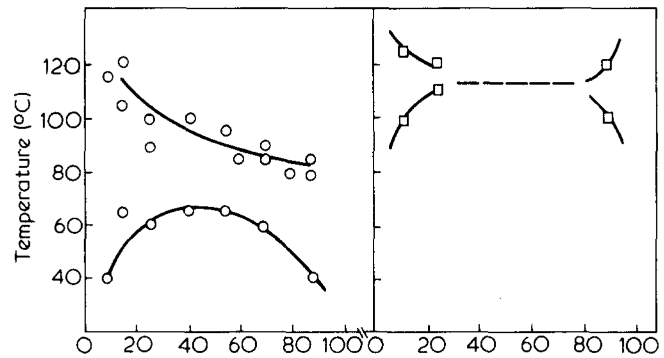

Figure 2 Phase diagram for blends of CPE 2 with PMMA (○) and for CPE 3 with PMMA (□)

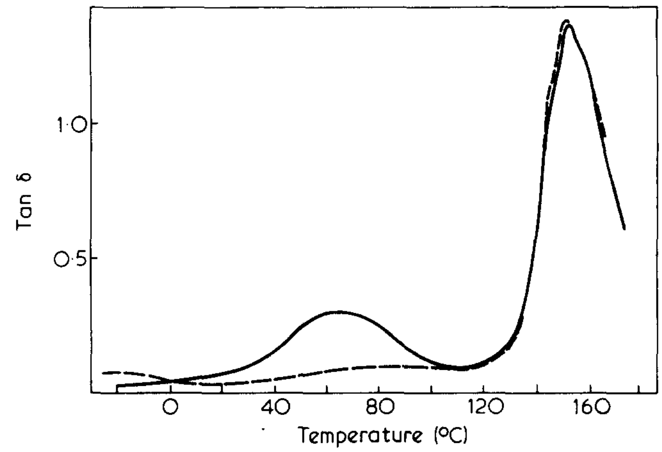

Figure 3 Dynamic mechanical results for a blend containing 25% w/w CPE 2 in PMMA (solid line) and 26% w/w CPE 1 in PMMA (broken line)

The resulting phase diagrams are shown in *Figure 2*. The samples prepared from polyethylene with the lower degree of chlorination show both upper critical and lower critical phase behaviour. The samples prepared from polyethylene with a higher degree of chlorination all appear to show similar 'hour glass' phase diagrams. One example of these is shown in *Figure 2*. The broken lines in the intermediate portion show where the samples were becoming clearer before becoming cloudy again, no horizontal region of very low scattering was found. This region is again made less certain due to possible 'orange peel effects'.

The results were checked by dynamic mechanical analysis. This can only be done where a single T_g is detectable within the compatible region at the frequency of testing, and we might expect to find this in the central region of the phase diagram for the samples from polyethylene with a lower degree of chlorination. The results for a sample containing 25.0% (w/w) (CPE 2) chlorinated polyethylene in PMMA is shown in *Figure 3* when scanning through temperature at this composition we observe the T_g for a compatible mixture at 60°C. Because the polymers are incompatible over other regions we see other spurious peaks. *Figure 3* also shows the curve obtained for an incompatible mixture prepared from the higher chlorinated polyethylene for comparison.

The fact that polymers of this molecular weight can exhibit an upper critical solution temperature as well as a lower critical solution temperature has important implications for the various theories of polymer compatibility which attempt to explain these phenomena.

Conclusion

It has been shown that poly(methyl methacrylate) is compatible with chlorinated polyethylene at some degrees of chlorination and over some temperature ranges. Some of these mixtures have been found to exhibit an upper critical solution temperature.

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Preparation of polystyryl-1,5-naphthyridine, polystyryl-pyrido[2,3-b]pyrazine and some of their copper(II) complexes

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Introduction

Polymers containing chelating ligands have found numerous applications in solid phase and organic syntheses[1,2]. When coordinated to the appropriate metal ions, these systems can function as 'immobilized' homogeneous catalysts possessing the activity of their soluble analogues while having the added advantage of ease of recovery from the reaction mixtures. Polymer-bound chelates have also been shown to selectively recover specific metal ions from metal ion mixtures[3]. Such polymers thus combine the selectivity characteristic of liquid–liquid extractions with the mechanical convenience and flexibility inherent in solid–liquid systems.

Although chelating resins employing phosphine ligands have been widely investigated in several catalytic studies during the past decade[4,5], very little work has been done using nitrogen heterocycles, some of the most versatile chelating systems known. 2,2'-Dipyridine has been attached to an insoluble polystyrene support and its potential as a polymer-bound chelate demonstrated[6]. We have recently reported the attachment of 1,8-napthyridine (NAPY) to polystyrene-2% divinylbenzene copolymer beads and the preparation of a number of transition and

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lanthanide metal complexes of the polymer[7]. In order to further the investigation of chelating systems and to prepare new polymer systems which contain the potential of stepped bridging to metal ions, we have attached 1,5-naphthyridine and pyrido[2,3-b]pyrazine to polystyrene-2% divinylbenzene copolymer beads.

Experimental

The polystyrene-2% divinylbenzene copolymer beads were purchased from Eastman laboratories. 1,5-Napthyridine (1,5-NAPY) was synthesized according to the method reported by Hamada and Takeuchi[8]. Pyrido[2,3-b]pyrazine (PPZ) was prepared using the procedure of Leese and Rydon, which was slightly modified by increasing the extraction time from 4 h to a minimum of 48 h[9]. Brominated polystyrene (SBr) containing 25% brominated phenyl residues, was prepared using the procedures suggested by Farrall and Fréchet[10]. All other chemicals and solvents were reagent-grade and used without further purification. Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories. Metal ion loadings of the modified polymer beads were determined by titrating the metal ion solutions before and after exposure to the polymer with 0.01 M EDTA using murexide (ammonium purpurate acid) as the indicator. Infra-red spectra were obtained by use of a Digilab FTS-20 Fourier transform spectrophotometer modified to record spectra by diffuse-reflectance[11]. Samples for i.r. analyses were prepared by grinding the polymer beads with KCl in a ball mill.

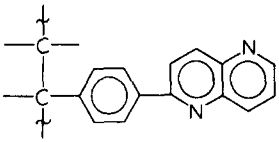
Poly(styryl-1,5-napthyridine), (S-1,5-NAPY). The bromination-lithiation steps of this preparation were carried out in an atmosphere of helium. The brominated polystyrene [4 g] (1.86 mmol Br/g) beads were swollen in 100 ml of benzene. Ten ml of a 2.2 M solution of *n*-butyllithium in hexane was added and the suspension stirred at 60 C for 3 h. A colour change from pale-yellow to salmon-pink was observed at this point. Solid 1,5-napthyridine (5.0 g, 0.039 mol) was added and the resulting purple suspension was heated to reflux for 3 h. The mixture was cooled to room temperature and bubbled with air for 12 h. The golden-brown polystyryl-1,5-napthyridine (S-1,5-NAPY) beads were recovered by filtration; washed with 500 ml portions of tetrahydrofuran, benzene, ethyl acetate, methanol-water (1:1), and methanol and dried at 60 C under reduced pressure for 24 h. Analysis found: C, 86.68; H, 7.16; N, 1.21; Br, 2.69.

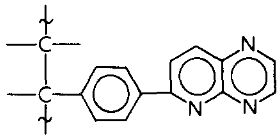
Poly(styryl-pyrido[2,3-b]pyrazine), (SPPZ). A procedure similar to that for the preparation of S-1,5-NAPY was repeated in which pyrido[2,3-b]pyrazine (5.0 g, 0.038 mmol) was employed instead of 1,5-naphthyridine. SPPZ is brick red in colour. Analysis found: C, 84.01; H, 6.90; N, 3.16; Br, 3.22.

Polymer-bound metal complexes. In a typical experiment, 500 mg of the S-1,5-NAPY beads were soaked in 50 ml of ethyl acetate containing 0.05 M copper(II) nitrate for 2 h with occasional shaking. The resulting polymer-bound metal complexes were isolated by filtration, washed with ethyl acetate and tetrahydrofuran, and dried at 60°C under reduced pressure for 24 h. The percent metal composition of the copper(II) complexes of S-1,5-NAPY and SPPZ are indicated in *Table 1*. The copper(II) complexes of SPPZ are olive brown in colour while those of S-1,5-NAPY are dark green-gold.

Results and Discussion

Attachment of 1,5-NAPY and PPZ to the free phenyl residues of PS-2% DVB is accomplished by the bromination-lithiation pathway[10]. The amount of ligand attachment may be inferred from elemental analysis. Results indicate 0.43 mmol of 1,5-NAPY per gram of polymer which is roughly equivalent to one 1,5-NAPY per 20 phenyl residues. This represents a 23% conversion of brominated phenyl groups. Elemental analysis indicate 18% of the brominated sites remain unchanged. The presence of a considerable amount of LiBr in the polymer washings leads to the conclusion that 59% of the brominated sites participated in phenyl-phenyl crosslinking. The attachment of 0.75 mmol of PPZ per gram of polymer or roughly one PPZ for every 11 phenyl residues corresponds to a 40% conversion of brominated phenyl groups. Analysis indicates 22% of the original brominated residues remain unchanged while 38% appear to have participated in crosslinking.


S-1,5-NAPY


SPPZ

The behaviour of 1,5-NAPY and PPZ in the lithiation reaction is markedly different from that of NAPY which was found to convert 80% of the phenyl groups of SBr and leave no residual bromine in the polymer[7]. Since there is no significant disparity in the electron densities at the 2-positions of these three heterocycles[12,13], the reason for the reaction difference may lie in the prevention of the compounds from reaching the reaction site. This could occur as the result of the phenyl-phenyl cross linking, which was observed in S-1,5-NAPY and SPPZ but not SNAPY, closing pathways into the polymer beads.

Except for the appearance of a shoulder at 810 cm^{-1} which is assigned to a C-H out of plane bending mode of the respective heterocyclic residues, the infra-red spectra of S-1,5-NAPY and SPPZ are very similar to that of their

Table 1 Copper(II) loadings of S-1,5-NAPY and SPPZ

	Quantity bound to polymer					
	S-1,5-NAPY			SPPZ		
Metal salt	% Metal	mmol metal/ g S-1,5-NAPY	mmol 1,5-NAPY/ mmol metal	% Metal	mmol metal/ g SPPZ	mmol PPZ/ mmol metal
$Cu(NO_3)_2$	0.50	0.08	5.38	3.83	0.68	1.10
$CuCl_2$	2.98	0.50	0.86	4.94	0.87	0.86
$Cu(BF_4)_2$	1.78	0.30	1.43	4.09	0.76	0.99

precursor SBr[14,15]. The absence of water in the two polymers and their copper complexes is verified by the lack of absorptions in the 3600–3100 cm^{-1} region of their spectra[16]. Polymer complexation of copper(II) causes the appearance of a shoulder in the spectra at 1630 cm^{-1} which occurs due to a shift in a skeletal mode of the heterocycles[14,15].

The polymer bound nitrate complexes exhibit increased band intensities in the 1400–1000 cm^{-1} region which are due to nitrate modes superimposed on the skeletal vibrations of the polymer[17,18]. The intensities in this region increase proportionally with nitrate salt loading. The observation of a single band of medium intensity at 1740 cm^{-1}, which represents the $\nu_1+\nu_4$ combination band, leads to the conclusion that the nitrate is ionic[18]. Under anhydrous conditions $Cu(NO_3)_2$ contains covalent nitrate groups. The exceptionally low affinity of S-1,5-NAPY toward $Cu(NO_3)_2$ in contrast with SPPZ and SNAPY suggests the necessity of a chelate group in order to displace the nitrate from the metal.

The spectra of the $Cu(BF_4)_2$-polymer complexes exhibit an increased intensity at 1070 cm^{-1} and the appearance of a new band at 530 cm^{-1} which are ascribed to the ν_3 and ν_4 modes of ionic tetrafluoroborate, respectively[19]. The intensities of both of these absorptions vary with the amount of salt loading. The chloride complexes, as expected show no anion related bands in the region 450–3200 cm^{-1}.

Compounds having the formulae: $Cu(1,5\text{-NAPY})Cl_2$[20], $Cu(PPZ)Cl_2$[21], $Cu(1,5\text{-NAPY})(NO_3)_2$[22] and $Cu(PPZ)(NO_3)_2$[22] are formed from reactions of the free heterocycle with the appropriate copper salt. All of these complexes have polymeric structures which contain stepped bridging heterocycles and covalently bound anions. In all complexes PPZ and 1,5-NAPY behave in an identical manner. Since the copper nitrate complexes of SPPZ and S-1,5-NAPY contain ionic nitrate, the constraints of the polymer backbone have resulted in a new type of geometry about the metal. Even though the SPPZ-$Cu(NO_3)_2$ complex has the 1:1 ligand to metal ratio found in $Cu(PPZ)(NO_3)_2$, the significant difference between the behaviour of S-1,5-NAPY, and SPPZ as well as the presence of ionic nitrate leads to the conclusion that the chelating ability of SPPZ is of major importance in its complexes.

The fact that the polymers contain only 5–9% of the phenyl groups functionalized would seem to rule out complexes of copper chloride which exhibit an octahedral geometry composed of bridging chloride and heterocycles similar to that found in complexes with the free heterocycles. Such a geometry in the polymer would only be possible if the beads were highly functionalized in localized regions and/or an exceptionally high degree of flexibility occurs in the swollen state in spite of the increased rigidity imposed by the additional crosslinking that occurred during functionalization.

Both S-1,5-NAPY and SPPZ exhibit a loading dependence on counter ion similar to that observed with SNAPY: $Cl^- > BF_4^- > NO_3^-$ (*Table 1*)[7]. The loading ability as measured by mol of metal per gram of polymer relative to a fixed anion is: SPPZ > SNAPY > S-1,5-NAPY. Although only data for $CuBr_2$ with SDIPY is available, it appears that its loading ability falls between SNAPY and S-1,5-NAPY[6,7]. However, each polymer contains a different number of ligands per gram of polymer and the positions of the nitrogens in the heterocycles afford PPZ and 1,5-NAPY the opportunity to bind two metals per ligand while NAPY is limited to a single metal. if loading ability is judged by mol of metal per mol of ligand we find SPPZ > S-1,5-NAPY > SNAPY; while the order SPPZ > SNAPY > S-1,5-NAPY is obtained if we normalize mol of metal per mol of ligand by the potential number of metals each ligand could complex. All three methods of measuring loading ability indicate the superiority of SPPZ. It appears that the presence of both chelate and bridge sites for metal attachment contribute to making SPPZ the most promising metal complexing agent of these polymers.

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