

Nucleation Behavior of Sheared Poly(ethylene Oxide) Melts

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Synopsis

The nucleation behavior of a poly(ethylene oxide) melt is measured as the material crystallizes under defined conditions of shear and temperature. Polarized light microscopy is used as the measuring technique. A strong dependence of nucleation rate on supercooling and imposed stress was found. This behavior is explained in terms of stress-induced supercooling of melts. A correlation between the nucleation behavior and morphology of the sheared material is attempted.

INTRODUCTION

Little research has been reported on the effect of stress on the nucleation rate during crystallization of polymer melts. Most work reported has been on the effect of stress on overall transformation rates¹⁻⁶ or qualitative nucleation rates⁷ in elastomers. Qualitative results have also been reported for stirred dilute solution crystallization.^{8,9}

Work that has been carried out on melts has dealt with describing overall kinetics for crosslinked systems¹⁰ or induction times for crystallization.¹¹⁻¹⁴

The purpose of the research presented here was to study the nucleation behavior of a polymer melt as it crystallized under well-defined temperature and shear conditions.

The material used was Carbowax 20-M supplied by Dr. F. E. Bailey of Union Carbide Corporation. The sample had a \bar{M}_n of 38,300 and a \bar{M}_w of 506,000 as determined by GPC analysis. The instrument used to conduct the experiments was a parallel-plate rotary shearing device which has been described elsewhere.¹⁵

EXPERIMENTAL

The method of data collection used for the nucleation studies was to mount the previously described shearing device on the stage of a polarizing microscope and photograph the material at predetermined time intervals as it crystallized under shear. The photographs were then analyzed for the number of crystalline entities.

The experiments are carried out several times with the microscope focused

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at different depths within the sample. Crystallization experiments at shear rates of 0, 8, 12, and 22 sec^{-1} have been conducted at temperatures of 50.4°, 51.6°, and 53.8°C.

RESULTS

Plots of the number density of particles as a function of time for the various combinations of temperatures and shear rates were made, and it was found that a linear function provided the best fit to the data. Values for the slopes of the least-squares best fit of the data and, hence, the nucleation rates are given in Table I. It appears that increasing the shear rate increases the apparent rate of nucleation.

TABLE I
Nucleation Rate as a Function of Shear Rate and Temperature

Temp., °C	$\dot{\gamma}$, sec^{-1}	Number of Particles, $\text{sec}^{-1} \text{ cm}^{-3}$
53.8	0	630 ± 63
53.8	8	848 ± 53
53.8	12	957 ± 125
53.8	22	1230 ± 232
51.6	0	1510 ± 100
51.6	8	2520 ± 140
51.6	12	3060 ± 380
51.6	22	4338 ± 675
50.4	0	2400 ± 350
50.4	8	7600 ± 1200
50.4	12	9980 ± 1900
50.4	22	16,386 ± 3900

DISCUSSION

Turnbull and Fisher¹⁶ have derived a theoretical treatment of the nucleation phenomena present during phase transitions of materials. Their result may be approximated by

$$\dot{N} = N_c \exp\left(\frac{-\Delta E - \Delta F^*}{RT}\right) \quad (1)$$

where \dot{N} is the nucleation rate, N_c is a constant, k is Boltzmann's constant, T is the temperature, ΔE is the free energy of activation for transport across the nucleus-mother phase interface, and ΔF^* is the free energy of formation of a critical-sized nucleus. This relation predicts that just below the melting point of the material, the nucleation rate has a negative temperature coefficient. This portion of the nucleation rate-temperature curve is controlled by the ΔF^* term. At temperatures just above the glass transition temperature of a polymer, the nucleation rate has a positive temperature coefficient. This portion is controlled by the transport term. At some temperature between those of melting and glass transition, the terms balance each other to give a maximum nucleation rate. This overall behavior produces a bell-shaped curve with limits at the melting point and glass transition temperatures.

Hoffman and Lauritzen^{17,18} have theoretically treated the kinetics of polymer nucleation and crystallization in light of the work of Turnbull and Fisher. Their major effort was directed toward evaluating the free energy of formation term, ΔF^* . The analysis is based on considerations of the bulk and surface free energies of the nucleating or crystallizing material. Various arrangements of the crystallizing polymer chains, such as folded or bundle-like, and methods of nucleation, such as heterogeneous and homogeneous, were considered.

Application of the free-energy terms derived by Hoffman and Lauritzen to the Turnbull-Fisher equations yield expressions of the form

$$\dot{N} = N_c \exp [-\Delta E/RT - UT_m^2/T(\Delta T)^2] \quad (2)$$

or

$$\dot{N} = N_c \exp [-\Delta E/RT - UT_m/T(\Delta T)] \quad (3)$$

where ΔT is the supercooling, T_m is the equilibrium melting temperature, and U contains lateral- and end-interfacial free energies of the nuclei. Equation (2) corresponds to the homogeneous formation of a three-dimensional nucleus while (3) is for the formation of a monolayer nucleus. In theory, plots of \dot{N} versus $T_m^2/T(\Delta T)^2$ or $T_m/T(\Delta T)$ should yield a straight line depending on the nucleation mechanism. These plots were made for the data collected in the present research. In this case, as is usually true for other systems, the goodness of fit was indistinguishable between the two cases. These results are shown in Figure 1 for the $T_m/T(\Delta T)$ plot. The fit for the quiescent case was quite good. The sheared cases could not be fitted with a linear relation and, hence, nonlinear best-fit curves are drawn through the points. As can be seen, as the temperature is lowered and, hence, the stress on the system at each shear rate increased, the deviation from the quiescent cases becomes greater. The same trend is followed at each of the shear rates.

Equations (2) and (3) may be written in general terms as

$$\ln \dot{N} = \left[\ln N_c - \frac{\Delta E}{RT} \right] - Uf(\Delta T) \quad (4)$$

where $f(\Delta T)$ is the functional temperature dependence previously discussed. This is the form in which the equations were previously cast for Figure 1. If it is assumed that eq. (4) still describes the behavior of $\ln \dot{N}$ (that is, there is not an additional factor) under shear conditions, it would appear that the transport energy is decreasing with increasing stress while the term containing the bulk and interfacial energies is becoming larger.

The alternate approach may be taken that the deviations from the quiescent case are due to the stress supercooling of the system. Here, T_m is always taken as the value for the quiescent case. This approach will be adopted in a later section. It may be pointed out here that comparisons of the stress supercoolings necessary to produce the behavior in Figure 1 compare favorably with those predicted by an alternate (though probably less accurate) nonlinear extrapolation treatment of the experimental data.

Flory⁴ and Krigbaum and Roe⁵ have treated the effect of stress on the melting point of crosslinked systems. Flory's analysis will not be considered here, as certain assumptions concerning crystalline orientation in the stressed

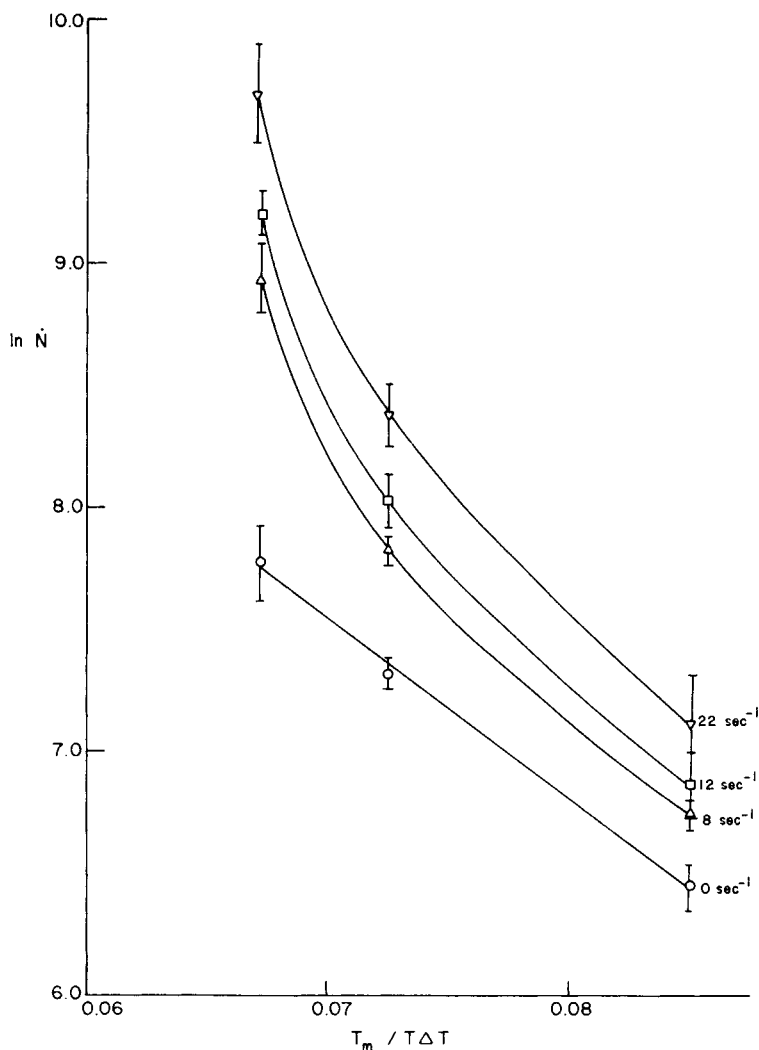


Fig. 1. Log_e of nucleation rate as a function of $T_m/T(\Delta T)$ for shear rates of 0, 8, 12, and 22 sec^{-1} for Carbowax 20-M.

system are not felt to be valid in this system. Haas and Maxwell¹³ adopted the analysis of Krigbaum and Roe in order to treat their stress crystallization data. These investigators have expressed the Krigbaum-Roe theory as

$$\Delta T = \Delta T_i + (T_m^0/\Delta H_m) (\tau^2/2G_s)$$

where ΔT is the effective supercooling of a system, ΔT_i is the initial supercooling of the system due to temperature decrease only, T_m^0 is the quiescent thermodynamic melting point of the material under consideration, ΔH_m is the heat of fusion per statistical segment, τ is the shear stress imposed on the system, and G_s is the elastic shear modulus. Hence, the additional supercooling of the material due to stress may be given by

$$\Delta T_a = (T_m^0/\Delta H_m) (\tau^2/2G_s).$$

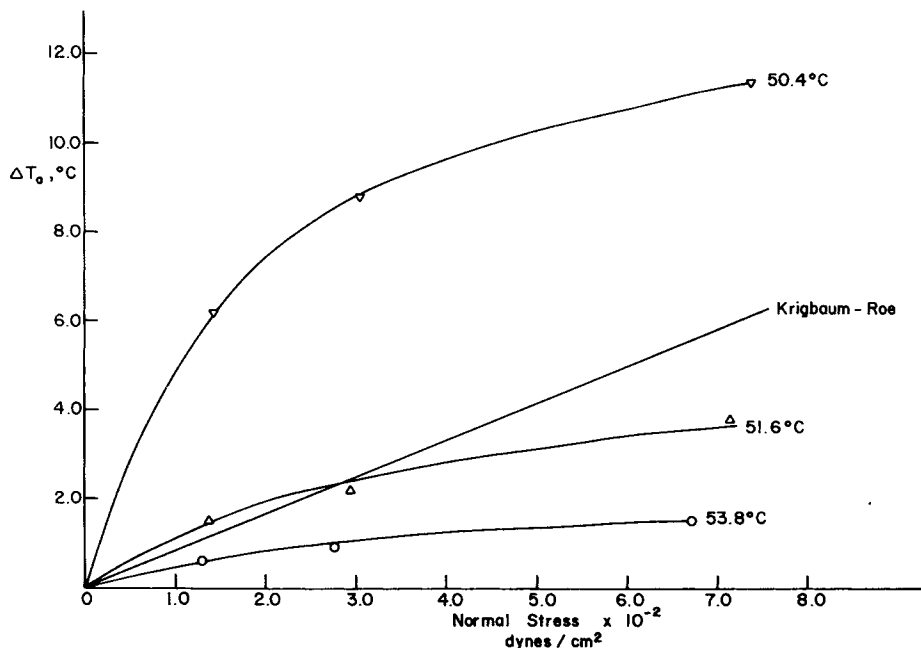


Fig. 2. Observed additional stress supercooling as a function of normal stress at the temperatures of 53.8°, 51.6°, and 50.4°C for Carbowax 20-M compared to the predictions of Krigbaum and Roe.

The term τ^2/G_s must be evaluated. This may be done by utilization of the Weissenberg hypothesis that

$$N_s/\tau^2 = 2/G_s$$

and N_s is the normal stress imposed on the system. It has been found by White and Metzner¹⁹ that there is a slight deviation from a linear relationship between τ^2 and N_s below a shear rate of 50 sec^{-1} for a parallel-plate geometry. That is, the value of N_s predicted from $2 \tau^2/G_s$ by the Weissenberg hypothesis is slightly below that observed. With this deviation in mind, the relationship

$$\tau^2/2G_s = N_s/4$$

may be cast. Hence, the additional supercooling due to stress may be given by

$$\Delta T_a = T_m^0 N_s / 4 \Delta H_m$$

which reduces to

$$\Delta T_a = 8.33 \times 10^{-3} N_s$$

upon substitution for the appropriate value of T_m^0 and ΔH_m .²⁰ Values of N_s have been measured with the Weissenberg rheogoniometer for the Carbowax 20-M used in this research.

In order to compare the results predicted by the Krigbaum-Roe relationship to the values observed in this research, it is necessary to find a suitable

means of measuring the supercooling imposed by shearing the material. This may be obtained from the nucleation rate data in Figure 1. The least-squares best fit line to the quiescent case may be used to measure the additional supercooling at each sheared condition by answering the question, "At what supercooling would the system have to be in the quiescent state to produce the nucleation rate observed in the sheared state?" Once this supercooling is determined, the additional supercooling due to the stress imposed on the system may be had from the difference between the actual temperature at which the system was crystallized and the equivalent temperature at which the observed nucleation rate would have occurred under quiescent conditions. This experimental approach and the Krigbaum-Roe theory are consistent with an increase of nucleation rate with shear due to an increase in melting point. The results of this analysis and those predicted by the Krigbaum-Roe treatment are given in Figure 2. Agreement is somewhat better than that found by Haas and Maxwell who found the predicted values to be almost an order of magnitude less than those observed.

The relation derived by Krigbaum and Roe was done for a crosslinked elastic system. It must be considered how this relates to the system presently being studied.

The elastic nature of the system may be treated by the method of Philippoff.²¹ Let the recoverable shear in a flowing system be given by N_s/τ . The reversible elastic energy of the flowing material is defined by

$$E = \frac{1}{2} G_s (N_s/\tau)^2.$$

If the Weissenberg hypothesis is again invoked, this relationship reduces to

$$E = N_s.$$

Hence, the reversible elastic energy of the system may be expressed as the normal force of the system as has been done in the previous treatment of the Krigbaum-Roe theory.

The crosslinked nature of the PEO melt is due to chain entanglement. It has been shown by Porter and Johnson²² and Teramoto and Fujita²³ that the critical entanglement molecular weight for PEO is approximately 10,000. As has been shown, the molecular weight of the material used for this study is well above that value.

It should be noted that the supercooling predicted by the Haas and Maxwell treatment of the Krigbaum-Roe theory is independent of the actual temperature at which the data are taken. This is reasonable for a vulcanized system in which the molecular chains between crosslinks may not relax from their extended state. Considering Figure 2, this does not appear to be the case for an uncrosslinked melt.

Lodge,²⁴ Philippoff,²⁵ and Peterlin²⁶ have attempted to correlate the flow birefringence of a sheared system with the applied stress. It was found that the stress-optical coefficient (ratio of birefringence to stress) was constant regardless of the concentration (ranging from a few tenths of a per cent to pure material), molecular weight, or temperature of the material. Assuming that the measured birefringence is due to the sum of the polarizabilities of the chain segments, the constancy of the stress-optical coefficient indicates that

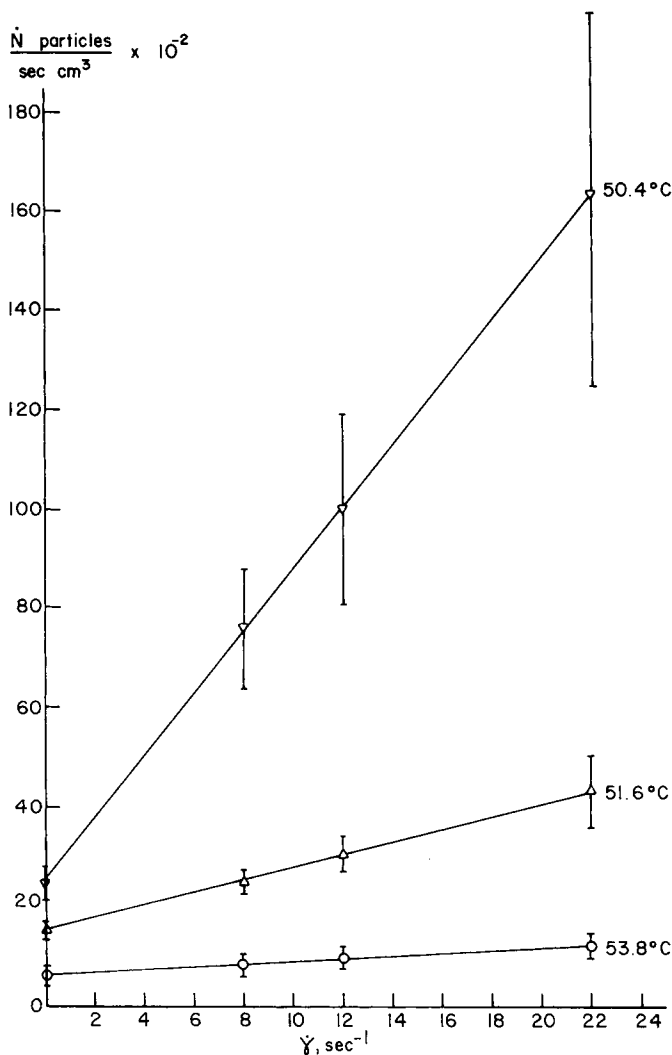


Fig. 3. Nucleation rate as a function of shear rate at 53.8°, 51.6°, and 50.4°C for Carbowax 20-M.

regardless of the condition of the sheared material, as long as an equal amount of stress is supported by the various systems, the average orientation of the segments is the same. This would seem to support the temperature independence of the Krigbaum-Roe theory for the case of uncrosslinked melts.

The additional supercooling due to stress has been measured in this research by comparing the nucleation rates of sheared and unsheared samples at equal initial supercoolings. It is felt, for the system studied here, that imposition of a stress leads to mutual alignment of the polymer chains through the elastic nature of the melt.

By the stress-optical coefficient, equal stresses at different temperatures lead to the same average orientation of polymer chains. This would imply the same mutual alignment.

The Turnbull-Fisher equation states that the higher the crystallization

temperature, the larger the critical sized nucleus required for crystallization to proceed. Hence, even though the same mutual alignment, at equal levels of stress, may be supported at two different temperatures, the effect on nucleation rate at the higher temperature will be lessened by the requirement of a larger critical sized nucleus.

The probability of the formation of a critical-sized nucleus is further decreased through stress relaxation of the polymer chains. As the temperature is increased, the stress relaxation times at a given level of stress decrease. Because the residence time for each statistical segment in a given favorable configuration is less, the probability of forming a critical sized nucleus is further decreased.

Hence, even though a given level of stress will impose the same overall orientation in a system regardless of the temperature, the probability of this orientation leading to the formation of a critical-sized nucleus decreases as the temperature is increased. This is due to the negative temperature coefficient of the nucleation process and the shorter stress relaxation times of the polymer chains. Therefore, for uncrosslinked melts, the crystallization temperature independence of the supercooling term in the Krigbaum-Roe theory cannot be correct. This behavior is reflected in Figure 2.

Hence, it appears that the increase in the nucleation rate of the sheared system considered here may be described largely in terms of stress supercooling. An adequate theoretical description of this behavior include the effect of temperature on the relaxation of the entangled chains. An added complication for a low strength material such as PEO may also be shear fracture.

It has been further observed that the nucleation rate as a function of shear rate may be fitted by a straight line at each temperature of crystallization. These results are shown in Figure 3. It would appear from these plots that the slopes at each temperature would be a function of the supercooling. Attempts to describe the functional relationship of the slope to the supercooling in terms of a polynomial in ΔT have not proven successful. Hence, the value of the slope at each supercooling is dependent on ΔT as well as some other factor such as the stress relaxation of the system.

Krueger and Yeh²⁷ have carried out shear crystallization experiments on polyethylene using a concentric cylinder shearing dilatometer. It is claimed that the total strain on the system at the induction of crystallization, $\dot{\gamma}t_i$, is a function only of temperature and is independent of shear rate. Here, t_i is the induction time for crystallization and $\dot{\gamma}$ is the shear rate.

We will now attempt to rationalize the Krueger-Yeh results. By Figure 3, it can be seen that the nucleation rate under sheared conditions, at a constant temperature, may be expressed as $\dot{N} = a + b\dot{\gamma}$. Since a is equal to the nucleation rate at zero shear, it will be equivalent to the result of the Turnbull-Fisher equation. For the temperature range studied by Krueger and Yeh, a is apparently a negligible term as they state that the system can be maintained, under quiescent conditions, at the desired shear crystallization temperature for 2 hr without any change in the final experimental results.

Assume that t_i always occurs at the same volume fraction of transformed crystalline material, C_i . Let it also be assumed that, because an induction time is being observed, the amount of transformed material is very small and that impingement of crystalline regions is negligible. This means that at t_i ,

the induction time, $\Sigma N_j v_j$ (N_j is the number density of crystalline regions of volume v_j) is constant irrespective of temperature and $\dot{\gamma} t_i$.

We follow Mandelkern²⁸ and let

$$C_i = \Sigma N_j v_j = AG^m \int_{\tau=0}^{t_i} (dN/dt) (t_i - \tau)^m d\tau$$

where in a system at time t_i , $(dN/dt) d\tau = b\dot{\gamma}d\tau$ is the number of nuclei introduced in time interval between τ and $(\tau + d\tau)$ with $\tau < t_i$; G is the growth rate of the growing crystalline regions; and m and A constants reflecting their dimensionality and mode of growth. This expression integrates to

$$C_i = \frac{A}{m+1} [G(T, \dot{\gamma})]^{m+1} b(T) \dot{\gamma} t_i^{m+1}.$$

If $G(\tau, \dot{\gamma})$ has some functional dependence on $\dot{\gamma}$ as does \dot{N} , as shown in Figure 3, then the shear rate dependence of G is large enough so that $G(T, \dot{\gamma}) = G'(T) \cdot \beta \dot{\gamma}$, where β is a constant of sufficient size that $G(T, \dot{\gamma} = 0)$ is small compared to $G(T, \dot{\gamma})$. In this situation,

$$C_i = \frac{A}{m+1} [G'(T)]^{m+1} b(T) \beta^{m+1} (\dot{\gamma} t_i)^{m+1}.$$

Thus, $\dot{\gamma} t_i$ depends only on temperature as found by Krueger and Yeh. It is worth noting that the unusual observation of these two investigators seems to demand a strong dependence of both nucleation and growth rate on shear.

Kobayashi and Nagasawa¹² have attempted to predict the increase of nucleation rate with shear in crystallizing polymers. Their approach is based on expressing the increased nucleation rate through the addition of a shear entropy term to the Turnbull-Fisher equation. In turn, the entropy of the sheared system is expressed in terms of the strain on the system. An attempt was made to apply this analysis to the data gathered in this research. The strain on the system was expressed in terms of the recoverable shear strain τ/G_s . Unfortunately, there was very poor correlation between the predicted and observed results.

Due to the very strong dependence on the nucleation rate-versus-shear rate curves on supercooling, it again appears that additional information regarding the relaxational processes in the system is necessary to adequately describe the behavior.

It should be recalled that, for the shear rates and temperatures considered, the rheological behavior of the PEO used is Newtonian. This lack of shear-thinning behavior would tend to indicate a lack of flow orientation of the molecules. Hence, in the Newtonian region studied, molecular orientation leading to increased nucleation rates should probably be ascribed to elastic behavior of the melt.

CONCLUSIONS

It has been shown by this research that for an uncrosslinked melt of poly(ethylene oxide), relatively low shear rates and stresses will produce changes in the nucleation rate of the crystallizing material. Because this research was carried out under Newtonian conditions, it would appear that the observed

effects are due to orientation of the molecular chains through the elastic nature of the melt rather than flow orientation.

This elastic orientation leads to an additional supercooling of the system similar in nature to that postulated for crosslinked systems by Flory and by Krigbaum and Roe. For the case studied here, the crosslinks in the system are in the form of chain entanglements in the melt which is reflected by stress relaxation. Hence, the theories of Flory and of Krigbaum and Roe would have to be modified to take into account the relaxation processes.

Additional effective crosslinking may occur as the system crystallizes due to the action of the crystallites as pseudocrosslinks. This would lead to an increasing supercooling due to increasing stress.

The additional supercooling due to shear is reflected in the increased rates of primary nucleation. The fine lamellar textures of the crystallizing and crystallized material suggest increased secondary nucleation rate due to shear.¹⁵ The strong dependence of the change in nucleation rate with shear rate on initial supercooling is another indication of the role relaxational processes must play. The importance of the stress on the system, rather than the shear rate, is also demonstrated by the rapidly increasing effect of shear as the supercooling and, hence, stress on the system is increased.

Orientation of the shear crystallized material appears to be minimal as evidenced by DSC and x-ray analysis.¹⁵ The row-like structures observed are similar to those of Andrews; however, they do not constitute a large fraction of the total morphology. They appear to be a surface phenomena in this material. Orientation of the gross sheaf-like morphology during crystallization does occur, as evidenced by polarized light microscopy and light scattering. It has not been determined whether the shear conditions produce selective growth rates in the material as postulated by Baranov, Volkov, Farshyan, and Ya.²⁹ The orientation of these sheaf-like structures with their long axes perpendicular to the flow direction can be described in terms of hydrodynamic theory. The similarity of the morphology produced by these hydrodynamic factors to those postulated by Keller and Machin³⁰ for material crystallized under low stress deserves further research and consideration.

In conclusion, it appears that the major effect of the relatively low stresses on the system studied was to increase the nucleation rate of the system through elastic orientation of the molecular chains. This has been demonstrated by both direct measurement and morphological studies. It does not appear that the shear conditions studied in this system produce long-range crystalline order or high degrees of orientation.

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