Ligand Field Stabilization in Nickel Complexes That Exhibit Extraordinary Glass Transition Temperature Enhancement

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ABSTRACT: A thermodynamic interpretation of the ligand field stabilization energy appropriate to pseudo-octahedral d^8 complexes is employed to estimate the synergistic enhancement of the glass transition temperature in blends of nickel acetate with poly(4-vinylpyridine) (P4VP). The maximum enhancement of T_g is ≈100 °C, which occurs at a metal/polymer-repeat-unit concentration of approximately 1:2 on a molar basis. This suggests that the nickel cation coordinates to two pyridine ligands under favorable conditions. Energetic considerations coupled with the crystal structure of nickel acetate tetrahydrate suggest that pyridine ligands replace weak-base waters of hydration in the coordination sphere of the metal center. "Effective" coordination cross-links form when the pyridine pendant groups reside on different macromolecular chains. Ligand field stabilization energies (LFSE) are calculated for two hydrated nickel acetate model complexes that coordinate to either one or two pyridine groups in a pseudo-octahedral mixed-ligand arrangement. These models simulate the formation and disruption of coordination cross-links, and the LFSE's are consistent with the fact that cross-link dissociation is an endothermic process. The positive quantity $R\{T_g(\text{blend}) - T_g(\text{undiluted P4VP})\}$ represents thermal energy that must be supplied to dissociate coordination cross-links. The simple coordination-interaction model equates this thermal energy to the LFSE difference between the two nickel acetate model complexes mentioned above. The concentration dependence of the synergistic T_g response is formulated via the quadratic $x(1-x)$ following the Margules symmetric model for nonideal energetics, where x represents the mole fraction of the metal salt. The experimental enhancement of T_g represents 70% of the prediction based on LFSE's of the pseudo-octahedral model complexes. Reasons for the discrepancy between experiment and prediction are discussed in terms of microstructures not accounted for by the simple model.

Introduction

This research contribution presents experimental results for blends of nickel acetate and poly(4-vinylpyridine) that exhibit some of the most remarkable enhancements in glass transition temperature reported to date.[1] The strategy focuses on coordination complexes as a mechanism for compatibilization and thermal synergy. Recently, Khandwe et al.[2] synthesized poly(butanethiooxamides) that form coordination complexes with acetates and chlorides of the following divalent transition metals; cobalt, nickel, and copper. Thermogravimetric analysis revealed that these metal salts enhance the thermal stability of the polymers. Weight loss occurred at higher temperature and the enhanced thermal stability was most pronounced for d^8 Ni^{2+} complexes.[2] Allan and co-workers prepared and characterized coordination complexes of poly(4-vinylpyridine) with zinc chloride[3] and cobalt bromide.[4] In both cases,[3,4] far-infrared spectroscopy was employed to identify vibrational absorptions that are characteristic of metal–halogen and metal–nitrogen bonds. Tetrahedral coordination was proposed for the zinc and cobalt complexes in agreement with far-infrared data.[3,4] Previous work originating in this laboratory employed low-molecular-weight zinc salts (i.e., zinc acetate, zinc laurate, zinc stearate) and zinc-neutralized ethylene/methacrylic acid copolymers in solid-state blends with poly(4-vinylpyridine) (P4VP).[5-7] Thermal synergy was observed in blends containing zinc acetate,[5,6] and mechanical synergy was measured in blends with the zinc ionomer (SURLYN 1706).[1,7] However, the maximum enhancement in glass transition temperature for zinc acetate/P4VP is 15–25 °C relative to the T_g of undiluted P4VP.[6] Since there is no energetic stabilization due to the ligand field in d^{10} (Zn^{2+}) complexes,[8] thermal synergy in blends of zinc acetate and P4VP cannot be attributed to the effect of ligand field stabilization on thermochemical properties. When zinc acetate is replaced by nickel acetate, the ligand field stabilization energy (LFSE) is comparable to the ligand field splitting.[9] In this research contribution, it is proposed that the LSFE for pseudo-octahedral mixed-ligand d^8 complexes represents a potential molecular thermodynamic interpretation of macroscopic thermal properties.[6,10]

One advantage of employing low-molecular-weight d-block metal salts is that coordination and symmetry in the undiluted crystalline state is known prior to blending via X-ray diffraction data. Hence, in the case of nickel acetate tetrahydrate, the results of Van Nierkerk and Schoening[11] and Downie et al.[12] suggest that two acetate anions and four waters of hydration represent the initial six ligands in a slightly distorted pseudo-octahedral arrangement as illustrated in Figure 1. When nickel coordinates to pyridine pendant groups in the macromolecular chain during solution blending, this occurs via ligand substitution as the pyridine nitrogen lone pairs replace weak-base waters of hydration in the coordination sphere of the nickel cation, even though all hydrogen atoms of the water molecules are extensively hydrogen bonded in the crystal.[12] An empirical "group-contribution" scheme is employed to calculate the ligand field splitting[9] and the LSFE for nickel acetate coordinated to either one or two pyridine groups. The difference between the LFSE's for these two complexes is employed via a Margules-type excess energetic model[13] to account for nonidealities in the mixing process and the synergistic increase in the glass transition temperature.

Experimental Considerations

Materials and Sample Preparation Methods. Nickel acetate tetrahydrate was purchased from Aldrich Chemical Co. (Milwaukee, WI) as a light-green powder. Poly(4-vinylpyridine) (P4VP) was obtained from Scientific Polymer Products (Ontario, NY) with reported molecular weights of 50 000 and 200 000.

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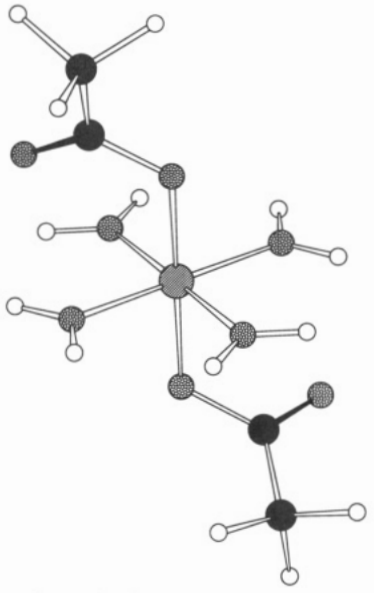

Figure 1. Pseudo-octahedral crystal structure of nickel acetate tetrahydrate, as determined from X-ray diffraction experiments (adopted from ref 12).

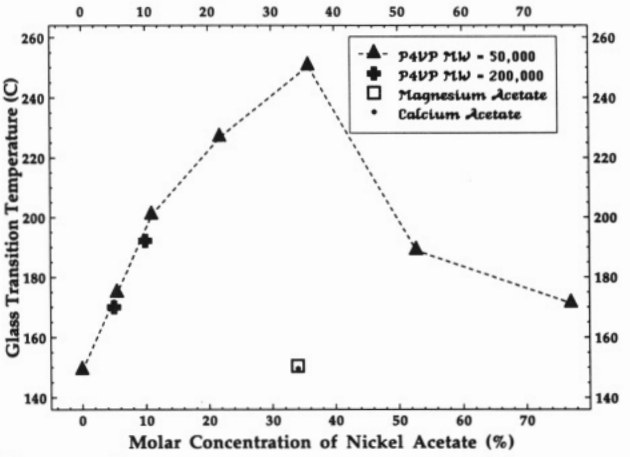

Figure 2. Glass transition phase behavior for blends of nickel acetate tetrahydrate with poly(4-vinylpyridine), illustrating synergistic thermal response. Data are included for two different molecular-weight samples of P4VP (50K and 200K). For comparison, glass transition temperatures are also provided for P4VP blends that contain either magnesium acetate tetrahydrate or calcium acetate hydrate when the metal/polymer-repeat-unit concentration is 1:2 on a molar basis.

All materials were used as received from the commercial distributors. d-Block coordination complexes of nickel acetate and P4VP were prepared via solution blending for 24 h in 3% (v/v) acetic acid to generate 2% (w/v) solutions. Most of the solvent evaporated at ambient temperature in a fume hood, and the solid residues exhibited a gradual color change from light-blue green to emerald green with increasing concentration of nickel acetate. The final drying step was performed under vacuum at 145 °C for 24 h to produce blends of the same greenish color, independent of composition. The ≈150 °C glass transition temperature of P4VP is increased substantially by nickel acetate. Consequently, it is only possible to employ high-temperature compression molding for blends that contain relatively low nickel concentrations because the elevated T_g approaches the decomposition temperature of the metal salt, and optimal molding temperatures are typically 75–100 °C above T_g in the absence of crystallinity. When compression molding is feasible, films are produced that shrink considerably upon removal from the high-temperature press. Precipitation occurs when individual 2% (w/v) *methanol solutions* of nickel acetate and P4VP are mixed. When the initial solution concentration of nickel acetate was 34 mol % relative to P4VP, the green transparent precipitate obtained from *methanol* exhibited a glass transition temperature of 262 °C after drying.

Thermal Analysis. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-7 with the overall goal of generating the glass transition temperature phase diagram. After quenching from the molten state, glass transition temperatures were measured under helium and nitrogen purges at a rate of 20 °C/min *during the second heating trace in the calorimeter*. T_g was calculated at the midpoint of the heat capacity change between the liquid and glassy states, without complicating effects due to enthalpy relaxation. Differential power output was monitored via Perkin-Elmer's TAC 7/DX thermal analysis controller in conjunction with the DSC7 multitasking software on a 386/33 personal computer.

Results and Discussion

Glass Transition Phase Behavior. Synergistic thermal response is illustrated in Figure 2 for blends of nickel acetate with poly(4-vinylpyridine). The glass transition phase behavior reveals blend T_g's of vacuum-dried samples that are considerably higher than the T_g of undiluted P4VP. This is remarkable because most low-molecular-weight additives plasticize the host polymer and lower its T_g.[14] For all of the blends investigated, the step increment in specific heat at the glass transition remains relatively constant at a value of 0.28 ± 0.08 J/(K·g of P4VP). This is a typical range for the discontinuous observable ΔC_p of glassy polymers.[14] The maximum enhancement of the glass transition temperature in Figure 2 is ≈100 °C with respect to the thermal properties of undiluted P4VP (T_g ≈ 150 °C), and the optimal metal/ligand concentration is roughly 1:2 on a molar basis. For comparison, the glass transition temperatures of P4VP blends that contain either magnesium acetate tetrahydrate or calcium acetate hydrate at a metal salt concentration of 34 mol % are also included in Figure 2. It is evident that neither of the s-block salts perturbs T_g when the metal/polymer-repeat-unit concentration is 1:2 on a molar basis. This is attributed to the fact that Ca^{2+} and Mg^{2+} are classified as hard acids.[15] Hence, they prefer the "hard-base" acetate anions and the waters of hydration instead of the pyridine pendant group which is classified as a borderline base.[15] A molecular interpretation of the synergistic T_g–composition data presented in Figure 2 suggests that nickel coordinates to two pyridine ligands on different polymer chains, generating "coordination cross-links".[28] Pseudo-octahedral d^8 nickel complexes can accommodate at least two pyridine ligands which replace weak-base waters of hydration in the coordination sphere of the metal center. Ligand substitution of this nature leads to an increase in the ligand field splitting because pyridine is the strongest base, the acetate anion is intermediate, and the waters of hydration are the weakest of the three ligand bases under consideration.[16,17] This hypothesis of metal–ligand σ-bonding that focuses on the basicity of the ligands via Brønsted acid ionization constants[16] (i.e., pK_a values) and Gutmann donor–acceptor numbers[17] is consistent with hard-and-soft acid–base concepts.[15] The divalent nickel cation is classified as a borderline acid,[15] and it favors coordination to pyridine, which is a borderline base, instead of the hard-base acetate anions and waters of hydration. Hence, it is highly probable that the pyridine ligand (via its free electron pair) in the side chain of P4VP replaces waters of hydration in undiluted nickel acetate during blend preparation in acetic acid solution. Six-coordinate d^8 nickel complexes are strongly favored from an equilibrium viewpoint when good donor ligands such as pyridine are present.[18] Furthermore, metal–ligand σ-bonds between Ni^{2+} and water are weaker than those between the nickel cation and the acetate anion. This suggests that it is energetically favorable for nickel acetate tetrahydrate to shed some of its bound water molecules and

coordinate to one or more polymeric pyridine groups in the amorphous phase of this binary mixture. Consequently, coordination cross-links reinforce P4VP,[28] and the glass transition occurs at higher temperature.

Ligand Field Stabilization Model. The extraordinary synergistic thermal response illustrated in Figure 2 is rationalized in terms of thermodynamic aspects of the ligand field stabilization energy that is consistent with pseudo-octahedral d^8 complexes. It should be emphasized that the approach described below deviates considerably from well-known free-volume and configurational entropy models of the glass transition.[22-27] Energetic stabilization of complexes due to the presence of the ligands is invoked to explain the increase in T_g of P4VP via blending with nickel acetate. The absolute magnitude of T_g and the discontinuous observable ΔC_p at the glass transition are not predicted by the energetic ligand field stabilization model.

The starting point focuses on the five degenerate d-atomic orbitals of the free nickel ion. When six ligands are distributed octahedrally about the metal center, there is repulsion between the ligand electrons and the metal d-electrons which raises the energy of the d-orbitals. Most importantly, however, the Coulombic potential partially removes the orbital degeneracy[8,9] and splits the five metal d-orbitals into a set of three degenerate metal–ligand molecular orbitals, denoted by d_{xy}, d_{yz}, and d_{zx}, which are at lower energy relative to the degenerate pair denoted by $d_{x^2-y^2}$ and d_{z^2}. The latter molecular orbitals (i) have lobes that are directed along the metal–ligand bond axis, (ii) are of the correct symmetry to participate in metal–ligand σ-bonding, and (iii) are designated e_g under octahedral symmetry. The three degenerate orbitals at lower energy (i) have lobes that are directed to each side of the metal–ligand bond axes, (ii) are of the correct symmetry to participate in metal–ligand π-bonds, and (iii) are designated t_{2g} under octahedral symmetry. The energy difference between the t_{2g} and e_g molecular orbitals is called the octahedral ligand field splitting, and it is characteristic of both the metal center and the six ligands. Group-contribution empiricism is employed to predict the octahedral ligand field splitting[9] for nickel acetate tetrahydrate, nickel acetate trihydrate coordinated to one pyridine group, and nickel acetate dihydrate coordinated to two pyridine groups. The latter complex is representative of a coordination cross-link where nickel acetate forms a metal–ligand bond with pyridine side groups on two different macromolecular chains. Initially, group-contribution computations[9] are performed for the six-coordinate nickel acetate anion $[Ni(CH_3COO)_6]^{4-}$, the hexaaqua nickel cation $[Ni(H_2O)_6]^{2+}$, and the six-coordinate nickel pyridine cation $[Ni(C_5H_5N)_6]^{2+}$. The predicted ligand field splittings are 8544, 8900, and 11 125 cm^{-1}, respectively. The "rule of average environments" is subsequently invoked[9] which states that "*the ligand field splitting for a pseudo-octahedral mixed-ligand complex is a weighted average of the splittings calculated for each of the mono-ligand 6-coordinate complexes separately*". Hence, one estimates the pseudo-octahedral ligand field splitting Δ_0 for the three mixed-ligand complexes as follows: Δ_0 = 8781 cm^{-1} for $Ni(CH_3COO)_2(H_2O)_4$, Δ_0 = 9152 cm^{-1} for $Ni(CH_3COO)_2(H_2O)_3(C_5H_5N)$, and Δ_0 = 9523 cm^{-1} for $Ni(CH_3COO)_2(H_2O)_2(C_5H_5N)_2$. The next step is to calculate the ligand field stabilization energy based on estimates of the electronic energy level separation between the t_{2g} and e_g molecular orbitals. The ground-state electronic configuration[8] of a d^8 octahedral complex is designated $(t_{2g})^6(e_g)^2$. When eight metal d-electrons populate the t_{2g} and e_g molecular orbitals in this fashion, the electronic energy of the complex is lower than that if the electrons were placed in the five degenerate atomic d-orbitals of the free nickel ion. In other words, the energy of the eight metal d-electrons is stabilized in the coordination complex, hence the phrasing "ligand field stabilization energy (LFSE)". When the metal d-electrons are influenced by the Coulombic ligand field potential appropriate to an octahedral distribution of electron donors around the metal center, quantum mechanical calculations based on zeroth-order perturbation theory allow one to determine the energy levels of the t_{2g} and e_g molecular orbitals. Relative to the energy of the five degenerate atomic d-orbitals of the free metal ion, the t_{2g} orbitals are $0.4\Delta_0$ lower in energy, and the e_g orbitals are $0.6\Delta_0$ higher in energy.[9] Hence, the ligand field stabilization energy is $1.2\Delta_0$ when six metal d-electrons fill the t_{2g} molecular orbitals and the remaining two electrons populate the e_g set for an octahedral d^8 complex that does not distort to tetragonal or square-planar geometries.[8] On the basis of calculations of the ligand field splittings given above, the LFSE of $Ni(CH_3COO)_2(H_2O)_2(C_5H_5N)_2$ is 5.3 kJ/mol larger than the LFSE of $Ni(CH_3COO)_2(H_2O)_3(C_5H_5N)$.

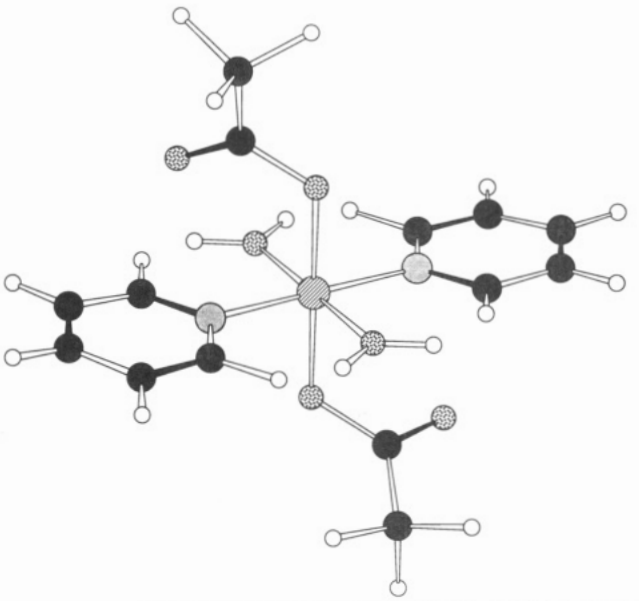

Figure 3. Proposed model for coordination cross-links where nickel acetate dihydrate forms metal–ligand bonds with pyridine nitrogen lone pairs on two different macromolecular chains.

The quantum mechanical calculations summarized above from classic inorganic chemistry[8] and ligand field theory[9] texts are correlated with the macroscopic glass transition phase behavior illustrated in Figure 2. The 101 °C enhancement in T_g of undiluted P4VP occurs when the metal–ligand concentration ratio is approximately 1:2 on a molar basis. In this respect, it is proposed that thermal synergy is a consequence of coordination cross-linking where the nickel cation forms metal–ligands bonds with two pyridine nitrogen lone pairs on different macromolecular chains.[28] This coordination complex is modeled by $Ni(CH_3COO)_2(H_2O)_2(C_5H_5N)_2$, and the proposed molecular structure is illustrated in Figure 3. The structure of the complex in Figure 3 that simulates coordination cross-links is based on the following facts: (i) the crystal structure of undiluted nickel acetate tetrahydrate is pseudo-octahedral[11,12] as illustrated in Figure 1, (ii) six-coordinate d^8 nickel complexes are strongly favored from an equilibrium viewpoint when good donor ligands such as pyridine are present,[18] even though the complex is completely amorphous, (iii) stronger metal–ligand σ-bonding occurs when pyridines replace weak-base waters of hydration in the coordination sphere of the nickel cation, and (iv) coordination cross-links were proposed by Ag-

new[28] more than 15 years ago for transition-metal complexes of nickel(II) chloride with poly(4-vinylpyridine). The onset of main-chain backbone motion in P4VP is severely restricted until enough thermal energy is supplied to (i) dissociate one nickel–pyridine bond for each metal center that is coordinated to two pyridine ligands from different macromolecular chains and (ii) induce the glass–rubber transition. The proposed model compound after dissociation is $Ni(CH_3COO)_2(H_2O)_3(C_5H_5N)$, because coordination of each metal center to one pyridine nitrogen lone pair only increases the length of the side group in P4VP, similar to a para-substituent on the phenyl ring of polystyrene. Interestingly enough, a *tert*-butyl [$C(CH_3)_3$] side group in the para-position of the styrene ring increases the glass transition temperature of polystyrene by ≈30 °C.[19,20] This is comparable to the T_g enhancement of P4VP by nickel acetate for the equimolar blend illustrated in Figure 2 where each nickel cation hypothetically coordinates to one pyridine ligand and the thermal synergy is ≈40 °C. Thermal energy required to dissociate coordination cross-links and induce the glass–rubber transition is estimated by RT_g(blend), where R is the gas constant. It should be emphasized that this quantity is concentration dependent, as illustrated in Figure 2. Thermal energy required to remove one pyridine ligand from the coordination sphere of the nickel cation on a molar basis and disrupt coordination cross-links is estimated by $R\{T_g$(blend) − T_g(undiluted P4VP)$\}$ where, once again, concentration dependence is prevalent. No effort is made to account for the concentration-dependent effect on T_g of P4VP due to a nickel acetate trihydrate pendant group in the para-position of the pyridine ring. This pendant group effect becomes more important when the nickel concentration exceeds 33 mol % and approaches 50 mol %.

A simple coordination-interaction model is formulated which accounts for the disruption of coordination cross-links and includes the ligand field stabilization energies for the two model complexes described above. The ligand substitution scheme is

$$Ni(CH_3COO)_2(H_2O)_2(C_5H_5N)_2 + H_2O \rightarrow Ni(CH_3COO)_2(H_2O)_3(C_5H_5N) + C_5H_5N \quad (1)$$

The energetics of the proposed ligand substitution are endothermic because (i) pyridine is a stronger base than water[16,17] and (ii) the complex on the left has an estimated LFSE that is 5.3 kJ/mol larger than that for the complex on the right of the above reaction. Free water and pyridine are included for completeness in postulating the form of the ligand substitution but are excluded from energetic considerations. The endothermic nature of the proposed scheme is consistent with the fact that (i) energy must be supplied to disrupt coordination cross-links and (ii) the glass transition temperature of P4VP/nickel acetate blends is enhanced relative to the T_g of undiluted P4VP. The energy input required to remove a pyridine ligand from the coordination sphere of the nickel cation and achieve the rubbery state is assumed to be proportional to the enhancement in T_g. Pyridine is a model ligand, and it is employed for simplicity to replace poly(4-vinylpyridine) which is electronically similar from the viewpoint of the nitrogen lone pair coordinating to nickel. The concentration dependence of the coordination interaction is adopted from the Flory–Huggins lattice theory[21] for nonideal mixing energetics of polymer/small-molecule blends with $RT\chi$ replaced by −5.3 kJ/mol and the polymer segment fraction replaced by the mole fraction of the repeat unit. The difference between the use of mole fraction vs volume fraction for the concentration dependence of nonideal mixing energetics is somewhat equivalent to the difference between the Margules and van Laar models[13] for the excess free energy of mixing. In this respect, the proposed model matches the characteristics of the Margules model. Hence, with the aid of ligand field stabilization, the enhancement of T_g(P4VP) due to the metal salt is estimated from the following energetic equality:

$$R\{T_g(\text{blend}) - T_g(\text{P4VP})\} = 5.3\ (\text{kJ/mol})\beta x(1-x) \quad (2)$$

where x represents mole fraction. The empirical parameter β is included in eq 2 to account for at least three possible scenarios that have been overlooked by the simple energetic model. First, ligand field splitting calculations appropriate to small-molecule crystalline coordination complexes[9] have been adopted to predict stabilization energies for amorphous polymer/metal-salt blends. There is no requirement that nickel acetate must coordinate to P4VP with long-range crystallographic order and complete pseudo-octahedral symmetry. Distortions to tetragonal and square-planar geometries are not uncommon in d^8 complexes to lower the energy of the electronic configuration.[8] Hence, β accounts for amorphous imperfections, and the possibility that distortions to lower symmetry prevail. Second, when nickel coordinates to two pyridine ligands, there is no guarantee that the ligands reside on different macromolecular chains producing "effective" cross-links. Intramolecular loops form if both ligands originate in the same chain, and T_g is not expected to increase much, if at all, due to "ineffective" cross-links. Hence, β accounts for the fraction of *effective* intermolecular coordination cross-links. Finally, it has been mentioned that nickel acetate trihydrate pendant groups in the para-position of the pyridine ring could affect the glass transition temperature of P4VP, and, understandably, in a concentration-dependent manner. When and if this type of coordination occurs for nickel acetate concentrations below 35 mol %, then this microstructural imperfection is also lumped into the parameter β. It is encouraging that the best-fit value of β is 0.7 for pseudo-octahedral symmetry with a Δ(LFSE) of 5.3 kJ/mol. This suggests that the experimentally measured enhancement in T_g represents 70% of the prediction based on the octahedral ligand field model. If tetrahedral coordination of the nickel cation is assumed, (i) the electronic configuration of the eight metal d-electrons in the molecular orbitals of the complex is $e^4(t_2)^4$, (ii) tetrahedral ligand field splittings are $^4/_9$ as large as the corresponding octahedral ligand field splittings,[9] (iii) the LFSE for the electronic configuration $e^4(t_2)^4$ is 80% of the tetrahedral ligand field splitting,[8] and (iv) the Δ(LFSE) parameter is 2.4 kJ/mol for the disruption of coordination cross-links which is consistent with the ligand substitution scheme given by eq 1. If tetrahedral parameters for nickel acetate coordinated to either one or two pyridine ligands are employed in the energetic model given by eq 2, then the best-fit value of β is 1.6 to generate agreement between prediction and experimental glass transition temperature data. This is physically unrealistic because crystal field coordination parameters should not *underestimate* bonding in the amorphous phase by roughly 60%. In light of the glass transition data for nickel acetate and P4VP illustrated in Figure 2, linear least-squares analysis indicates that the ligand field stabilization energy difference, Δ(LFSE), consistent with the dissociation of coordination cross-links should be greater than 3.8 kJ/mol, as illustrated in eqs 3–5 if the parameter β in the energetic model has a physically realistic upper limit of 100% (i.e., 1.0). Analysis of the glass transition data via eqs 3–5 provides further justification for the fact that tetrahedral coordination of nickel acetate to the pyridine pendant groups is

Energetic Ligand Field Model

$$R\Delta T_g = \beta\{\Delta(\mathrm{LFSE})\}x(1-x) \quad (3)$$

Minimization Function

$$\sum_{i=1}^{n}\{R(\Delta T_g)_i - \beta[\Delta(\mathrm{LFSE})]x_i(1-x_i)\}^2 \quad (4)$$

Least-Squares Result with $\beta \leq 1$

$$\Delta(\mathrm{LFSE}) \geq \frac{R\sum_{i=1}^{n}(\Delta T_g)_i x_i(1-x_i)}{\sum_{i=1}^{n} x_i^2(1-x_i)^2} = 3.8\ \mathrm{kJ/mol} \quad (5)$$

not favored because the Δ(LFSE) parameter is only 2.4 kJ/mol based on tetrahedral ligand field splittings. Measured and predicted synergistic enhancements in T_g are plotted in Figure 4 as a function of blend concentration with $\beta = 0.7$ for pseudo-octahedral symmetry and a Δ(LFSE) of 5.3 kJ/mol. Comparisons are only provided from 0–35 mol % nickel acetate because a stoichiometric imbalance which favors the metal salt could pave the way for additional microstructures whose explanations require sophisticated and possibly intractable theoretical developments.

Conclusions

Ligand field stabilization and coordination cross-linking offer plausible explanations for the observed synergistic enhancement of the glass transition temperature in blends of nickel acetate with poly(4-vinylpyridine). When the metal/polymer-repeat-unit concentration is roughly 1:2 on a molar basis, the enhancement of T_g(P4VP) is approximately 100 °C. This is remarkable because most "additives" lower the glass transition temperature of the host polymer. The thermal synergy illustrated in Figures 2 and 4 is a manifestation of the fact that (i) the disruption of coordination cross-links is endothermic and (ii) the glass–rubber transition cannot be induced until at least one nickel–pyridine bond from each metal center coordinated to two pyridine ligands on different chains is dissociated to allow unrestricted motion of the polymer backbone. A simple "back-of-the-envelope" model is proposed that focuses solely on energetics to predict the enhancement of T_g. The experimental data represent 70% of the expectations based on empirical ligand field splitting calculations for d^8 pseudo-octahedral mixed-ligand complexes without tetragonal or square-planar distortions. The adjustable parameter (i.e., $\beta = 0.7$) accounts for amorphous imperfections that result in deviations from complete pseudo-octahedral symmetry, intramolecular coordination cross-links that are deemed ineffective, and nickel acetate trihydrate pendant groups coordinated to the pyridine nitrogen free electron pair in P4VP that could have a concentration-dependent effect on the glass transition temperature. Metal–ligand coordination is an attractive strategy to produce compatibilized blends with enhanced macroscopic physical properties, particularly when coordination cross-links and coordination pendant groups are present.

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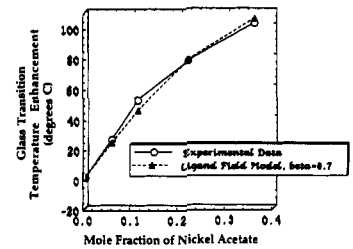

Figure 4. Concentration dependence of the glass transition temperature enhancement of P4VP induced by nickel acetate in solid-state coordination complexes. Experimental measurements are compared with the prediction based on the energetic ligand field stabilization model.

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