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APPLICATION OF CONTACT SHIFT REAGENTS TO THE NMR SPECTRA OF POLYMERS

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The nuclear magnetic resonance spectra of molecules containing functional groups possessing a basic lone-pair of electrons are shifted downfield by tris (dipivalomethanato) europium and upfield by tris (dipivalomethanato) praseodymium. The largest shifts are obtained for alcohols but esters, ethers,[1] and lactones[2, 3] also give contact shifts.

We now find that these lanthanide shift reagents may be successfully applied to polymers. Figure 1 shows the displacement of the methylene peak in the NMR spectrum of poly (ethylene oxide): the single peak is shifted to high or low field as expected. Hence paramagnetic shift reagents should be of general applicability in improving the resolution of NMR spectra of polymer systems, as we now illustrate for poly (methyl methacrylate).

The europium shift reagent in deuteriochloroform caused considerable shifts for all the peaks of atactic poly (methyl methacrylate). As more reagent was added, the singlet due to the O-methyl protons broadened and the three initially overlapping peaks corresponding to the C-methyls in isotactic, heterotactic and syndiotactic triads were resolved. These triads may also be observed by the solvent effect of benzene without the addition of shift reagents;[4] by running the spectra in benzene in the presence of tris (dipivalomethanato) europium the peaks for the carbomethoxy protons are separated even further (Figure 2). Raising the temperature caused a slight upfield shift, but the peaks sharpened up considerably.

Figure 3 shows the relative shift of the peaks of atactic poly (methyl methacrylate) as more europium shift reagent is added. The C-methyl proton peaks are affected most, and the broad methylene peak more than the O-methyl peaks. For the C-methyl and especially for the O-methyl protons, the isotactic triad peaks are affected more than the heterotactic and the syndiotactic peaks are moved least. The europium atom is associated with the lone-pair of electrons on the carbonyl oxygen; the nearer a proton is to the europium atom, the greater the shift produced in the NMR spectrum for that proton. Models indicate that larger shifts would be expected for methyls or carbomethoxy groups in isotactic triads.

Tris (dipivalomethanato) praseodymium causes upfield shifts in all peaks of atactic poly (methyl methacrylate). Again the peaks of the isotactic triad are shifted more than the heterotactic with the syndiotactic moved least; hence, the various peaks for the methyl and carbomethoxy protons are less well resolved in the presence of this shift reagent.

The spectra were run on a Varian HA100 100 MHz instrument. When deuteriochloroform was used as solvent TMS was employed as reference and lock signal; for benzene solutions the lock signal was the solvent.

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FIGURE I

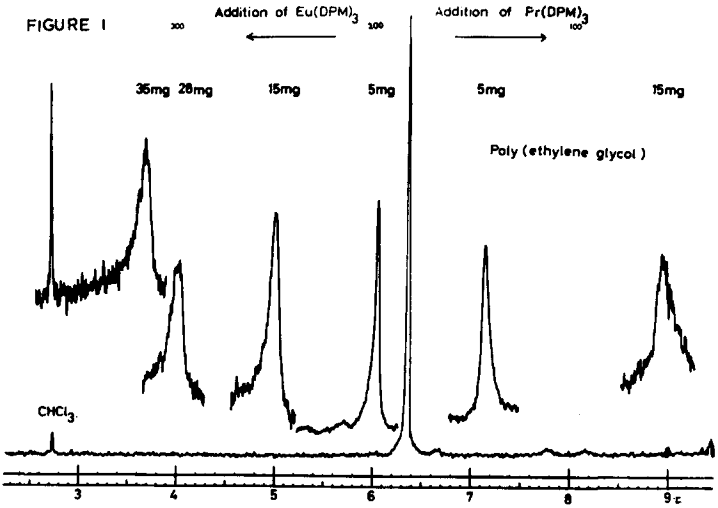

FIGURE 2

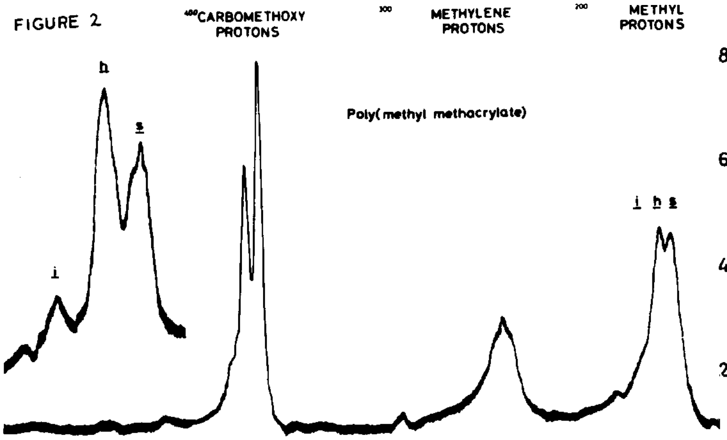

Figure 3.