

# This Week's Citation Classic

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Hoffman J D, Williams G & Passaglia E. Analysis of the  $\alpha$ ,  $\beta$ , and  $\gamma$  relaxations in polychlorotrifluoroethylene and polyethylene: dielectric and mechanical properties. *J. Polym. Sci. C* (14):173-235, 1966.  
[National Bureau of Standards, Washington, DC]

Linear semicrystalline polymers without independently rotatable side groups generally exhibit three major dielectric and mechanical relaxation effects denoted, in order of their appearance with descending temperature, ' $\alpha$ ,' ' $\beta$ ,' and ' $\gamma$ .' This paper deals largely with the detailed molecular origin of each of these effects, mostly in terms of simple molecular models consistent with the chain-folded lamellar morphology known to exist in such systems. [The SCI® indicates that this paper has been cited over 180 times since 1966.]

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"This paper has been highly cited because it was the first comprehensive attempt to explain, in a unified manner, the physical basis of the three major mechanical and dielectric relaxation effects that appear in many crystalline polymers. Prior to our paper, theoretical interpretations were mostly limited to essentially qualitative arguments.

"As was attested by numerous papers already in the literature, there was no doubt as to the reality in the experimental sense of both mechanical and dielectric relaxation effects bespeaking the presence of the so-called ' $\alpha$ ,' ' $\beta$ ,' and ' $\gamma$ ' relaxations in semicrystalline polymers, but the molecular origin of those important effects was not, in our view, in a coherent condition. In addition, the nomenclature was not very consistent. The basic position we took was to first ascertain which phase was the seat of each relaxation effect. Polyethylene (PE) and polychlorotrifluoroethylene (PCTFE) were chosen as model compounds, partly because considerable dielectric<sup>1</sup> and mechanical data for specimens of various degrees of crystallinity were available, and partly because they were *linear polymers without independently rotatable side groups*. The latter property was rightly viewed as important because earlier authors had attributed some

of the principal relaxations entirely to movable side groups when in fact PE and PCTFE, which possessed no such groups, clearly exhibited the  $\alpha$ ,  $\beta$ , and  $\gamma$  effects.

"Some of the interpretation in our paper was done in terms of the then new chain-folded lamellar morphology. We feel that this lent credence to our results. It was shown that the high temperature relaxation, which we denoted ' $\alpha_c$ ,' had its origin in the lamellar crystalline part of the semicrystalline polymer; the subscript ' $c$ ' in our notation means 'crystalline.' A theoretical model based on a 'rotation-translation' motion was proposed to explain the molecular origin of  $\alpha_c$ . We still think of the  $\alpha_c$  interpretation as a substantial contribution. The next lower temperature relaxation was denoted ' $\beta_a$ ,' whose seat was shown to be the amorphous part of the semicrystalline polymer and involving the onset of the glass transition at  $T_g$ ; the subscript ' $a$ ' stands for 'amorphous.' To our knowledge, this interpretation has not been disputed. The lowest temperature relaxation was generally denoted ' $\gamma$ ' and appeared to us, especially because in the light of very extensive dielectric data<sup>1</sup> and a number of experimental observations in mechanical relaxation, to consist of two closely related effects, one of them,  $\gamma_c$ , of crystal origin, and the other,  $\gamma_a$ , of amorphous phase origin. The  $\gamma$  effect was generally attributed to short-range 'jump rope' type motion of the chain backbone involving only a few chain segments. In the amorphous phase ( $\gamma_a$ ) this general interpretation appears to have stood up, and there now exists a considerable literature on the details, though the term 'crankshaft' rather than 'jump rope' is now commonly employed to describe them.

"Thus it was clearly recognized by us that a completely amorphous flexible chain linear polymer would exhibit two relaxation effects, namely,  $\beta_a$  and  $\gamma_a$ . The crystalline component of  $\gamma$ , called  $\gamma_c$ , was treated with a detailed molecular model where the jump rope type motion was allowed in the vicinity of the vacancies caused by chain ends or sunken chain folds in the crystalline lamellae. The existence of  $\gamma_c$  has been disputed, and a friendly discussion still prevails on this point. We would add that we still like our notation, though it is employed with less than complete regularity."

1. Scott A H, Scheiber D J, Curtis A J, Lauritzen J I, Jr. & Hoffman J D. Dielectric properties of semicrystalline polychlorotrifluoroethylene. *J. Res. Nat. Bur. Stand.* 66A:269-305, 1962.