molecular origin of the empirical C_2 term in the Mooney-Rivlin equation.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation and the ARPA Materials Research Council Contract No. DAHC 15-71-C-0253 with the University of Michigan.

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Ole Kramer
Chemistry Laboratory III
The University of Copenhagen
2100 Copenhagen ϕ, Denmark

John D. Ferry*
Department of Chemistry and Rheology Research Center
University of Wisconsin
Madison, Wisconsin 53706

Received September 24, 1974

On the Anisotropy of Composite Networks

Recently the elastic behavior of some specially prepared polymer networks was reported by Kramer, *et al.*[1] These networks, cross-linked in states of strain just above the glass transition temperature, were analogous to composite networks[2] in that an entanglement structure provided a stress level during cross-linking; the entanglements served as first stage cross-links.

These networks, prepared from polybutadiene, were mechanically anisotropic, with a lower modulus along the initial direction of stretch than in the transverse direction. Such anisotropy is in the opposite sense to that previously reported for true composites of rubber,[3] where the modulus along the transverse direction is lower. The theory of composites, based on Gaussian chains, cannot account for such anisotropic behavior.[2,4-6]

We wish to point out, however, that composite theory derived from non-Gaussian statistics does predict anisotropic elastic behavior.[7,8] One such model,[8] a composite network composed of a most probable chain contour length distribution of non-Gaussian chains undergoing an affine deformation, is in qualitative agreement with the experimental results of Kramer, *et al.*[1] Therefore, to the extent that entanglement–cross-link composites are comparable to cross-link–cross-link composites, we view their data as being an experimental validation of our theoretical results.[8] Since the theoretical anisotropy arises from the use of the most probable contour length distribution, a monodisperse system being isotropic, it is suggested that chain length distributions can have important bearings on the mechanical behavior of elastomers. The data reported by Kramer, *et al.*,[1] tend to add substance to this conclusion.

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K. J. Smith, Jr.*
Department of Chemistry
College of Environmental Science and Forestry
Syracuse, New York

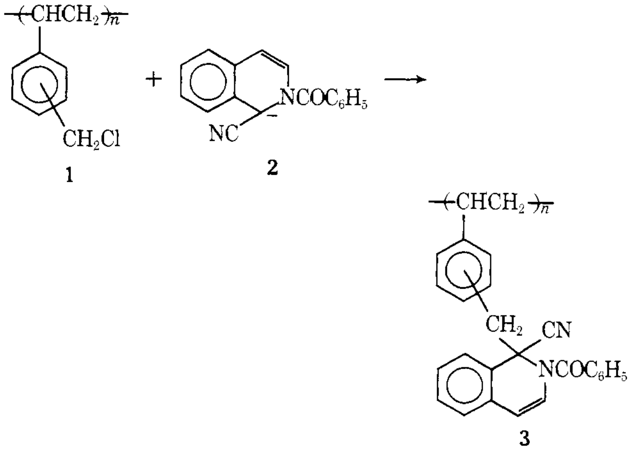
R. J. Gaylord
Department of Metallurgy and Mining Engineering
University of Illinois at Urbana-Champaign
Urbana, Illinois

Received July 22, 1974

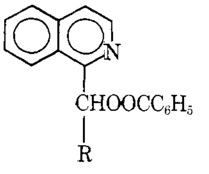
Chemical Modification of Polymers. IV. Another Example of Facile Nucleophilic Attack on a Polymer by a Reissert Anion

Recent progress in the field of chemical reactions of polymers[1,2] brought to our attention the opportunities for controlled alteration of chemical and physical properties of polymers. Our studies[3-5] have concentrated on polymeric reactions in solution. This allows more facile and complete analysis of the reaction process and products, while at the same time affording polymers of potentially greater utility than insoluble polymers.

In the previous report in this series the reaction of Reissert compounds and polymers bearing displacable halogens was examined and shown to be an excellent means of attaching aza-aromatic moieties to polymers.[5] Specifically, poly(vinylbenzyl chloride) (1) was reacted with the anion (2) of 2-benzoyl-1,2-dihydroisoquinaldonitrile. Displacement of chloride ion occurs, resulting in formation of poly[1-(vinylbenzyl)-2-benzoyl-1,2-dihydroisoquinaldonitrile] (3).



Other reactions of Reissert compounds[6] seem to be adaptable to grafting reactions of polymers. Among these is the reaction of aldehydes. The Reissert anion **2**, for instance, reacts with aldehydes (RCHO) to produce ester **4**



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via an intramolecular rearrangement with loss of cyanide