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THE EPR SPECTRUM OF γ-IRRADIATED POLYMETHYL METHACRYLATE SPECIFICALLY DEUTERATED IN THE METHYLENE GROUP

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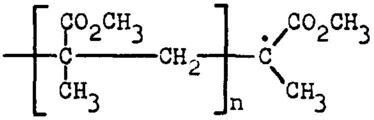
COMMERCIAL polymethyl methacrylate (PMMA) on exposure to any kind of ionizing radiation[1-3] or to mechanical damage of the polymer chain[4] gives at room temperature always the same well known EPR spectrum. Identical spectrum is obtained on polymerizing methyl methacrylate (MMA) and trapping free radicals in the polymer gel.[5,6]

As has been shown by Abraham et al.[7] and by Ingram et al.[8] the most probable structure of the macroradical is the following one:



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[1] E.E. Schneider, M.J. Day and G. Stein, *Nature* **168**, 645 (1951).

[2] C.H. Bamford and J.C. Ward, *The Fifth International Symposium on Free Radicals*, Uppsala, July 1961.

[3] A. Charlesby and M.G. Ormerod, ibid.

[4] S.J. Bressler, S.N. Zhurkov, E.N. Kazbekov, E.M. Saminskii and E.E. Tomashevskii, *Zhur. Tekh. Fiz.* **29**, 358 (1959).

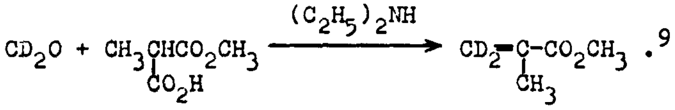
[5] R.J. Abraham and D.H. Whiffen, *Trans. Faraday Soc.* **54**, 1291 (1958).

[6] S.J. Bressler, E.N. Kazbekov and E.M. Saminskii, *Vysokomolekulyarnye Soedineniya* **1**, 132, 1374 (1959).

[7] R.J. Abraham, H.W. Melville, D.W. Ovenall and D.H. Whiffen, *Trans. Faraday Soc.* **54**, 1133 (1958).

[8] D.J.E. Ingram, M.C.R. Symons and M.G. Townsend, *Trans. Faraday Soc.* **54**, 409 (1958).

In order to elucidate the nonequivalence of interaction of protons with the unpaired electron in the free radical concerned we synthesized MMA specifically deuterated in the methylene group according to the following scheme:



$$CD_2O + CH_3\underset{CO_2H}{CH}CO_2CH_3 \xrightarrow{(C_2H_5)_2NH} CD_2{=}\underset{CH_3}{C}{-}CO_2CH_3$$.[9]

The infrared spectra of "normal" and deuterated MMA prove the specificity and the practically quantitative degree of deuteration. The absorption band at 3010 cm^{-1}, assigned to the stretching vibration C-H of $=CH_2$ group and other bands due to deformation vibrations C-H of the same group in the regions 1410 cm^{-1}, 660 cm^{-1} and 600 cm^{-1} [10] disappear in the spectrum of deuterated MMA and a new band due to C-D stretching vibration occurs at 2230 cm^{-1}. Absorption bands of stretching and deformation vibrations C-H of $-CH_3$ groups remain unchanged.

The monomer thus obtained was block polymerized at 60°C during 400 minutes with dibenzoyl peroxide as initiator (36 mmol/l.) and thereupon γ-irradiated with a dose of $2,64 \cdot 10^{18}$ eV/ml. at $11,7 \cdot 10^{16}$ eV/min.ml. by a ^{60}Co source.

In Fig. 1 the EPR spectra of "normal" (a) and deuterated (b) PMMA, polymerized and irradiated at identical conditions, are shown.

The obtained spectra prove unequivocally the interaction equivalence of the methyl protons, that gives evidence of the correctness of Ingram's[8] hypothesis about free rotation of the

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[9] C. Mannich and K. Ritsert, Ber. 57, 1116 (1924).

[10] G. Salomon, C.J. Schooneveldt - Van der Kloes and J.H.L. Zwiers, Rec. trav. chim. 79, 313 (1960).

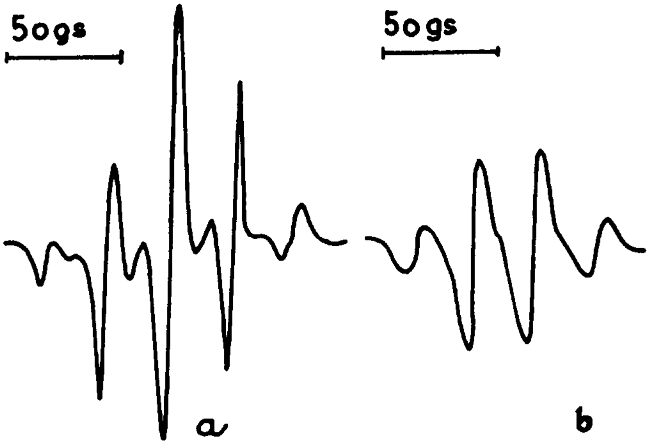

FIG. 1

methyl group around the C-C bond with a frequency higher than 10^7 rev./sec. The interaction with one deuteron broadens the spectral lines; the broadening at maximum slope amounts to 4 ± 2 gauss.

The quartet in the EPR spectrum of "normal" PMMA arises from the interaction with the methyl protons only. Should this quartet originate from an interaction with two protons of the methyl group and one proton of the methylene group, there would have to be a weaker triplet superimposed upon the quartet in the EPR spectrum of deuterated PMMA; this is, however, not the case. Most likely the quartet of "normal" PMMA arises in such a conformation of the macroradical where the axis of the unpaired electron orbital just halves the angle between the methylene C-H bonds.

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