Synthesis of Bifunctional Interpenetrating Polymer Networks as Ion-Complexing Agents

Introduction. Interpenetrating polymer networks (IPNs) are an important category of polymers with properties which can be quite different from their component networks. A review article[1] and monograph give thorough overviews.[2] Briefly, one polymer network is prepared in the presence of another with no covalent cross-links binding them together. The physical entanglement which thus arises minimizes their phase separation since each network is independently cross-linked. As one of many examples, the formation of styrene-based IPNs with polar ligands has been studied.[3-6]

Bifunctional polymers prepared from polystyrene by the covalent bonding of two types of ligands have been found to complex certain metal ions synergistically.[7] The covalent attachment of ligands onto polymer supports may, however, involve a number of low-yield reactions, and a more straightforward method would need to be developed. The modification of polystyrene beads through IPN formation with ligands which can participate in metal ion complexation reactions is presented in this paper. The goal of this study is to synthesize IPNs with a range of binding constants for a given metal ion in order to define the conditions necessary for maximized cooperative bifunctional interactions. In the present paper, the second network is bifunctional; another type of bifunctional IPN, also under study, is that with each network having a different functional group.

Synthesis. Sequential IPNs were prepared from polystyrene xerogel[8] beads (250–425-μm diameter) cross-linked with 2% divinylbenzene (DVB). The beads were swollen with 4.25 M toluene solutions of two monomers for 24 h yielding swelling ratios of 4.0–4.9 depending on the monomers. The toluene solutions also contained 10% DVB and 2% AIBN (based on monomer weight). The monomer uptake and the theoretical capacities of the polymers were calculated after the beads were filtered from the solution. Polymerization was carried out by suspension in an aqueous phase which contained stabilizers to eliminate agglomeration of the beads and to minimize loss of monomers which were water soluble. After 12 h at 80 °C, the beads were recovered from the aqueous phase, washed with water, extracted in a Soxhlet apparatus for 24 h, and conditioned with successive 1 L elutions of H_2O, NaOH, H_2O, HCl, and H_2O. Characterization of the IPNs included determining their capacities and analyzing their FTIR spectra.

Two monomer pairs have been studied: *N*-vinylimidazole (VI)/ethyl acrylate (EA) and 4-vinylpyridine (VP)/EA. In each case, the former monomer coordinates with metal ions while the latter, after hydrolysis, can ion exchange. The bifunctional IPNs thus operate by both access (ion exchange) and recognition (coordination) mechanisms characteristic of the phosphorus-based ion exchange/coordination resins as previously developed.[9]

Characterization. The IPN capacities are given in Table I. The ester capacity of all acrylate-containing resins

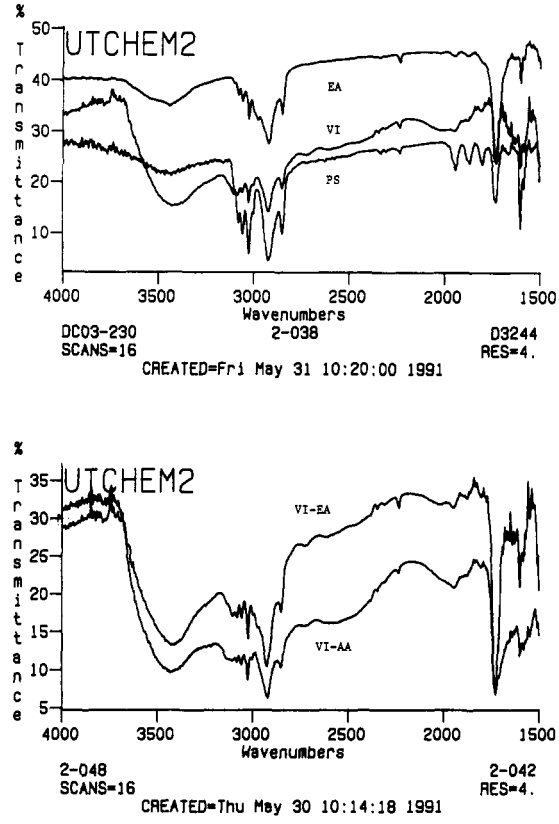

Figure 1. Infrared spectra of polystyrene (PS), *N*-vinylimidazole (VI) IPN, ethyl acrylate (EA) IPN, VI/EA IPN, and VI/acid IPN.

was calculated from the subsequent hydrolyzed acid capacity. Comparison of calculated with experimental capacities points to very high levels of incorporation during IPN formation. Figure 1 shows IR spectra of polystyrene and various IPNs within the 4000–1500-cm^{-1} region. The polystyrene is clearly modified by the presence of the VI and EA polymer networks. The VI/EA spectrum contains elements of its components, and comparison of it with its hydrolyzed product, VI/acid, shows a broad peak centered at 2500 cm^{-1} in the latter spectrum, indicative of hydrogen bonding[10] between the acid and acid/imidazole ligands. The IPN matrix thus retains enough flexibility for interligand association—as would be needed for cooperative effects in metal ion complexation reactions. Identical conclusions may be drawn from the pyridine-based spectra.

Results. The metal ion complexing abilities of the IPNs were evaluated from their Cu(II) and Co(II) binding constants after a 24-h contact time using buffered pH 5 solutions. The *y*-reciprocal form[11] of the Langmuir isotherm was used in determining the binding constants (eq 1); c is the milliequivalents of substrate remaining per

$$(c/r) = (1/S_t)c + (1/K_{11}S_t) \quad (1)$$

milliliter of solution, r is the milliequivalents of bound

Table I
Capacities (mequiv/g) of IPNs Prepared from Amine–Acrylate Monomers[a]

	VP	VP/EA	VP/acid	EA	acid	VI	VI/EA	VI/acid
base[b]	6.63[d]	3.06[d]	3.25			4.38[e]	2.62[f]	3.33
COOR[c]		2.35[e]	2.50	4.63	5.32		2.38[g]	2.55

[a] VP = 4-vinylpyridine; EA = ethyl acrylate; acid = hydrolyzed ester (i.e., carboxylic acid); VI = *N*-vinylimidazole. [b] Amine capacity, either pyridine or imidazole. [c] Ester or acid capacity. [d] 100% of calculated capacity based on monomer uptake. [e] 85% of calculated capacity based on monomer uptake. [f] 87% of calculated capacity based on monomer uptake. [g] 80% of calculated capacity based on monomer uptake.

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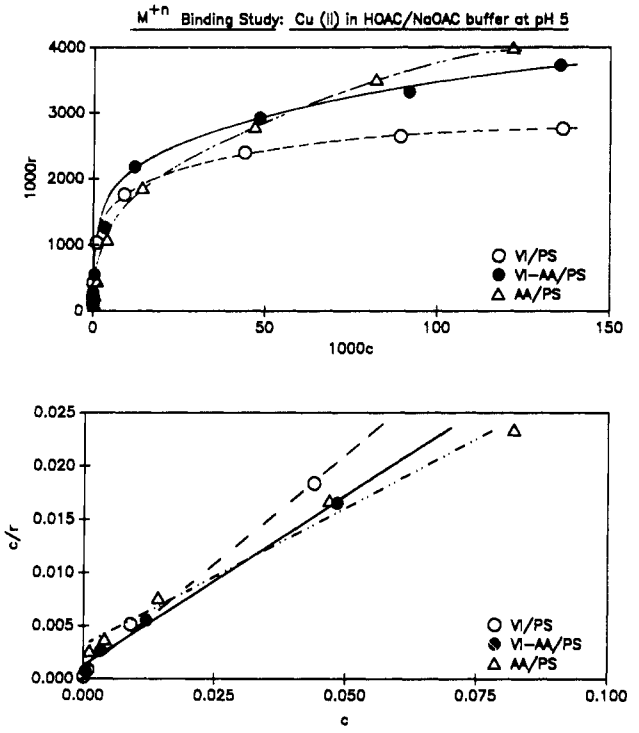

Figure 2. Adsorption isotherm and y-reciprocal plots for Cu(II) binding with VI, VI/acid, and acid IPNs.

substrate per gram of polymer, S_t is the saturation capacity (mequiv/g), and K_{11} is the binding constant assuming 1:1 complex formation.[12] Points for the y-reciprocal plot are taken from the adsorption isotherm within 20–80% of saturation as recommended by Deranleau.[13]

A portion of the Cu(II) adsorption isotherms and the y-reciprocal plots for the VI, VI/acid, and acid IPNs are shown in Figure 2. The K_{11} values are 617, 252, and 51 M^{-1} for the three IPNs, respectively. The saturation capacities show increasing values (2.8, 3.3, and 4.6 mequiv/g, in the same order as above). The VI/EA IPN has a much lower Cu(II) saturation capacity (0.62 mequiv/g) but a binding constant which is almost identical (257 M^{-1}) to the VI/acid IPN. The monofunctional EA IPN has no Cu(II) affinity. The K_{11} values for Co(II) are 99, 76, and 19 M^{-1} for the VI, VI/acid, and acid IPNs, respectively, with saturation capacities all at 2.9 (±0.1) mequiv/g. The Cu(II) K_{11} values for the VP and VP/acid IPNs are 77 and 65 M^{-1}; they are 15 and 20 M^{-1}, respectively, for Co(II).

Discussion. IPN formation maintains ligand accessibility and selectivity, thus allowing for its general application to the synthesis of polymer-supported reagents. The linearity of the y-reciprocal plots indicates 1:1 complex formation. The imidazole IPN displays quite different ion-binding behavior compared to the pyridine IPN. Additionally, the imidazole IPN binds Cu(II) more strongly than Co(II) in spite of an identical saturation capacity for the two ions. The bifunctional IPN microenvironment is different from that of the monofunctional IPNs: the Cu(II) binding constant for the VI/acid IPN is 252 M^{-1} compared to 617 M^{-1} for the VI IPN. This would suggest that the imidazole and acid ligands are proximate enough within the IPN to form a different environment for binding to the metal ion. The lower K_{11} value for the VI/acid IPN is due to the polarity of the acid ligand, rather than to irreversible hydrogen bonding, since the VI/EA IPN gives an almost identical binding constant. A complete study of the metal ion kinetics will be reported. Kinetic studies to date with a limited number of IPNs show that a 24-h contact time is sufficient (note that the Cu(II) saturation capacity for the acid IPN approaches its maximum capacity (4.6 vs 5.3 mequiv/g)).

The IPN binding constants are consistent with results from soluble analogues.[14] Acetic acid has a first formation constant of 51 M^{-1} with Cu(II) and 6.5 M^{-1} with Co(II) from solutions with an ionic strength of 1 M. The corresponding values for pyridine are 363 and 15 M^{-1} for copper and cobalt, respectively, from 0.5 M ionic strength solutions. The lower binding constant for copper with the VP IPN may indicate a steric hindrance to complexation. Extending the contact time to 7 days (from 24 h) does not lead to a significant change in the binding constant. (No imidazole–copper complex formation data have been located.)

Conclusion. Bifunctional IPNs have been synthesized as metal ion complexing agents. The ligands within such a network retain their ability to selectively complex metal ions as measured by their binding constants. Further studies with monomer pairs which lead to IPNs in which the ligand interactions enhance the extent of metal ion complexation will be reported in due course.

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References and Notes

(1) Klempner, D.; Berkowski, L. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1987; Vol. 8.
(2) Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum: New York, 1981.
(3) Millar, J. R. *J. Chem. Soc.* **1960**, 1311.
(4) Sperling, L. H.; Friedman, D. W. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 425.
(5) Kolarz, B. N. *Angew. Makromol. Chem.* **1980**, *90*, 167.
(6) Hatch, M. J. U.S. Patent 3,041,292, June 26, 1962.
(7) Alexandratos, S. D.; Quillen, D. R.; Crick, D. W. *Ind. Eng. Chem. Res.* **1991**, *30*, 772.
(8) Sederel, W. L.; De Jong, G. J. *J. Appl. Polym. Sci.* **1973**, *17*, 2835.
(9) Alexandratos, S. D.; Quillen, D. R.; Bates, M. E. *Macromolecules* **1987**, *20*, 1191.
(10) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 954.
(11) Connors, K. A. *Binding Constants*; Wiley: New York, 1987.
(12) Klotz, I. M.; Walker, F. M.; Pivan, R. B. *J. Am. Chem. Soc.* **1946**, *68*, 1486.
(13) Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044.
(14) Kotrly, S.; Sucha, L. *Handbook of Chemical Equilibria in Analytical Chemistry*; Ellis Horwood: Chichester, U.K., 1985.

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