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ESR STUDIES OF MOLECULAR MOTION OF POLY [2,2-BIS(3-FORMYL-N-HEXYLENDIIMINE-4-ACETOXY PHENYL)] PROPANE

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ABSTRACT - The ESR spectra of spin probe doped in poly [2,2-bis(3-formyl-n-hexylendiimine-4-acetoxy phenyl)] propane (XII) were recorded in solid and studied over a temperature range -196 to 56 °C. At lower temperature (-196 °C), the spectrum reflects the complete development of the anisotropic hyperfine interaction. As the temperature was raised the ESR spectra became narrow indicating some movements in the solid phase. The Brownian diffusion model gives, an activation energy of 5.4 kJ / mole which is very close to that found for segmental reorientation in molten state polymers, indicating that the motional freedom of this polymer in solid state is as high as in the high molecular weight liquid.

INTRODUCTION

Spin labelling technique has been successfully used for investigation of molecular motion of some polymers [1-8]. This technique has, however, been restricted to polymers having reactive functional groups which can be converted to nitroxide radical. On the other hand, spin probe technique can be considered to be another approach by which to study the molecular motion of solid polymers. Several reports on this field were published [9-12] in recent years but appropriate spin probes with high molecular weight have not been attempted.

In the present study we examined ESR spectra of spin probe (3-spiro-[2-N-oxyl-3,3-dimethyl-oxozolidine]) 5α-cholestane dissolved in polymer (XII) over awide range of temperatures in order to obtain detailed information about the rotational freedom exhibited by polymer (XII). This radical was chosen from the available nitroxide because it is rigid (high molecular weight) and stable over a wide range of temperatures.

EXPERIMENTAL

Polymer XII was synthesised as shown in scheme (1) , from reaction of 0.2 mole 2,2-bis(3-formyl-4-hydroxyphenyl) propane (X) in xylene , 0.2 mole of 1,6-diaminohexane and few drops of 95% volume formic acid. The polymerisation was carried out by heating the reaction mixture at 100 °C for 5 hrs with rapid stirring. The resulting solid (XI). was filtered, washed with distilled water and then purified by reprecipitation from absolute ethanol by distilled water. The

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