The Nuclear Magnetic Resonance Spectrum of Poly-*N*-vinylcarbazole

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Summary The n.m.r. spectrum of poly-*N*-vinylcarbazole is assigned and discussed on the basis of a polymer chain with restricted internal rotations.

THE n.m.r. spectrum of the poly-*N*-vinylcarbazole has been reported by Heller.[1] The assignment of the spectrum has not, however, been reported hitherto.

We have now assigned a peak at τ 8·5 (2H) to the methylene protons, the two peaks at τ 6·4 and 7·3 (1H altogether) to a methine proton, a peak at τ 5·0 (approximately 1H) to an aromatic proton, and the several τ 3 peaks to the remaining aromatic protons (approximately 7H). When poly-*N*-vinylcarbazole is deuteriated at the methylene protons, the methylene peak disappears but both methine peaks remain unchanged. [$\beta\beta$-$^2H_2$]-*N*-Vinylcarbazole was synthesized by the dehydration of *N*-hydroxyethylcarbazole prepared by the $LiAlD_4$ reduction of *N*-ethoxycarbonylmethylcarbazole. Samples of the poly-*N*-vinylcarbazole were prepared by thermal polymerization and by cationic polymerization (BF_3,Et_2O). The relative intensities of the methine peaks differ somewhat between samples produced by the two methods.

The difference in τ value for the two methine proton peaks seems too large to be attributable to different triad tacticity as is usual in some polymers with very "flexible" random coil conformations. Restricted internal rotation of the poly-*N*-vinylcarbazole molecule in solution may explain the fact that the methine protons have such different τ values. The extremely large upfield shift of one aromatic proton to τ 5 may also be explained by the effect of the neighbouring carbazyl groups' belonging to a chain molecule with restricted internal rotation.

Our recent *X*-ray examination[2] of the heat-annealed and stretched poly-*N*-vinylcarbazole indicated the presence in the molecules of sequences of the isotactic 3/1 helix and the syndiotactic 2/1 helix with lateral order but without longitudinal order. Examination of models indicates that in the isotactic 3/1 helix, the internal rotation of the polymer chain may be restricted almost completely because of the extreme bulkiness of the pendant carbazyl groups. In the syndiotactic 2/1 helix partial internal rotation of the polymer chain seems possible, although the rotation does not give freely rotating completely "flexible" random coil conformations. Thus, motion of the poly-*N*-vinylcarbazole molecule in solution seems to be possible on the n.m.r. time scale, to give more or less distinct n.m.r. peaks. Examination of models indicates that the shielding is expected to be very large for one proton of the carbazyl group belonging to the 2/1 helix part of the molecule and in some of the three protons belonging to the carbazyl group in the 3/1 helix part. This may explain the presence of approximately one anomalous τ 5 aromatic proton in poly-*N*-vinylcarbazole. The rigidity of the poly-*N*-vinylcarbazole molecule in solution has also been discussed by Hughes and North.[3]

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[1] J. Heller, D. O. Tieszen, and D. B. Parkinson, *J. Polymer Sci., Part A*, 1963, **1**, 125.

[2] A. Kimura, S. Yoshimoto, Y. Akana, H. Hirata, S. Kusabayashi, H. Mikawa and N. Kasai, to be published in *J. Polymer Sci., Part B., Polymer Letters*.

[3] J. Hughes and A. M. North, *Proc. Chem. Soc.*, 1964, 404.