Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 12 Oct 2011.

To cite this article: Roger L. Clough (1979): Computer Modeling of Polymer Radiation Chemistry, Molecular Crystals and Liquid Crystals, 52:1, 267-268

To link to this article: http://dx.doi.org/10.1080/00268947908071743

Mol. Cryst. Liq. Cryst., 1979, Vol. 52, pp. 267–268

Printed in Holland

Computer Modeling of Polymer Radiation Chemistry†

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(*Received June 16, 1978*)

Subjection of polymeric materials to high energy radiation leads to a variety of changes in the molecular structure and these changes can substantially affect macroscopic properties. Considerable experimental work has been done to identify and measure these structural alterations, and much evidence indicates that free radicals are the principal reactive intermediate involved.

We have developed a computer program to model the full range of radiation-induced chemical reactions which occur in one polymer system, polyethylene. The program is based on kinetics for free radical reactions of low molecular weight hydrocarbons, which have been studied extensively in the gas and liquid phases. The overall form of the kinetic expressions includes provision for steps involved in the transport of reactive radical sites in the solid phase. This internal movement can be rate limiting and includes diffusion of small radicals and movement of chain-centered radicals by hydrogen abstraction from neighboring chains.

The program follows the complex network of chemical reaction pathways throughout the irradiation period, as the basic structure of the polymer is continuously altered. Variables in the program include temperature, irradiation rate, and details of the initial polyethylene structure such as chain end double bonds and branching. The mathematics of the program constitute a series of coupled differential equations containing activation energy parameters for the competing reactions. The range of the timescale involved covers some 20 orders of magnitude, as does the range of coefficient terms in the various rate equations. Such a set of differential equations is called stiff, and requires use of a special integration technique with variable calculative

† Work supported by U.S. Department of Energy and U.S. Nuclear Regulatory Commission.

step size. The output follows structural variables including volatile gas evolution, concentrations of different double bond sites, net chain scission, net crosslinking, and concentrations of the various types of free radical sites, as a function of time.

Our work to date demonstrates that such mathematical modeling is a viable approach to understanding the complex problem of polymer radiation, and is consistent with the view that major structural events can be accounted for in terms of classical radical reactions. Comparison of computer-generated results with experimental data on polyethylene irradiation has yielded good correlations in reproducing trends in structural changes, with magnitudes within reasonable agreement in most cases. Computer runs replicating a range of experimental conditions have been evaluated and correlated with experimental results including ESR work, infrared measurements, out-gassing determinations, crosslinking yields and bulk physical property measurements.

The computer approach is being used for sorting out the relative contributions of the various reaction pathways. Additionally, the program has been applied to questions concerning dose rate effects, annealing effects, and combined environment (radiation-thermal) synergistic effects.