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ESR Study of the Spin Labeled Polyethylene Crosslinking System

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INTRODUCTION

There exist only a few methods to investigate the crosslinks in polymeric systems (determination of gel-fraction, modulus of elasticity, etc.). We have developed a new spin labeling technique (ROCKENBAUER et al., 1978) which in special cases makes possible the application of ESR spectroscopy to study the crosslinks of solid polymers. For spin labeling we used nitroso compound reacting in an auto-initiated way, where one of the nitroso molecules initiated the hydrogen abstraction from the polymer while the other one trapped the polymeric radical. Consequently two nitroso molecules should be present in the vicinity of the group to be nitroxide labeled (SIMON et al., 1980). In the present paper we apply the method for studying the chemically initiated crosslinking in polyethylene.

EXPERIMENTAL

Low-density polyethylene (PE) TIPOLOEN 30015, and Luperco 500-R dicumyl peroxide (DCP) m.p. 39-40° were used in the experiments. Powdery PE and DCP (in acetone) in adequate proportion were blended and vacuum dried, then moulded into 0.5 mm sheets (at 120°, 1 min) using Fontijne SRA-100 moulding press. Crosslinking was carried out in the same machine. To follow the crosslinking gel-fractions were determined by extraction with xylene using Soxhlet apparatus. 2,4,6-tribromo-nitrosobenzene was synthetised by the method of (HOLMES et al., 1960). ESR measurements were performed on a JEOL JES-FE-3X spectrometer with 100 kHz field modulation.

RESULTS AND DISCUSSION

For the ESR investigations the crosslinked PE samples were swollen in benzene solution of 2,4,6-tribromo-nitrosobenzene (TBNB) at 70°, in oxygen-free atmosphere. The ESR spectrum obtained consists of two six-line pattern in superposition (Fig.1), and can be assigned to two different radicals. The spectra can be interpreted as a hyperfine structure of one nitrogen and one β-hydrogen atoms. The nitrogen couplings are nearly equal but the hydrogen couplings are significantly different in the two signal components ($a^{\beta}_{H} \approx 10$ G and 6.7 G, resp.). It was found that the relative intensity of the broader signal ($a^{\beta}_{H} \approx 10$ G) in-

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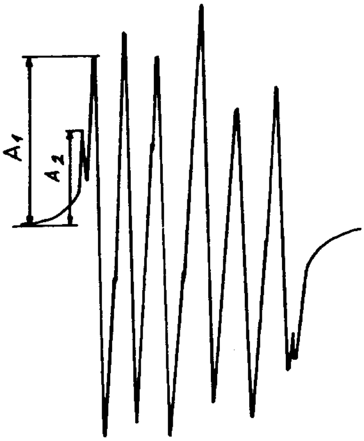

Figure 1

ESR spectrum of a spin labeled PE taken at 70°. A_1 is the height of the first line of the narrow signal, A_2 is that of the broader signal.

creases with the extent of crosslinking (Fig.2).

In order to elucidate the origin of the two different radicals model experiments were performed with a normal (n-heptane) and a branched (3-ethyl-pentane) hydrocarbons. In both cases six-line spectra with different widths were detected indicating that TBNB can abstract hydrogen and trap only radicals formed on the secondary carbon atoms. The coupling constant of β-hydrogen for 3-ethyl-pentane is higher (a_H^β = 6.0) than that of for n-heptane (a_H^β = 4.7 G). These observations can be explained by steric effects. Namely, the two ortho-bromo atoms hinder the nitroso compound to access to the tertiary carbon atoms. Furthermore, the more bulky is the group linked to the -NO the more restricted is the internal motion of CH_β group, which leads to the enhanced hydrogen coupling (ROCKENBAUER et al., 1978).

On the basis of the above conclusions the broader signal of the labeled PE was assigned to the nitroxide radical bound to the secondary carbon atom adjacent to the branches or crosslinks. The narrow signal was assigned to the nitroxide radical bound to the secondary carbon atom on the linear segment of PE chain.

In spite of the relative low concentration of "branches" in the crosslinked polymer the two type of radicals have commensurable concentrations (Fig.2). This fact can be explained by selective radical formation due to the effect of cavity constructed by the crosslinked segments of PE, which in turn leads to an increased local concentration of the nitroso molecules and consequently enhances the probability of the consecutive hydrogen abstraction and radical trapping.

The above outlined ESR method has the following features:

i In contrary to other methods it ensures the study of crosslinking of polyethylene in solid at slightly elevated temperatures far below the melting point;
ii If the chemical initiation of crosslinking proceeds when gel fractions has been completed, the relative intensity

A_2/A_1 shows further increases. Therefore it can be applied to study the crosslinking process even when the gel-fraction measurement is no longer informative (Fig.2).

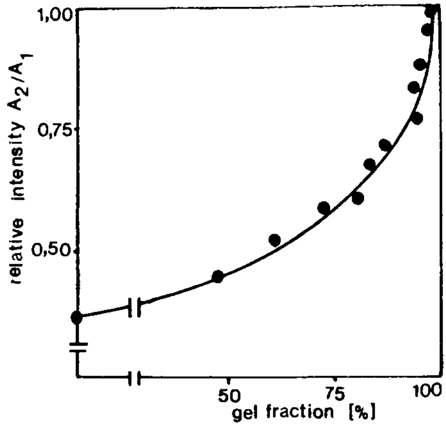

Figure 2. Relative intensity of the signals in ESR spectrum vs. gel-fraction in crosslinked polyethylene.

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