Microstructure of *N*-Picolylpolyurethane Transition Metal Complexes

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ABSTRACT: Spectroscopic methods are used to investigate coordination structure of *N*-picolylpolyurethane transition metal complexes (PUPYM, M = Co^{2+} and Ni^{2+}). Geometrical arrangement of ligands in first-shell coordination sphere of metal ions is postulated to be tetrahedral CoL_2Cl_2 and octahedral $NiL_2Cl_2Z_2$, where L is the picolyl group and Z is a hydrate. From extended X-ray absorption fine structure (EXAFS) analysis, bond lengths for metal−chlorine and metal−ligand of PUPYM are similar to those of small molecular weight transition metal complexes. A two-phase model of PUPYM, which best describes the experimental data of DMTA and SAXS, is proposed. One microphase is the hard domain of self-segregated hard segments brought about by metal−ligand interaction, and the other phase is the matrix of soft segments. Transition metal ion−ligand moieties and their interactions dominate the macroscopic thermal behavior of PUPYM. The ligand field stabilization energy difference (ΔLFSE) between metal d-electrons in complexes with two picolyl ligands in the coordination sphere of metal ions and complexes maintaining one picolyl ligand as coordination pendent group is calculated on the basis of observed coordination structure, and it represents the energy supplied to split coordination cross-links. ΔLFSE of polyurethane nickel(II) complex is larger than that of the cobalt(II) complex. Since the mobility of hard segments is in inverse proportion to the strength of coordination cross-links, a higher α-transition temperature of $PUPYNi^{2+}$ with respect to $PUPYCo^{2+}$ is found as expected.

Introduction

In the previous paper we have reported the preparation of polyurethane transition metal complexes by chemical modification of commercial available polyurethane and blending with metal chlorides.[1] Replacement of hydrogen atoms of carbamate groups in the polyurethane main chain with picolyl groups can lead to microscopic homogeneous *N*-picolylpolyurethane. When cobalt(II) ions were introduced into this sample, a dramatic change of morphology was found, and a two-phase separated material was obtained as proved by SAXS pattern. Coordination interaction between metal ions and pendent pyridine groups in hard segments was postulated to be the driving force for microphase separation of hard segments from soft segments. It was found that nickel(II) complex of *N*-picolylpolyurethane exhibited a distinct mechanical property with respect to the cobalt(II) complex, which seemed relative to the different strength of metal−ligand interactions. Since the cations in the *N*-picolylpolyurethane matrix played an important role in the macroscopic properties of the blends, extended X-ray absorption fine structure (EXAFS) determination, as well as other spectroscopic methods, will be performed to give an insight into their local structure.

Experimental Section

The schematic structure of *N*-picolylpolyurethane with 50 mol % of N-substitution is shown in Figure 1. *N*-Picolylpolyurethane transition metal complexes (PUPYM, M = Co^{2+} and Ni^{2+}) were prepared by mixing the DMF solution of *N*-picolylpolyurethane with $CoCl_2{\cdot}6H_2O$ and $NiCl_2{\cdot}6H_2O$, and the stoichiometric ratio of N-substituted picolyl groups to metal ions was 2:1.

Far-IR spectra of PUPYM films were determined at room temperature on a Bruker IFS66V vacuum-type FTIR spectrophotometer.

Ultraviolet−visible absorption spectra of PUPYM films on slicking quartz glass were recorded with a Shimadzu UV-3100 double-beam type spectrometer.

EXAFS measurements were carried out on BEPC 4W1B at Beijing Synchrotron Radiation Laboratory. Data were acquired in the vicinity of the K-edge of cobalt and nickel atoms at room temperature. Two software packages were used for data analysis to obtain quantitative information about local atomic structure surrounding an absorption atom, including nearest-neighbor distance, coordination number, etc. One software package (EDAPN), available from the Institute of High-Energy Physics, was used for analysis of experimental data. It followed a standard procedure, i.e., preedge and postedge background removal, extraction of EXAFS oscillation $\chi(k)$, Fourier transformation, isolation of each shell, back-transformation, and determination EXAFS parameters. Feff5,[2,3] available from the University of Washington, was used to theoretically calculate the EXAFS spectra.

Dynamic mechanical thermal analysis (DMTA) data were evaluated with a Rheovibron DDV-II dynamic viscoelastomer (Toyo Baldwin Co.).

Small-angle X-ray scattering (SAXS) was performed with a Rigaku D/MAX-RA rotating anode X-ray generator with a copper target, at 40 kV cathode potential and 150 mA emission current. The X-rays were collimated into a beam 10 mm × 70 μm with a Kratky camera, and the scattered X-rays were detected with a SC-30 scintillation counter probe. Cu Kα X-rays were selected by detector pulse-height analysis. Data were corrected for sample transmittance and scattering from the empty camera.

Results and Discussion

Geometric Arrangement of Ligands in PUPYM. Metal ions incorporated into a *N*-picolylpolyurethane matrix will be surrounded by a layer of polymer chains designated as immobilized layer, and the interaction between possible polymeric ligand groups and metal

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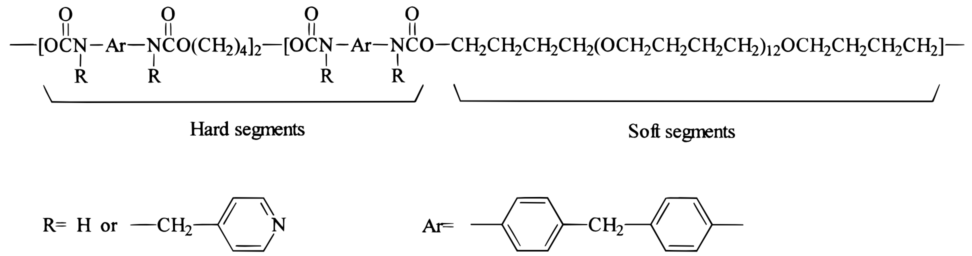

Figure 1. Structure of *N*-picolylpolyurethane.

ions will result in the change of vibration mode of ligand groups and local surrounding of metal ions. The absorption bands of the pyridine carbon–nitrogen stretch in *N*-picolylpolyurethane cobalt(II) and nickel(II) complexes are found at higher wavenumbers (1618 cm^{-1}) than the absorption when coordination is absent (1600 cm^{-1} in PUPY). This demonstrates that pyridine groups participate in metal–ligand π-bonding.[4] Observed middle infrared spectroscopic behavior of $PUPYCo^{2+}$ and $PUPYNi^{2+}$ indicates that two pyridine groups occupy two sites in the first-shell coordination sphere of metal ions.[1] Steric hindrance prevents metal ions from coordinating to more than two picolyl side groups. It is notable that immobilized polymer chains by metal ions are mainly picolyl-containing hard segments (schemed in Figure 1), and this means that cobalt(II) and nickel(II) complexes provide coordination cross-links between adjacent pendent groups of *N*-picolylpolyurethanes.

From X-ray and other measurements, metal halide complexes of small molecular weight pyridine and other nitrogen-donor ligands are well-known to be tetrahedral ML_2X_2, monomeric octahedral ML_4X_2, polymeric octahedral ML_2X_2 (halogen bridged), planar ML_2X_2, etc, where X is halogen atom and L is a nitrogen-donor ligand. Therefore, it is impossible to predict the possible geometric arrangement of ligands in the first-shell coordination sphere of metal ions in *N*-picolylpolyurethane metal complexes. Fortunately, systematic studies indicate that transition metal complexes with different stereochemistries can be distinguished by their electronic absorption spectra, far-infrared spectra, or magnetic behavior.

Figure 2 shows the far-infrared spectra of *N*-picolylpolyurethane metal complexes. For the tetrahedral complex $CoCl_2(pyridine)_2$, two infrared-active cobalt–chlorine (ν_{Co-Cl}) vibrations can be found at 344 and 304 cm^{-1}. The infrared spectra of the polymeric octahedral complex $CoCl_2(pyridine)_2$ (chloride bridged) consist of badly resolved bands in the 200–260 cm^{-1}. In *trans*-octahedral $CoCl_2(pyridine)_4$ and tetrahedral $CoCl_4^{2-}$, ν_{Co-Cl} is at 230 and 300 cm^{-1}, respectively.[5] The position of cobalt–chlorine vibration frequencies at 351 and 312 cm^{-1} of $PUPYCo^{2+}$ suggests a tetrahedral arrangement of ligands in the first-shell coordination sphere of cobalt(II) ions. Nickel–chlorine vibration frequencies occur at 327 and 297 cm^{-1} in tetrahedral $NiCl_2(\alpha\text{-picoline})_2$, 246 cm^{-1} in polymeric octahedral $NiCl_2(pyridine)_2$, 246 cm^{-1} in monomeric octahedral $NiCl_2(pyridine)_4$, and 403 cm^{-1} in planar $NiCl_2(PMe_3)_2$. The broad band at 230 cm^{-1} in $PUPYNi^{2+}$ (Figure 2) is assigned to the nickel–chlorine vibration of octahedral coordinated nickel(II) ions. This conclusion is also substantiated by ultraviolet–visible spectra shown in Figure 3. Metal ions in tetrahedral complexes exhibit a much stronger absorption ($\epsilon \approx 10^{2-3}$) than that in octahedral complexes ($\epsilon \approx 10^1$) due to the absence of center of symmetry.[6] Compared with the tetrahedral cobalt(II) complex, the octahedral nickel(II) complex exhibits a weaker band at about 600 nm, which is nearly invisible.

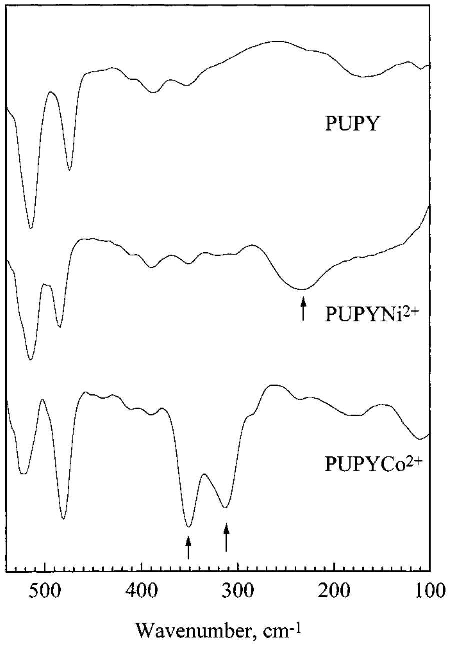

Figure 2. Far-infrared spectra of *N*-picolylpolyurethane and metal complexes.

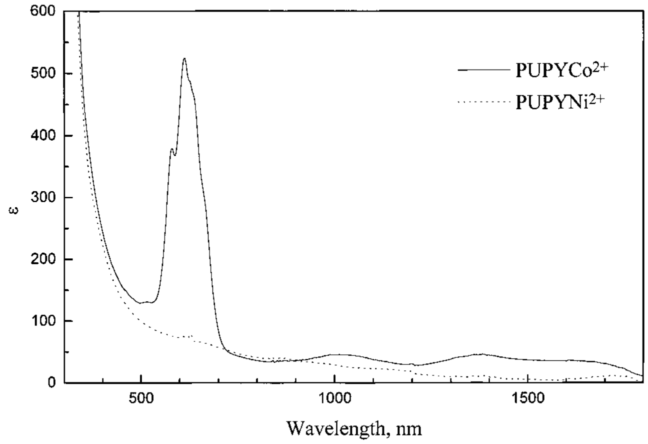

Figure 3. Ultraviolet–visible–near-infrared spectra of *N*-picolylpolyurethane cobalt(II) and nickel(II) complexes.

So, the conclusion is that exact arrangement of ligands in the first-shell coordination sphere of cobalt(II) ions in $PUPYCo^{2+}$ is CoL_2Cl_2, where L is the picolyl group. This means, in complexation with *N*-picolylpolyurethane, cobalt(II) chloride hexahydrate undergoes a geometric perturbation from octahedral to tetrahedral symmetry. In the nickel(II) complex, a coordination number of 6 is observed, and this means two picolyl side groups in polyurethane displace two waters of hydration in the first-shell coordination sphere of octahedral nickel(II) chloride hexahydrate. An octahedral NiL$_2$Cl$_2$Z$_2$ should be expected in PUPYNi^{2+}, where Z is mostly like to be water of hydration. To the different coordination behavior of these two metal ions with *N*-picolyl groups, a reasonable interpretation was that nickel (d^8) ions give higher ligand-field stabilization energy in octahedral form and lower stabilization in tetrahedral form than cobalt (d^7) ions. Therefore, the occurrence of tetrahedral complexes is less likely with nickel(II) than with cobalt(II) ions.

EXAFS Analysis. In theory, extended X-ray absorption fine structure (EXAFS) can be described as an electron diffraction process where the electron source is the absorbing atom. An X-ray photon excited a core electron of the absorbing atom into an escaping photoelectron state. The outgoing photoelectron wave interferes with the wave backscattered from surrounding atoms. These scattering characteristics generate the oscillatory structure $\chi(k)$, where k is the photoelectron wave vector. The EXAFS signal $\chi(k)$ contains much quantitative information concerning the local structure near an absorbing atom. This includes near-neighbor distances, coordination numbers, and the static and vibration disorder in bond distances, measured as the Debye−Waller factor.

Extracting EXAFS information with precision requires a comparison with an accurately known reference system or “standard”, either experimental or theoretical. The conventional procedure of extracting structural information in real space is based on Fourier-transforming the normalized oscillatory part of the X-ray absorption coefficient.[7] The peak in the Fourier transform occurs at a distance that is shifted from the correct distance by typically 0.2−0.3 Å. These shifts can be measured by performing the Fourier transform first on a system with known distances, and then they were used to predict distance in unknown systems. A second approach to obtain interatomic distance is curve fitting based on the transferability of experimentally determined phase shifts.[8,9] By parametrizing the phase-shift function by a linear and quadratic term, the phase-shift function can be extracted by best fitting the data directly. The phase-shift functions extracted from the same atomic pairs in different chemical environments are in excellent agreement with each other, and the phase shift extracted from one system can be used to predict distance in another system with an accuracy of 0.01−0.02 Å. Besides the experimental reference system to extract structural information, theoretical standards including tables of XAFS phases and amplitudes[10,11] and computer codes such as FEFF5 for ab initio single-scattering calculations can also be adopted. The application of EXAFS to ionomers[12−15]and macromolecular metal complexes[16−18] has been described previously. Nevertheless, EXAFS analysis gives only inconclusive results if the possible coordination structure in the macromolecular metal complexes is not accurately established by other spectroscopic methods described above.

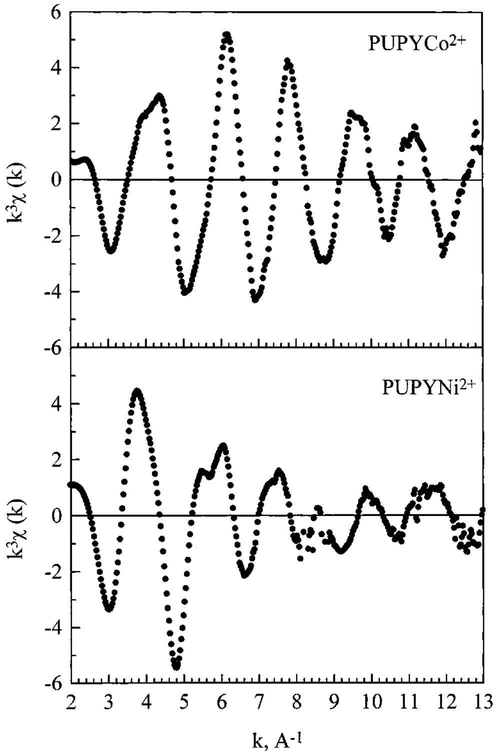

Figure 4. EXAFS spectra: $k^3\chi(k)$ versus k curves obtained from raw experimental data.

k^3-weighted EXAFS spectra of *N*-picolylpolyurethane cobalt(II) and nickel(II) complexes are shown in Figure 4, presenting the experimental $k^3\chi(k)$ versus k curves which are converted from the original measured $\mu(E)$ versus E curves by EDAPN software package and reported without Fourier filtration. There is a qualitative difference in oscillatory structure, either peak shapes or location of peaks, between cobalt(II) and nickel(II) complexes, in support of the idea that local structures about cobalt(II) and nickel(II) ions are different. To determine the nearest-neighbor distances, contribution of the first-shell coordination sphere to the experimental data is isolated by using Fourier filtration. Figure 5 shows Fourier filtered experimental data for PUPYM (dots). For comparison, the FEFF5 simulated EXAFS function (solid line) is also shown. The optimized structure parameters for FEFF5 calculation, including bond distances and Debye−Waller factor, are listed in Table 1. The agreement between the FEFF5 simulated and measured EXAFS spectra is very satisfactory over the full range of the curves. Some discrepancies in simulation partly arise from the approximate treatment of the molecular potential by FEFF5 calculation and the choice of E_0 in the experimental data analysis. The error can also be ascribed to the structural imperfections in the samples, such as geometric distortions of central metal ions to lower symmetry and coordination pendent groups that contain only one picolyl side group.

Reported interatomic distances are 2.437 Å for nickel−chlorine and 2.133 Å for nickel−nitrogen in *trans*-octahedral Ni(pyridine)$_4$Cl$_2$,[19] 2.26 Å for cobalt−chlorine, and 1.95 Å for cobalt−nitrogen in tetrahedral Co(*p*-toluidine)$_2$Cl$_2$.[5,20] The nickel−oxygen distance is 2.05 Å in octahedral NiCl$_2$·6H$_2$O.[21] It is notable that bond lengths for metal−chlorine and metal−ligand of PUPYM are similar to those of small molecular weight transition metal complexes.

Two-Phase Model for PUPYM. Incorporation of a small amount of ionic groups or fine particles into polymers will affect the structure and physical properties of the host materials in a similar way to our present system. Therefore, theoretical research in ionomers or filled polymers that exist Coulomb or van der Waals interaction was carefully reviewed.

Table 1. Optimized Structure Parameters for FEFF5 Calculation

	nitrogen		chlorine		oxygen			
sample	*R*, Å	σ, Å[a]	*R*, Å	σ, Å	*R*, Å	σ, Å	S_0^2 [b]	QF[c]
PUPYCo^{2+}	2.069	±0.053	2.251	±0.066			0.63	0.121
PUPYNi^{2+}	2.094	±0.088	2.411	±0.084	2.070	±0.073	0.60	0.146

[a] σ is the Debye–Waller factor that measures the static and thermal disorder in bond distances. [b] S_0^2 is the amplitude reduction factor that is due to excitations of electrons other than 1s electrons (for a K-edge) in the X-ray absorbing atom. [c] The quality factor of fit (QF) is defined as the square root of the ratio of the sum of the squares of the residue to the sum of the squares of the data.

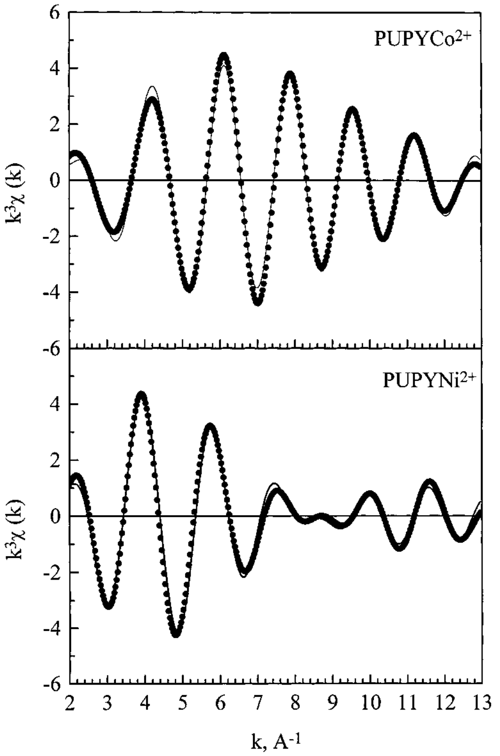

Figure 5. EXAFS spectra: $k^3\chi(k)$ versus *k* curves obtained from (a) FEFF5 theoretical calculation using the parameters in Table 1 (solid line) and (b) Fourier-filtered experimental data (dot).

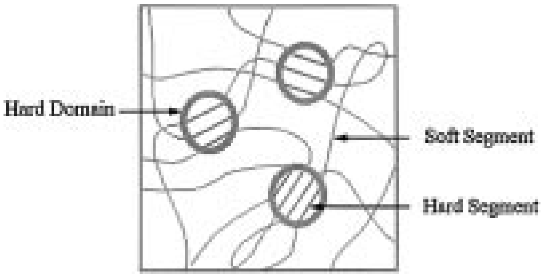

Figure 6. A two-phase model of *N*-picolylpolyurethane transition metal complexes: one microphase is the hard domain of self-segregated hard segments brought about by metal–ligand interaction, and the other phase is the matrix of soft segments.

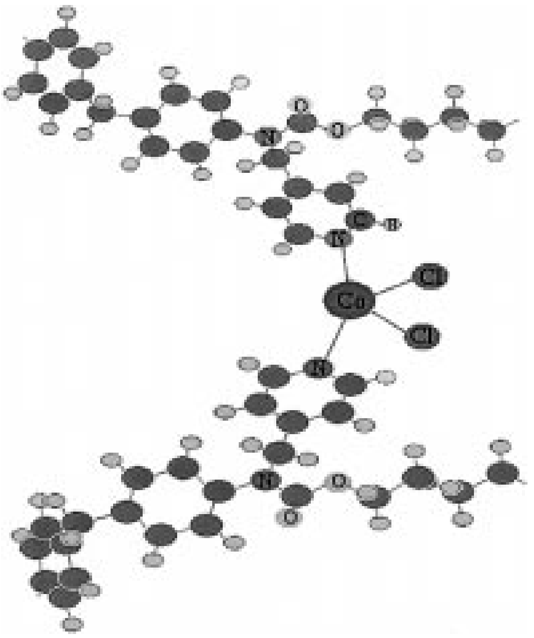

Figure 7. Schematic diagram of the hard domain brought about by coordination interaction between cobalt(II) ions and picolyl groups of hard segments.

Polymers with up to 10 mol % of pendent acid groups that are neutralized partially or completely are termed as ionomers. Efforts have been directed at delineating the very complex nature of their ionic interaction and microstructure,[22] and extensive studies support the idea that Coulomb interactions cause aggregation of the ionic groups. Ion-rich microdomains act as cross-links and are responsible for the behavior of thermoplastic elastomers over some range of temperature.

Eisenberg et al. have proposed a multiplet-cluster model (or EHM model) for random ionomers.[23] Salt groups exist in two different environments. Isolated multiplets, i.e., an aggregation of several ion species, disperse in the hydrocarbon matrix. Associated multiplets including hydrocarbon material, termed as clusters (about 5 nm in size), result in a separated microphase rich in ions. Multiplets reduce the mobility of vicinal polymer chains and increase their glass transition temperatures, while polymer chains restricted by clusters give rise to a new T_g.[24] The existence of two glass transition temperatures in fine silica-filled polymers suggested that a similar model is operative in this system.[25]

A proposed two-phase model of *N*-picolylpolyurethane transition metal complexes is shown in Figure 6. Once cations are incorporated into PUPY matrix, they are surrounded by an immobilized layer of hard segment chains and form a hard domain. In analogy with multiplets brought about by electrostatic binding in random ionomers, a hard domain in the recent system is postulated to be brought about by coordination interaction (Figure 7). Cations act as a cross-linkage between two pendent picolyl groups that provides a driving force for hard segments separating from soft segments to form a microphase separated material. Soft segments attached to the surface of a hard domain form a coating. The anchoring chains close to the surface are regarded as loosely bounded, while the mobility of chains far from the surface is slightly reduced by the anchoring effect. The difference between multiplets and hard domain lies in two ways. In multiplets only ionic moieties are involved, and no microphase separation is caused. On the contrary, hard segments are involved

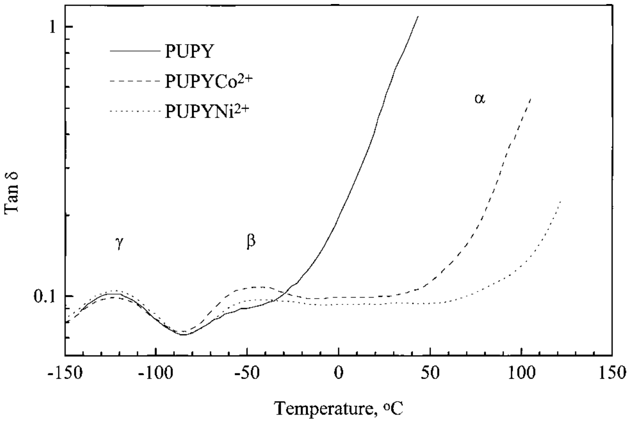

Figure 8. The tan δ versus temperature curves for *N*-picolylpolyurethane and transition metal complexes: α-, β-, and γ-transition are assigned to the motion of hard segments, glass transition of soft segments, and the Schatzki type crankshaft motion of the sequence of CH_2 groups on the soft segments.

in the hard domain and form a microphase separated from soft segments.

DMTA and SAXS Analysis. Dynamic mechanical properties of *N*-picolylpolyurethane transition metal complexes are investigated. The mechanical loss (tan δ) versus temperature curves are shown in Figure 8. In $PUPYNi^{2+}$, the γ-transition occurring at about −120 °C is assigned to the Schatzki type crankshaft motion of the sequence of CH_2 groups on the soft segments. The β-transition taking place at about −40 °C is ascribed to the glass transition of soft segments. $PUPYCo^{2+}$ exhibits a glass transition of soft segments at the same position. According to our model, it is expected that coordination interaction mainly affects the motion of hard segments and has little effect on the mobility of soft segments. Therefore, $PUPYNi^{2+}$ and $PUPYCo^{2+}$ have similar glass transition temperatures of soft segments. From small-angle X-ray scattering measurements, $PUPYNi^{2+}$ shows a scattering pattern of a distinct peak with respect to PUPY, and the shape is nearly identical to that of $PUPYCo^{2+}$.[1] This means the distribution mode of the hard domain is identified with each other in these samples.

Ligand Field Stabilization Energy (LFSE). The α-transition in *N*-picolylpolyurethane corresponds to the motion of hard segments. When complexation with cobalt(II) and nickel(II) ions, this transition shifts to higher temperatures. Since each metal center is coordinated to two picolyl ligands from different polyurethane chains, motions of hard segments in *N*-picolylpolyurethane cobalt(II) and nickel(II) complexes are severely restricted until sufficient thermal energy is supplied to break these coordination cross-links. This additional thermal energy for splitting coordination cross-links (Es) interprets the increase of α-transition temperature (Ts) in the presence of metal ions and can be estimated by Es = R[Ts(PUPYM) − Ts(PUPY)], where R is the gas constant. Ts enhancements are 78 °C for $PUPYCo^{2+}$ and 117 °C for $PUPYNi^{2+}$.

Belfiore has described a molecular thermodynamic interpretation of macroscopic thermal properties of macromolecular metal complexes.[26] According to this method, disruption of cross-links in $PUPYCo^{2+}$ can be described as a process that one picolyl ligand is removed from the coordination sphere of cobalt(II) ion. Metal complex species for $PUPYCo^{2+}$ before and after dissociation are CoL_2Cl_2 and $CoLCl_2Z$, respectively, where L is the picolyl group and Z is the water of hydration. Therefore, the splitting of the cobalt−ligand bond is schemed as $CoCl_2L_2 \rightarrow CoCl_2L(H_2O)$. Similarly, the splitting of the nickel−ligand bond is schemed as $NiCl_2L_2(H_2O)_2 \rightarrow NiCl_2L(H_2O)_3$.

Table 2. Estimation of Ligand Field Stabilization Energy Difference (ΔLFSE) between Metal d-electrons in Complexes with Two-Function Cross-Links vs Complexes Maintaining One Picolyl Ligand as a Coordination Pendent Groups

	g	f[a]	Δo (cm^{-1})	LFSE (cm^{-1})	ΔLFSE (kJ/mol)
$CoCl_2py_2$	9.3	1.015	9440	5041	3.56
$CoCl_2py(H_2O)$		0.955	8882	4743	
$NiCl_2py_2(H_2O)_2$	8.8	1.01	8888	10666	5.06
$NiCl_2py(H_2O)_3$		0.97	8536	10243	

[a] The "rule of average environments" is used to calculate Jorgensen's f parameters for mixed-ligand complexes based on a weight-average of the splittings of individual ligands.

Energy supplied to remove one picolyl side group ligand from the coordination sphere of metal ions is estimated by the ligand field stabilization energy difference (ΔLFSE) between metal d-electrons in complexes with two picolyl ligands in the coordination sphere of metal ions and complexes maintaining one picolyl ligand as coordination pendent group: $\Delta LFSE = LFSE(ML_2) - LFSE(ML)$.

Taking the concentration dependence of the coordination interaction into consideration, a simple energetic model is formulated which accounts for the disruption of coordination cross-links and includes the ligand field stabilization energy:[26]

$$R[\mathrm{Ts(PUPYM)} - \mathrm{Ts(PUPY)}] = \beta(\Delta \mathrm{LFSE})x(1 - x) \tag{1}$$

where x is the molar fraction of metal chloride in the hard domain. The empirical parameter β is included to account for the existence of imperfections that arise from geometric distortions of central metal ions to lower symmetry, intramolecular loops, coordination pendent groups, etc.

In favor of the LFSE calculation, pyridine is selected as a model ligand of the *N*-picolyl group. Quantitative calculation of LFSE for model compounds is shown in Table 2. LFSE is 120% of octahedral ligand splitting (Δ_O) for the octahedral nickel(d^8) complex. For the tetrahedral cobalt(d^7) complex, LFSE is 120% of tetrahedral ligand splitting (Δ_T) or 53.3% of Δ_O, since the tetrahedral ligand field splitting (Δ_T) is $^4/_9$ as large as the corresponding octahedral ligand splitting, when all the ligands are the same. Octahedral ligand splitting is estimated on the basis of Jorgensen's parameters:[27] $\Delta_0 = f \times g \times 1000\ cm^{-1}$, where g of Co^{2+} and Ni^{2+} is 9.3 and 8.8 and f of Cl^-, H_2O, and C_5H_5N is 0.79, 1.00, and 1.24, respectively. The "rule of average environments" is used to calculate the Δ_0 for mixed-ligand complexes based on a weight-average of the splittings of individual ligands.

Difference of ligand field stabilization energy of polyurethane nickel(II) complex is larger than that of the cobalt(II) complex. While mobility of hard segments is in inverse proportion to the strength of coordination interaction, $PUPYNi^{2+}$ has a higher α-transition temperature with respect to $PUPYCo^{2+}$ as expected.

The empirical parameter β obtained from eq 1 is 0.76 for $PUPYCo^{2+}$ and 0.80 for $PUPYNi^{2+}$ and is consistent with the value 0.7−0.8 for poly(4-vinylpyridine) nickel acetate[28] and cobalt chloride complexes.[29]

Conclusions

1. Spectroscopic methods are used to investigate the coordination structure of *N*-picolylpolyurethane transition metal complexes. Mid-IR, UV−vis, and far-IR spectra are applied to investigate the ligands, central cations, and the possible geometric arrangement of ligands in the first-shell coordination sphere. Thereafter, a detailed coordination structure is given by EXAFS on the basis of the above analysis. The geometrical arrangement of ligands in the first-shell coordination sphere of cobalt(II) and nickel(II) ions in *N*-picolylpolyurethane is tetrahedral CoL_2Cl_2 and octahedral $NiL_2Cl_2Z_2$, where L is picolyl groups and Z is hydrate. Calculated bond lengths for metal−chlorine, metal−nitrogen, and metal−oxygen atoms are similar to those of small molecular weight transition metal complex analogues.

2. A two-phase model of *N*-picolylpolyurethane transition metal complexes is proposed. One microphase is the hard domain of self-segregated hard segments brought about by metal−ligand interaction. The other phase is the matrix of soft segments. This model best describes the experimental data of DMTA and SAXS. Coordination interaction affects mainly the motion of hard segments and has little effect on mobility of soft segments. In polyurethane cobalt(II) and nickel(II) complexes, distribution modes of hard domain in soft segment matrix are identified with each other.

3. Transition metal ion−ligand moieties and their interactions dominate the macroscopic thermal behavior of PUPYM. The ligand field stabilization energy difference (ΔLFSE) between metal d-electrons in complexes with two picolyl ligands in the coordination sphere of metal ions and complexes maintaining one picolyl ligand as coordination pendent group is calculated on the basis of observed coordination structure. It represents the energy supplied to split coordination cross-links. ΔLFSE of polyurethane nickel(II) complex is larger than that of cobalt(II) complex. Since the mobility of hard segments is in inverse proportion to the strength of coordination cross-links, a higher α-transition temperature of $PUPYNi^{2+}$ with respect to $PUPYCo^{2+}$ is found as expected.

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