C, with an onset at 139 °C. The enthalpy is –80 cal/g. A thermogravimetric scan shows appreciable weight loss (approximately 30%) concurrent with this exothermic event and additional weight loss as the temperature increases further. The DSC results for Zr(bnuip)$_2$ show no exotherm (or endotherm) in this region; thus, we attribute the exotherm to the PTHF blocks. The oxygen atoms spaced regularly along the backbone makes PTHF (and this copolymer) particularly susceptibile to oxidative degradation. In the absence of an antioxidant, marked degradation of PTHF occurs in air just above 100 °C, whereas in vacuo, temperatures of 150 °C are required for complete decomposition.[10] Peroxides formed in air provide a weak linkage, which is easily broken upon heating.[11] Because no T_g was observed in the 50–250 °C DSC scan, a scan from –100 to +100 °C was run, but again no T_g was observed. The low molecular weight of the copolymer and the high crystallinity apparently precluded the observation of the T_g.

Conclusions

On the basis of our previous experience in this field and the characterizations noted above, Zr(bnuip)$_2$ is and eight-coordinate Schiff-base chelate complex. Furthermore, we have found that Zr(bnuip)$_2$ can react with polytetrahydrofuran (molecular weight of about 1000), which contains hydroxyl groups on both ends of the molecular chains. The copolymers of Zr(bnuip)$_2$ and poly(tetrahydrofuran) have been formed in this manner. Zr(bnuip)$_2$ should react easily with organic primary amines and other primary alcohols because of the active hydrogen atoms in these compounds and because of less steric hindrance than in secondary and tertiary amines in alcohols. Zr(bnuip)$_2$ should also react with other bifunctional oligomers and polymers that have end groups with active hydrogen atoms to form other linear zirconium-containing copolymers.

Acknowledgment. We thank the Office of Naval Research for partial support of this research. The detailed advice of the referees was also greatly appreciated.

---

(8) Wilkinson, G., Ed. *Comprehensive Coordination Chemistry*; Pergamon Press: New York, 1987; Vol. 2, p 730.

(9) Dreyfuss, P. *Poly(tetrahydrofuran)*; Gordon & Breach: New York, 1982.

(10) Farthing, A. C. In *Polyethers: I. Polyalkylene Oxides and Other Polyethers*; Gaylord, N. G., Ed.; John Wiley: New York, 1963; p 309.

(11) Davis, A.; Golden, J. H., *Makromol. Chem.* **1965**, *81*, 38.