

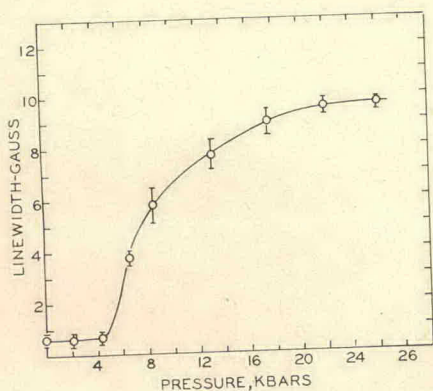


FIG. 7. ^1H linewidth vs pressure for polyethylene.

tion by the carbon skeleton of the polymer of a planar configuration.

The NMR linewidths vs pressure curve obtained in this study shows a discontinuity at 6-7 kbar which is probably the Teflon II-III transition. If the Teflon molecule does assume a planar structure this would be expected to restrict the motion of the chain and lead to an increase in the NMR linewidth. The rapid increase in linewidth which occurs at 11 kbar may be the higher incomplete transition reported by Beecroft and Swenson.¹⁶ To obtain an idea of the molecular structure at this point by broadline technique, accurate second moment values would be required. These would then be compared with values calculated from a model. Since the experiments were not conducted at a temperature sufficiently low to freeze out molecular motion, approximate corrections for this would have to be made. An estimate would also have to be made of the reduction in interatomic distances and the theoretical second moment corrected for this as well. Thus, while the exact nature of the molecular reorientation cannot be determined, the NMR results show that the transformation does involve a more severe restriction of chain mobility than the 6.5 kbar transition.

The Teflon linewidth obtained at atmospheric pressure at the conclusion of the high pressure run agreed with the

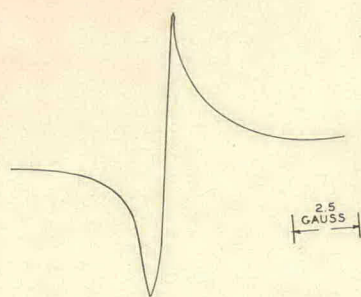


FIG. 8. NMR lineshape of polyethylene at 1 bar.

values obtained before the run. This indicates that the pressure induced changes are reversible; in agreement with the results obtained in other studies.

Linewidth vs pressure data for polyethylene are shown in Fig. 7. There is no measurable change in linewidth until a pressure of 5 kbar is reached. A rapid increase occurs above this pressure which finally levels off near 22 kbar. Lineshapes obtained at pressures of 1 atm and 26.4 kbar are shown in Figs. 8 and 9.

The polyethylene molecule is planar. It is not helical and there are no known phase transitions. Polyethylene and Teflon crystallize from the melt in the form of lamella or platelets.¹⁷ The polyethylene chains are folded back and forth perpendicular to the plane of the platelet. Bridgman's measurements on the compression of polyethylene¹⁰ do not reveal any phase transitions. The compression vs pressure curve does show a rounding off at the higher pressures similar to that exhibited by the NMR linewidth vs pressure curve. It appears then that while a phase transition may not occur at 5 kbar, the motion of the polyethylene chains is being severely restricted; this restriction may occur pri-

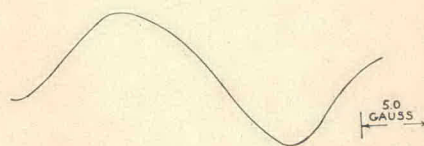


FIG. 9. NMR lineshape of polyethylene at 26.4 kbar.

marily in the amorphous region of the polymer. The pressure induced changes in polyethylene, like those in Teflon, appear to be reversible.

The high pressure system developed in this research is suited to spin echo, as well as broadline NMR measurements of T_1 , T_2 and coefficient of self-diffusion in solids.

The commercial availability of superconducting magnets opens up other possibilities. For example, if a 40 kG superconducting magnet were used instead of a 10 kG electromagnet, the magnetic resonance frequency for studying ^{133}Cs would be about 22.4 Mc instead of 5.6 Mc. The coil required would consist of 5 turns of wire instead of 20. Perhaps more important, the signal-to-noise ratio in a 40 kG field would be increased approximately eight times.

ACKNOWLEDGMENT

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¹⁷ P. H. Lindenmeyer, J. Polymer Sci. 31, 539 (1963).