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THE EFFECT OF LANTHANIDE SHIFT REAGENTS ON THE N.M.R. SPECTRUM OF STEREOREGULAR POLY (METHYL METHACRYLATE).

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Various lanthanide chelates have been found to induce large chemical shifts in the n.m.r. spectra of molecules containing functional groups with lone pairs of electrons[1-3]. We have been interested in the possibility of using these shift reagents to investigate the microstructure of stereoregular polymers since, with existing spectrometers, it is difficult to resolve (n)ad peaks beyond tetrads[4]. In this communication we report preliminary results for the effect of tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium and praesodynium, $Eu(fod)_3$ and $Pr(fod)_3$[3], on the n.m.r. spectrum of stereoregular poly (methyl methacrylate) (PMMA).

A sample of predominantly isotactic PMMA was prepared by the polymerization of methyl methacrylate in toluene at -78°C with n-butyllithium as catalyst. Spectra were recorded on a Varian HR-220 spectrometer at 120°C in o-$C_6H_4Cl_2$. The effect of $Eu(fod)_3$ upon the isotactic (i or mm), heterotactic (h or mr), and syndiotactic (s or rr) triads of the OCH_3 and CCH_3 peaks, and the mmm and rrr tetrads of the CH_2 group (other tetrad peaks were not as well resolved) is shown in Figure 1. Assignment of h and s OCH_3 triads may possibly be reversed since they are unresolved in the absence of $Eu(fod)_3$. The larger low field shifts for CCH_3 than OCH_3 peaks strongly suggests that $Eu(fod)_3$ complexes to the carbonyl oxygen of the ester group, as previously suggested[5]. The observed order of shifts for the CCH_3 groups, $s > i \gtrsim h$ leads to a crossover of h and s triad peaks (see Figure 2). The resolution of CCH_3 triads and pentads is actually decreased by added $Eu(fod)_3$ in the concentration range investi-

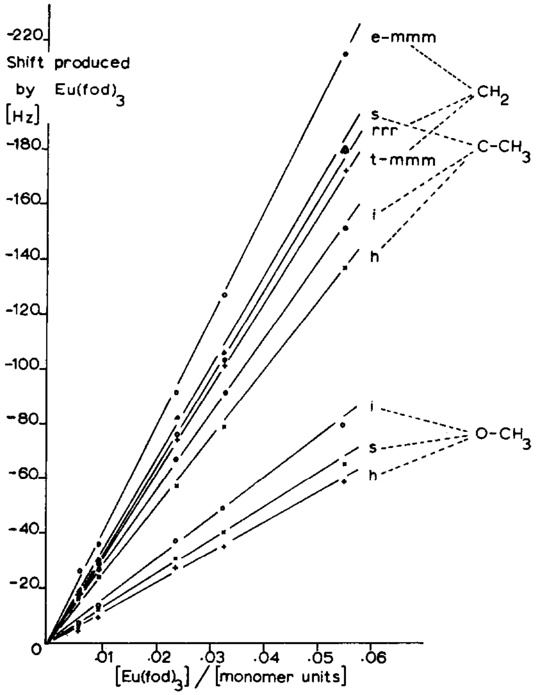


Figure 1: Chemical shifts in Hz (at 220 MHz) for PMMA protons as a function of [Eu(fod)$_3$] relative to shifts with [Eu(fod)$_3$] = 0.

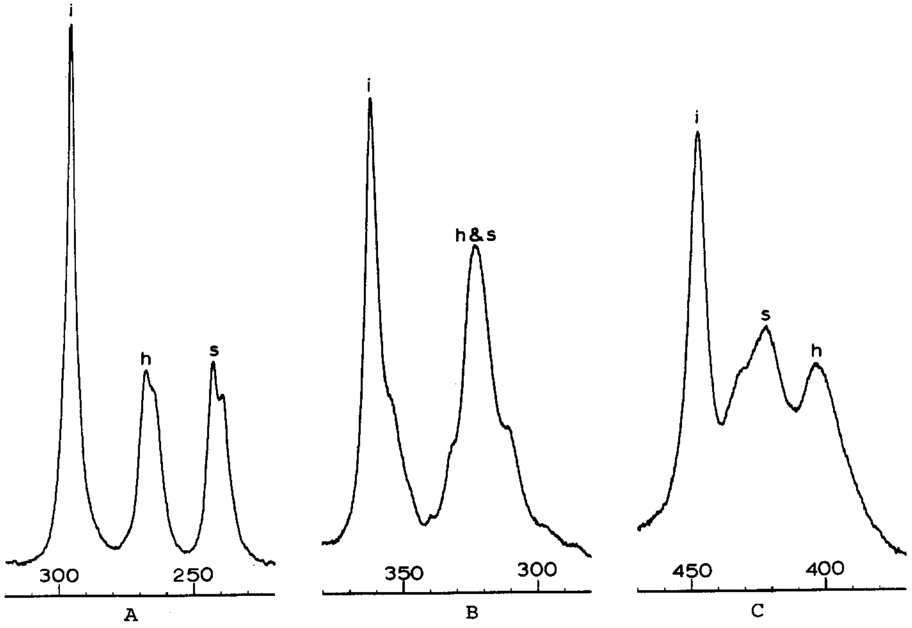
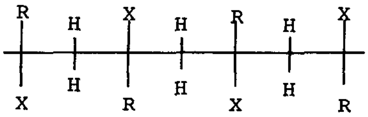


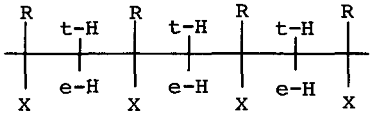
Figure 2: Spectra of CCH$_3$ triad peaks at different ratios of [Eu(fod)$_3$] to [polymer] (the latter expressed in concentration of monomer units).
(A) 0.009 (B) 0.023 (C) 0.054

gated. Resolution of tetrad CH_2 peaks is improved since the lowest field tetrad peak, the erythro proton of the mmm tetrad (on the same side of the backbone as the ester groups in the all-trans conformation)[4] is the most strongly shifted. $Pr(fod)_3$ gave better resolution of the CCH_3 triads by inducing high field shifts but the spectrum was complicated because CH_2 peaks overlapped with CCH_3 peaks. Our results differ significantly from those reported by Katritzky and Smith for atactic PMMA[5]. They reported shifts in the order i $CCH_3 >$ h $CCH_3 >$ s $CCH_3 > CH_2$, with improved resolution of the triad peaks. Since solvent, temperature and shift reagents were different in the two investigations, it is difficult to assign any single reason for the marked differences in results. However, we believe that it may primarily reflect the dependence of polymer conformation on tacticity. Lanthanide-induced shifts should be conformationally dependent since they depend upon both the distance and the orientation of the various protons relative to the paramagnetic center[6]. Our results suggest that shift reagents may be useful for investigating polymer conformation.

Examination of Fisher-Hirschfelder-Taylor space-filling models leads to the qualitative conclusion that a syndiotactic PMMA chain would prefer the all-trans conformation, thus placing a carbonyl group and consequently a paramagnetic center on both sides of each CCH_3 group (see below). Neither the all-trans form nor the $(g^+t)(g^+t)\ldots$ helical form of an isotactic sequence places two carbonyl groups in as close proximity to each CCH_3 group. Consequently, we believe that the order of shifts s $CCH_3 >$ i CCH_3 is reasonable, at least for stereoregular PMMA. For the all-trans isotactic sequence, it is readily apparent why the erythro mmm tetrad peak and the i OCH_3 peak should shift more than



Syndiotactic (rrr) tetrad



Isotactic (mmm) tetrad

(R CH_3, X $COOCH_3$, both sequences in all-trans conformations).

the other CH_2 and OCH_3 peaks. However, it should be emphasized that Katritzky and Smith also rationalized their observations from an examination of molecular models[5]. It is apparent that this approach does not lead to unambiguous conclusions. It is hoped that it will prove possible to reach more quantitative conclusions by combining the results of shift reagent studies with calculations of the types carried out by Flory[7] and Scheraga[8]. An investigation of this type is being undertaken.

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