257.Title: Comment on ldquoDynamic coupling of a small rigid probe to viscous ortho-terphenylrdquo

Author: Dzuba SA.

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Abstract: Huang and Richert recently have reported results of measurements of the dielectric relaxation of spin probe 2,2,6,6-tetramethyl-piperidine-l-oxyl (TEMPO) in supercooled ortho-terphenyl (OTP). For the time scale ranging from 100 mus to 1 s (temperature ranging from 268 to 248 K), they found that the tumbling mode of TEMPO is a true replica of the structural relaxation of OTP, and that both pure OTP and TEMPO in OTP trace the temperature dependence of the viscosity. It was pointed out that these results are in strong contradiction with the previously reported data of electron spin resonance (ESR) studies of TEMPO in OTP in which for the same temperatures the probe tumbling times were found to be smaller than 30 ns. The explanation of the contradiction suggested spinning modes around the dipole (nitroxyl) axis which are visible in ESR but do not manifest themselves in dielectric relaxation. Note in this respect that, as it is known for quite a long time, ESR spectra of nitroxide spin probes in highly-viscous state differ only slightly from the limiting case when motion is totally frozen out. Also, simulation of ESR spectra gives here almost undistinguishable results for different models of unrestricted orientational motion (Brownian diffusion, jumps, etc.). From the other side, now it is well established that ESR spectra in highly viscous regime may also be described by model of restricted small-angle rotations of the probe molecule (molecular librations). As reorientation angles for this type of motion do not exceed several degrees, this motion cannot manifest itself in dielectric relaxation (except for the terahertz range of frequencies where librations do show up). Nitroxide spin probes participate also in tumbling motion that is seen in dielectric relaxation and that obeys the temperature dependence of viscosity. But tumbling motion is too slow to be detected in ESR. So, the model of molecular librations is in agreement with ESR measurements and do not contradict dielectric relaxation data.