

# Analysis of the Flow Behavior of Irradiated Polyethylene through Transient Network Models

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## Synopsis

The chemical and physical properties of polymers can be dramatically affected by exposure to high-energy radiation. Two polyethylene samples (HDPE and LDPE) were irradiated with a  $^{60}\text{Co}$  source. Radiated samples with doses ranging between 0.5 and 5 Mrad were melted and their viscoelastic properties characterized. Results show the normal drastic changes in their flow behavior: higher viscosity and interesting changes induced in their elasticity, particularly in the case of LDPE. An explanation of the change in flow behavior is forwarded in terms of transient network models using the concept of creation and destruction of entanglements.

## INTRODUCTION

Ionizing radiation is a very powerful technique employed to generate useful and interesting effects in polymers.<sup>1-4</sup> Crosslinking, radiation induced polymerization, grafting, sterilization, cure of coatings, and degradation are among the principal industrial and commercial applications.<sup>5</sup> Nowadays, sales of irradiated plastic products have shown a consistent yearly growth of about 25% and hence their demand, manufacture, and use seem to be of continuously increasing importance.<sup>6</sup>

In the interaction of radiation with solid samples of polymers we can cite two principal competing effects: i.e., crosslinking and chain scission or degradation. Furthermore, the relative magnitude of one upon another depends on the type of polymer and working conditions.

The effect of radiation of polyethylene has demonstrated its ability to form crosslinks in comparison to its capacity to degrade. Therefore, this specific characteristic has substantiated its suitability to be used in thermo-shrinkable pipes and films and medical instrumentation as well.<sup>7</sup>

To elucidate the effect induced by the high energy radiation on polyethylene, many researchers have studied: (i) mechanisms involved in the formation, distribution, migration, and decay of radiation induced free radicals<sup>8-10</sup>; (ii) mechanisms involved in the production of crosslinks in the amorphous zones of the polymer<sup>11-14</sup>; (iii) modifications on the crystallinity and unit cell for a wide range of radiation dose<sup>15-20</sup>; and (iv) the effect of radiation on the mechanical properties of solid samples.<sup>21-23</sup>

In contrast to the extensive work reported in the above-cited areas, very few papers have been published on the description of the rheological behavior of irradiated polymer melts.

Recently, Markovic et al.<sup>24</sup> reported the effect of the degree of crosslinking

on the viscous behavior of polyolefins when subjected to a series of experiments in a torque rheometer and Fisher and Corelli,<sup>25</sup> focussed their work to study the viscous characterization of various previously irradiated polytetrafluoroethylene resins in a capillary rheometer. Unfortunately, none of these papers give information about the changes induced in the elasticity of the melt as a consequence of the irradiation. This information is certainly important to the evaluation of a successful processing and/or to complete the characterization of the irradiated materials.

In summary, and in view of the few amount of reported papers dealing with the area, it has to be mentioned that the rheological studies of irradiated melts discuss the results in terms of the general trends in the viscous behavior of the materials and nothing seems to be reported on the structural changes derived from brand new rheological theories of the flow of molten polymers.

This paper presents an analysis of the effect that irradiation has on the viscoelastic properties of polyethylene melts recognizing that: (i) the changes in viscoelastic behavior can be detected through the measurement of viscoelastic material properties; (ii) the possibility of quantifying molecular parameters of the melts (i.e., molecular weight between entanglements and segment length) through the predictions of transient network models, under the assumption that the crosslinked network produced by irradiation can be treated as an analogy of a highly entangled system.

### THEORETICAL BACKGROUND

The transient-network model provides a fundamental frame to analyze experimental results in highly entangled systems. Originally developed by Green and Tobolsky,<sup>26</sup> Lodge,<sup>27</sup> and Yamamoto,<sup>28</sup> this model fundamentally envisages a concentrated polymer solution composed of elastic segments or strands joined through temporary junction constantly undergoing creation and destruction processes. In Yamamoto's theory, a segment is represented by an end-to-end vector joining two entanglement points. The distribution function for the segments  $\psi$  follows the equation:

$$\frac{\partial \psi}{\partial t} + \nabla \cdot \dot{\mathbf{r}} \psi = G - \beta \psi \quad (1)$$

where  $\dot{\mathbf{r}}$  is the rate of the segment end-to-end vector, and  $G$  and  $\beta$  are the rates of creation and destruction of the network junction. Given a linear motion

$$\dot{\mathbf{r}} = \Gamma \cdot \mathbf{r} \quad (2)$$

where  $\Gamma$  is the velocity gradient tensor, eq. (1) can be solved for various flow situations and the macroscopic rheological functions can be evaluated by calculating the moments of the distribution function. In general,  $\beta$  has taken a variety of forms. Phan Thien-Tanner<sup>29</sup> proposed a linearized expression function of the mean squared extension of the segments; Murayama<sup>30</sup> added the first quadratic term of the mean extension of the segments;

Carreau<sup>31</sup> proposed that  $\beta$  may depend on the second invariant of the rate of deformation tensor; Tanner and Simmons<sup>32</sup> gave an expression for the "rupture time" that depends on the flow story through the scalar invariants of the rate of deformation tensor, etc. Fig. 1 shows the variation of the destruction function as a function of the mean end-to-end distance between entanglement points. Equations (1) and (2) depict the linear and quadratic forms of the destruction function as they vary with  $\langle r^2 \rangle$ . Equation (3) is the Warner's expression of  $\langle r^2 \rangle$ , corresponding to non-Gaussian statistics and similar to the inverse Langevin function. In most cases,  $G$  is assumed Gaussian for the initial distribution of the end-to-end distance of the segments.

The Gaussian form of the creation function is a consequence of the assumption that the segments are created at constant rate and that they have at the instant of creation, the same distribution of free chains. Integration over all configurations gives the following differential equation for the number of segments per unit volume:

$$\frac{dN_i}{dt} = \langle G(\mathbf{r}, N) \rangle - N_i \langle \beta \rangle \quad (3)$$

where  $N_i = \int \psi(r, t) d^3\mathbf{r}$  and  $\langle G(\mathbf{r}, N) \rangle$  is isotropic. Jongschaap<sup>33</sup> has shown that transient network models like those of Acierno<sup>34</sup> and Phan Thien and Tanner<sup>29</sup> can be derived from the general equation (1). Acierno's model can

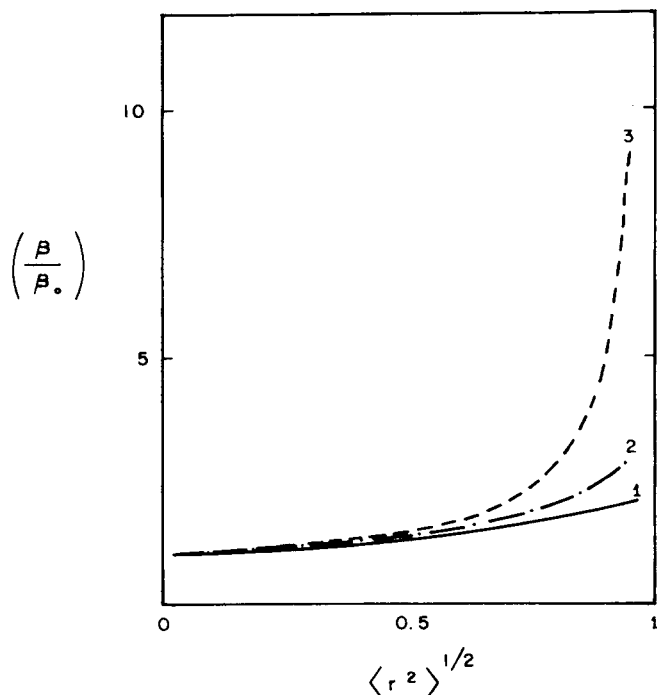


Fig. 1. Different expressions for the Destruction Function.  $\beta/\beta_0$ : (1)  $1 + \sigma\langle r^2 \rangle$ ; (2)  $1 + \sigma_1\langle r^2 \rangle + \sigma_2\langle r^4 \rangle$ ; (3)  $1/(1 - \langle r^2 \rangle)$ .

be obtained under the assumptions that:  $G$  and  $\beta$  do not depend explicitly on  $\mathbf{r}$  but only on average properties of the state of the fluid.

The basic equations of this rather successful model are

$$\tau = \sum_i \tau_i \quad (4)$$

$$\dot{\tau}_i + G_i \lambda_i \frac{D}{Dt} \left( \frac{\tau_i}{G_i} \right) = 2\lambda G_i \underline{\mathbf{D}} \quad (5)$$

$$G_i = G_{0i} x_i \quad (6)$$

$$\lambda_i = \lambda_{0i} x_i^{1.4} \quad (7)$$

$$\frac{dx_i}{dt} = \left( \frac{1-x_i}{\lambda_i} \right) - \frac{ax_i}{\lambda_i} \left( \frac{tr \tau_i}{2G_i} \right)^{1/2} \quad (8)$$

$G_{0i}$  and  $\lambda_{0i}$  are the equilibrium values of  $G_i$  and  $\lambda_i$ , and describe the fluid behavior in the limit of linear viscoelasticity. The structural variable  $x_i$  in eq. (6) is related to the  $N_i$  of eq. (3), and it describes how far from equilibrium is the existing structure. Comparison of eqs. (3) and (8) shows that eq. (8) contains a term which is the rate of destruction of the junctions due to the existing stress and the term corresponding to the rate of deformation due to thermal motion.

In steady shear the evaluation of eqs. (4)–(8) is straightforward and calculation of the structural variables is possible for given values of the shear rate. As Acierno et al. mentioned, the rate of destruction in simple shear is given as

$$\beta = ax_i \dot{\gamma} \quad (9)$$

where  $\dot{\gamma}$  is the shear rate. By assuming that  $\dot{\gamma}$  may depend on the trace of the stress tensor, they relate the destruction rate to the elastic content of the system. In fact, the Helmholtz free energy for transient network systems is given in terms of the excess free energy, i.e., it is a measure of the deformation of the network with respect to its equilibrium value. As it was suggested,  $\beta$  might be a function of the stress tensor, i.e., the end-to-end distance between entanglements, so the destruction function would be dependent on the entangled state of the network.

Experimentally, the entangled state of the network can be modified by irradiation, consequently altering the segment length and the molecular weight between entanglements. Evaluation of the destruction function on this systems provides information about the dependency of the destruction process on the deformation of the network due to the imposed flow in systems of different entanglement densities.

## EXPERIMENTAL PROGRAM

### Materials

Commercial samples of high and low density polyethylene manufactured by PEMEX-Mexico were used for irradiation. Some of its characteristics are given in Table I.

TABLE I  
Polyethylene Samples

Manufacturers code (Pemex, Mexico)	Density (g/cm <sup>3</sup> )	Melt index (g/10 min)
PX 20020 X (LDPE)	0.92	2.0
PADMEX 50003 (HDPE)	0.956	0.3

### Irradiation Method

The polymers were provided in pellet forms and were irradiated using a 29,100 C <sup>60</sup>Co source (Gamma Beam 650-Atomic Energy of Canada, Ltd.).

The total doses varied between 0 and 20 Mrad with a dose rate of 1.93 Mrad/h.

### Rheological Properties

It has to be mentioned that the rheological measurements were carried out for the samples irradiated with 0.5, 1, 3, and 5 Mrad. The samples irradiated at relatively high doses—10, 20 Mrad— could not be melted. This is an indication of a high degree of crosslinking.

The samples that could be molten after irradiation can be thought as

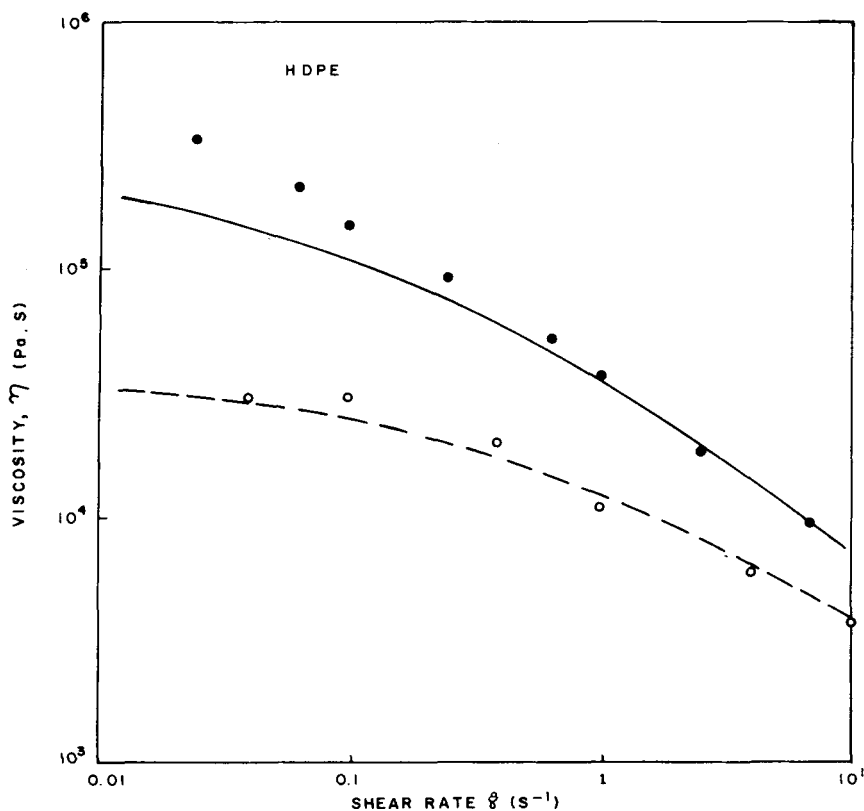


Fig. 2. Viscosity vs. shear rate for irradiated and non irradiated HDPE. T = 190°C. (○) 0 Mrad; (●) 5 Mrad; (- - -)  $a = 0.1$ ; (—)  $a = 0.275$ .

systems in which the radiation created mainly strong but temporal entanglement points as it will be discussed later.

The irradiated pellets were afterwards molten and shaped into thin discs suitable to fit the fixtures of a Rheometrics Mechanical Spectrometer. Two different test modes were used: simple shear (cone and plate) and small amplitude oscillatory shear (eccentric rotating discs—ERD<sup>35</sup>). In all cases the experimental temperature was set at 190°C. Figures 2–5 show the results of the measured  $\eta$  and storage modulus,  $G'$ , for the untreated and irradiated samples (case of 5 Mrad)

### Analysis of Rheological Data

The experimental curves of  $G'(\omega)$  and  $G''(\omega)$  were fitted to the  $n$ th order polynomials using an optimization computer subroutine known as BSOLVE.<sup>36</sup> These values were used later to calculate the relaxation function,  $H(\tau)$ , following the procedure outlined by Ferry.<sup>37</sup>

The transient network model of Acierno et al.<sup>34</sup> was chosen and complemented to further analyze the data. This model requires the use of a discrete linear relaxation spectrum in the form of a set of values of moduli,  $\lambda_{0i}$ , and relaxation times to  $\tau_{0i}$ .<sup>38</sup> The viscosity curves were used in conjunction with

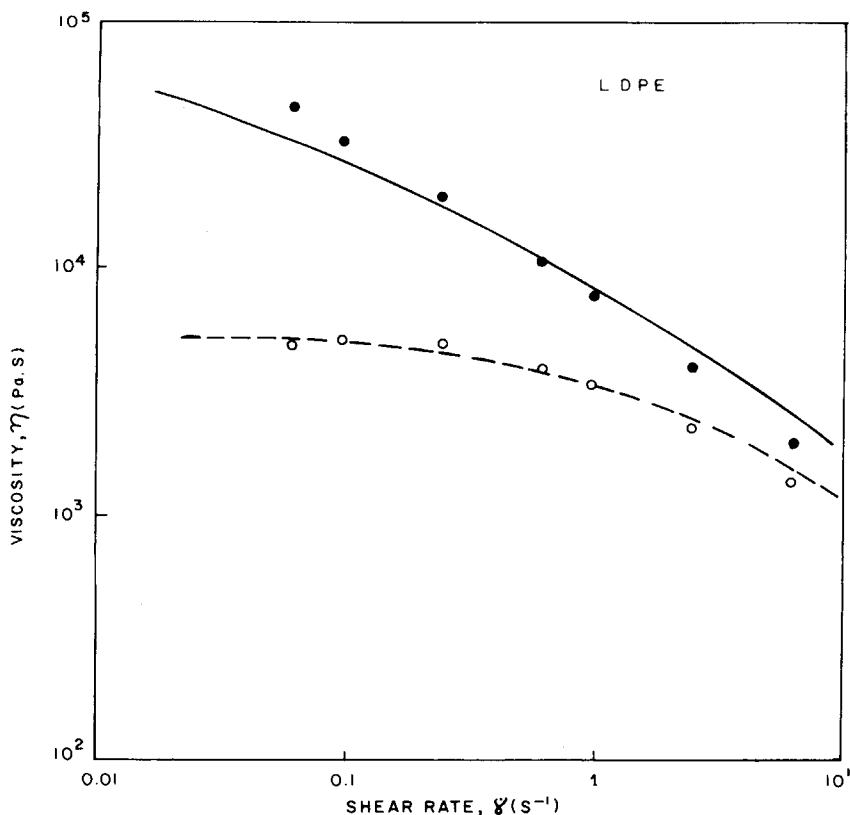


Fig. 3. Viscosity vs. shear rate for irradiated and non irradiated LDPE. T = 190°C. (○) 0 Mrad; (●) 5 Mrad; (---)  $a = 0.175$ ; (—)  $a = 0.4$ .

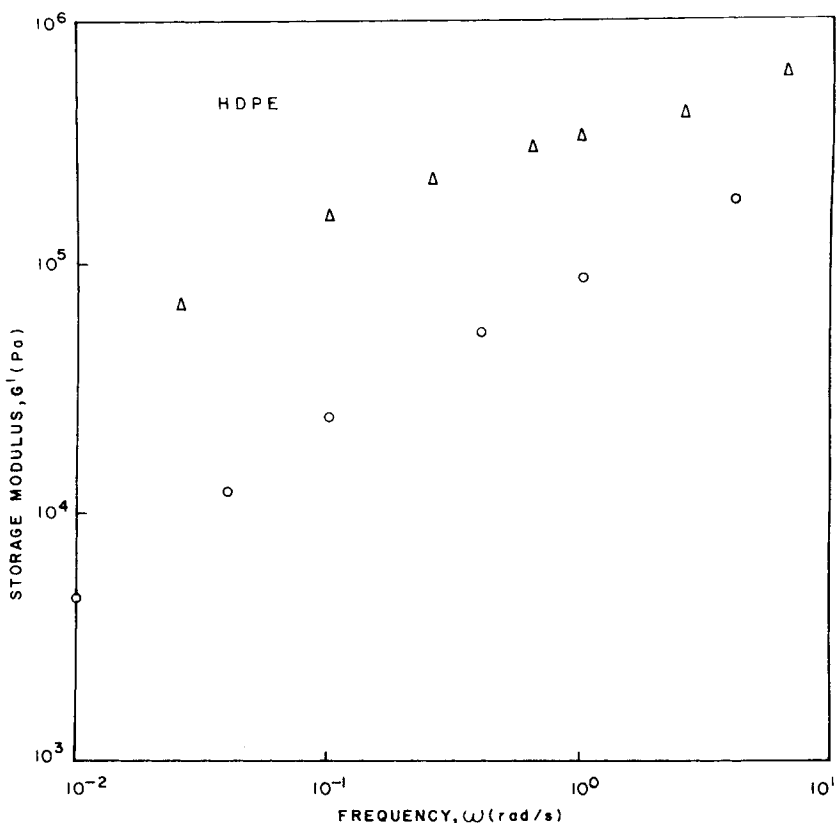


Fig. 4. Storage modulus vs. frequency for irradiated and nonirradiated HDPE.  $T = 190^\circ\text{C}$ . (○) 0 Mrad; (△) 5 Mrad.

the  $G_{0i}$  and  $\tau_{0i}$  values to calculate its adjustable parameter  $a$ . The details of this procedure may be found elsewhere.<sup>34</sup>

## RESULTS AND DISCUSSION

### Phenomenological Aspects

It is known that highly entangled systems present two different zones in the relaxation spectrum. The transition zone, corresponding to short configurational rearrangements between entanglements and the terminal zone, corresponds to relaxation process at long times beyond entanglement points. Thus, the viscoelastic properties of these systems in the terminal zone are dominated by the presence of entanglements, which strongly couples the configurational motions of neighboring molecules. Therefore, a system with more flow restrictions formed by irradiation will resemble a more entangled network which gets additional relaxation modes in the terminal zone. In the case of branched polymers (i.e., LDPE), the entangled effect will be higher than in linear polymers, like HDPE.

As mentioned before, the entanglements have a strong effect on the viscoelastic properties in the terminal zone, which reflect the longest-range

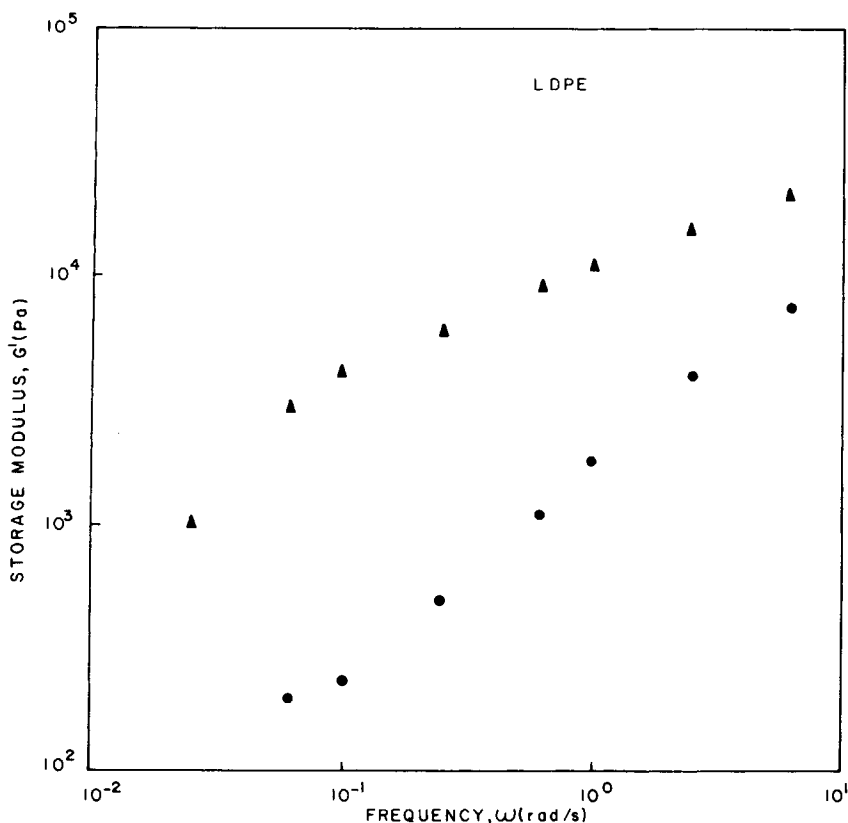


Fig. 5. Storage modulus vs. frequency for irradiated and nonirradiated LDPE.  $T = 190^\circ\text{C}$ . (●) 0 Mrad; (▲) 5 Mrad.

molecular motions. A typical nonlinear behavior in the terminal zone that reflects these molecular motions is the dependence of the non-Newtonian viscosity on the shear rate, at relatively low shear rates. Figures 2 and 3 depict plots of viscosity for high and low density polyethylene. The irradiated material presents a higher value of  $\eta_0$  (zero shear-rate viscosity) and a higher dependence on the shear rate. Explanation of the irradiation effect upon the viscosity can be given by comparing the structural properties of the two polyethylenes: HDPE presents a linear structure with small lateral branches. On the contrary, LDPE is a highly branched material with long lateral groups. The entangling process due to irradiation is believed to occur mainly in the amorphous or highly branched regions<sup>39</sup>; therefore, HDPE is less likely to be affected by irradiation.

The elastic properties represented by the storage modulus  $G'$  are given in Figures 4 and 5. The radiation dose increases the elasticity of the materials, this effect being stronger in the case of LDPE. This fact agrees with the possible formation of a secondary network between the branched and amorphous regions in the LDPE chain.

From the results shown in Figures 2-5 we can observe that the irradiated and nonirradiated materials achieve common values at high frequencies.



This corresponds to the transition region of the relaxation spectrum, where viscoelastic properties are dominated by short configurational rearrangements of molecular segments and the effect of entanglements is smaller than in the terminal region.

Between the transition region and the terminal zone, the spectrum passes through a region of slower relaxation called the plateau region. In this region  $G'$  is a weak function of the frequency, and it is possible to define a pseudoequilibrium modulus,  $G_N^0$ , related to the density of entanglement network strands. Furthermore, the modulus can be related to an apparent molecular weight between junctions<sup>40</sup>:

$$G_N^0 = \rho RT/M_e \quad (10)$$

Since  $\eta_0$  and  $G_N^0$  can be expressed in terms of the moments of the relaxation spectrum  $H(\lambda)$ , their values are controlled almost completely by the terminal processes. A lower value of  $G_N^0$  implies a decrease in entanglement density and consequently in the molecular weight between entanglements. The results shown in Figures 4 and 5 are in qualitative agreement with the above-mentioned facts, and they indicate an increase in molecular weight between entanglements proportional to the radiation dose.

### Transient Network Theories Correlations

Figures 6 and 7 show the calculated values of  $\beta$  taken from eq. (9) for both samples of polyethylene. The destruction function is plotted against the square root of the trace of the stress tensor, from data of the transition and terminal zone of the spectrum. Figure 6 shows the occurrence of large changes in the transition zone for HDPE. Given a value of  $\beta$ , the square root of the trace of the stress tensor is directly related to the segment distance. The irradiated sample has increased its entanglement density

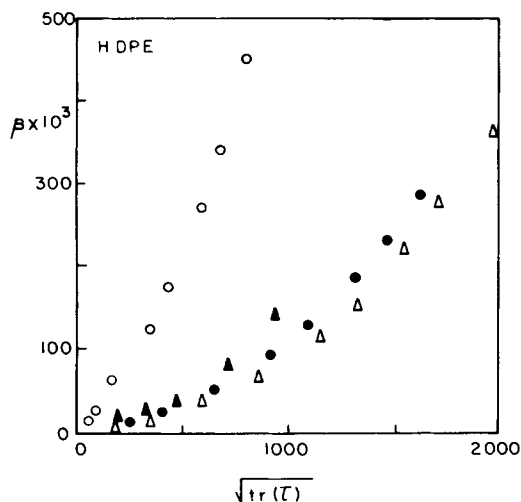


Fig. 6. Destruction function calculated from eq. (9): HDPE. (●) 0 Mrad (trans); (▲) 0 Mrad (term); (○) 5 Mrad (trans); (△) 5 Mrad (term).

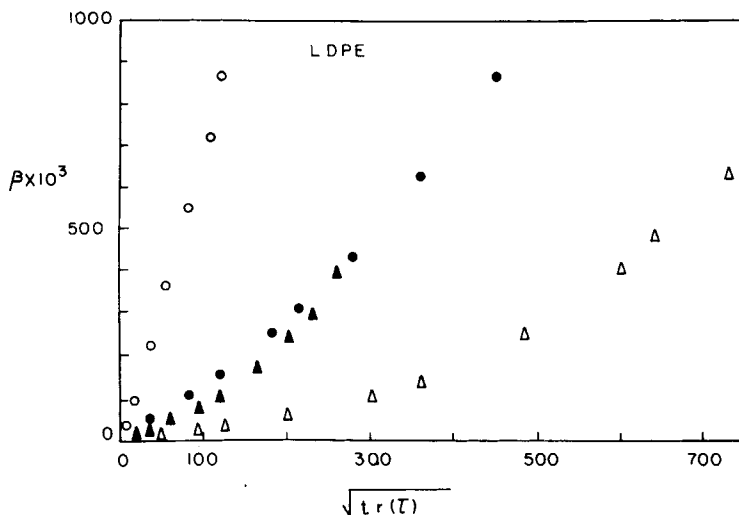


Fig. 7. Destruction function calculated from eq. (9): LDPE. (●) 0 Mrad (trans); (▲) 0 Mrad (term); (○) 5 Mrad (trans); (△) 5 Mrad (term).

decreasing the distance between entanglement points. This distance is two to three times smaller in the case of the irradiated sample. It is also interesting to compare the two samples in the transition and terminal zones. While the irradiated sample depicts large changes in structure, the sample without irradiation hardly modifies its structure. This fact shows that the new entanglements formed by irradiation are weaker and easier to destroy than the others.

A similar qualitative behavior is observed in the LDPE sample (Fig. 7); in this case the effect of irradiation is more pronounced. If we compare the transition and terminal zones for the irradiated sample, it turns out that the spacing between entanglements is about 10 times larger in the terminal zone (for a given  $\beta$ ) while the sample with no irradiation shows almost no change. This result gives additional evidence that the junctions formed on branched polymers by irradiation are weaker than the ones formed on more linear polymers. Comparison between the irradiated and nonirradiated samples in the transition zone shows a larger change in segment length than in the HDPE case. The difference is about 5 times for a given  $\beta$  value. Furthermore the irradiated samples show a much larger spacing in the terminal zone.

Figures 8 and 9 depict the degree of "anisotropy" due to deformation of the network strands and the continuing action of the destruction and deformation process upon the entangled network. They show directly the effect of the flow on the spacing between entanglements or segment lengths by plotting the trace of the stress tensor against the velocity gradient. The highest spacings are obtained in the terminal zone for the irradiated samples, being higher in the case of HDPE. The following conclusions can be inferred: the larger changes in network structure occur in the irradiated samples, achieving a common value at high velocity gradients.

Finally, Figures 10 and 11 show Acierno's model predictions of the first

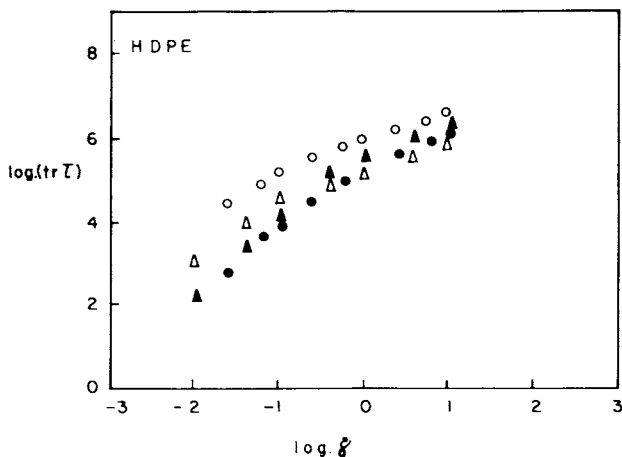


Fig. 8. Degree of anisotropy of the segment deformation: HDPE. Term: ( $\Delta$ ) 0 Mrad; ( $\circ$ ) 5 Mrad. Trans: ( $\blacktriangle$ ) 6 Mrad; ( $\bullet$ ) 5 Mrad.

normal stress difference  $N_1$  for the irradiated and nonirradiated polyethylenes. It is also shown how the relationship  $(N_1)_5/(N_1)_0$  varies with shear rate. This relation depicts variations between 7 and 40 for LDPE and between 2 and 6 for HDPE. This behavior reinforces the previous assumption concerning the formation of a secondary network more effective in the more amorphous material and the destruction caused by the flow of temporary entanglements at high shear rates.

### CONCLUSIONS

The viscoelastic properties of polyethylene melts which were previously irradiated (in the solid state) showed an increase in viscosity and storage modulus most probably caused by the creation of a network structure. The structure obtained at low radiation dose (up to 5 Mrad) appears to be reversible up to this dose and the material can still be melted. The irradiation

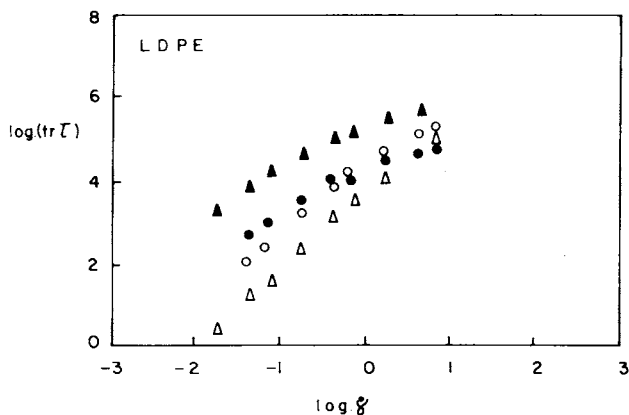


Fig. 9. Degree of anisotropy of the segment deformation: LDPE. Term: ( $\bullet$ ) 0 Mrad; ( $\blacktriangle$ ) 5 Mrad. Trans: ( $\circ$ ) 0 Mrad; ( $\Delta$ ) 5 Mrad.

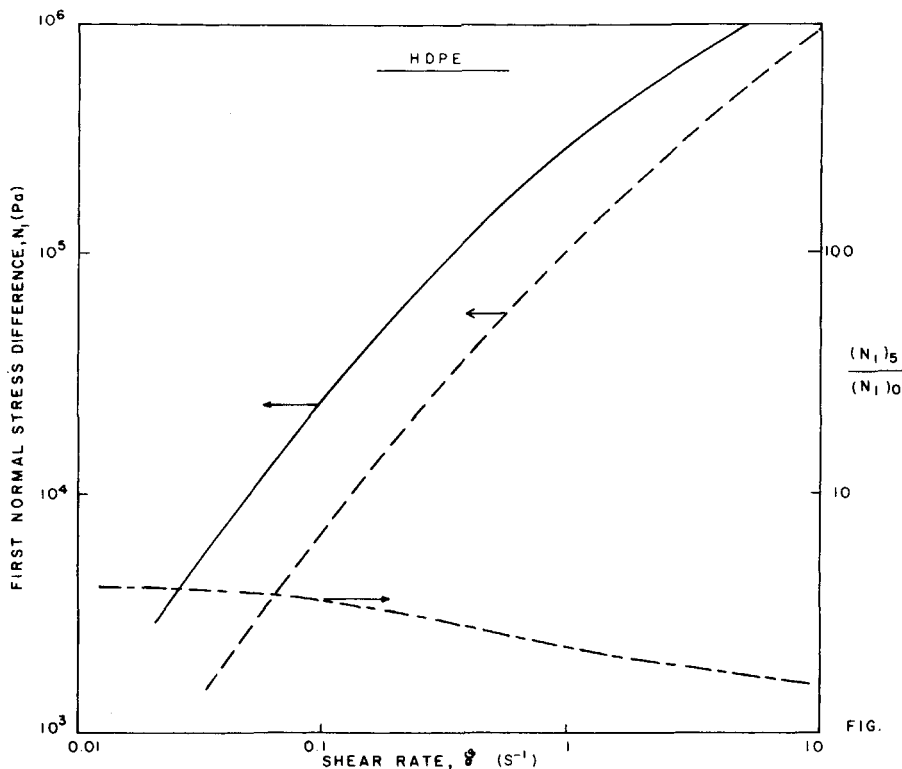


Fig. 10. Acierno's Model predictions of the first normal stress difference: HDPE.  $T = 190^{\circ}\text{C}$ . (- - -) 0 Mrad; (—) 5 Mrad.

tion effect has a stronger influence in the case of LDPE most probably due to the branched nature of this polymer.

The results of the present work suggest that transient network models are capable to explain certain aspects of the changes in the molecular structure through the analysis of the flow behavior of irradiated polyethylenes.

Furthermore, the viscoelastic testing might be a promising technique in order to establish the structural changes undergone by the irradiated samples.

#### APPENDIX: NOMENCLATURE

$a$	parameter in Acierno's model
$G$	creation function of the network segments
$G_0$	relaxation modulus at equilibrium conditions
$G_0^*$	pseudo equilibrium modulus
$G'$	storage modulus
$G''$	loss modulus
HDPE	high density polyethylene
LDPE	low density polyethylene
$M_e$	molecular weight between entanglements
$N$	number of segments per unit volume
$N_1$	first normal stress difference

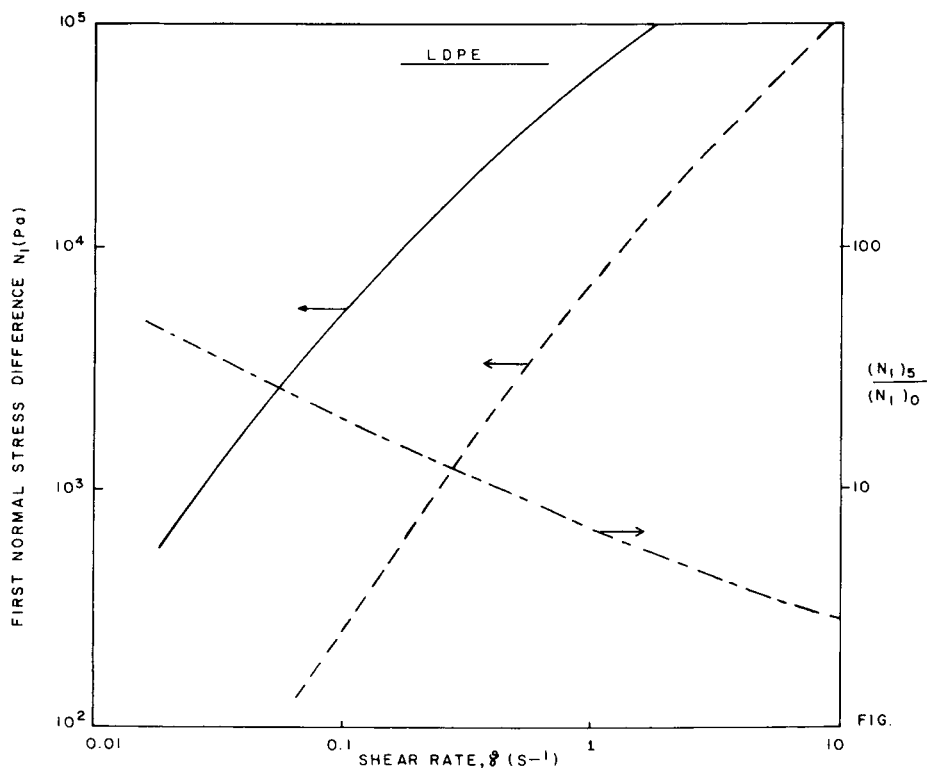


Fig. 11. Acierno's Model predictions of the first normal stress difference: LDPE.  $T = 190^{\circ}\text{C}$ .  
 (---) 0 Mrad; (—) 5 Mrad.

$R$	gas constant
$r$	end to end vector for the segments
$\dot{r}$	rate of change of the segment end-to-end vector
$T$	temperature
$t$	time
$x$	structural parameter in Acierno's model

### Greek Symbols

$\beta$	destruction function of the network segments
$\Gamma$	velocity gradient tensor
$\dot{\gamma}$	shear rate
$\eta_0$	zero shear viscosity
$\lambda$	relaxation time
$\psi$	distribution function of the segments
$\rho$	density
$\tau$	stress tensor
$\omega$	frequency

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