

**CRYSTALLIZATION KINETICS
OF POLYLACTIDE AND ITS BLENDS**

by

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Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Chemical Engineering

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August, 1986
Blacksburg, Virginia

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(ABSTRACT)

The purpose of this research was first, to investigate a polymerization method to produce polylactides of desired molecular weights. The polymers PLA-L and PLA-DL produced were then utilized to make blends of semicrystalline/amorphous components. The compatibility of the blends was investigated by determining their T_g with a DSC. However, because of the proximity of the T_g's of the two components, a new approach, which utilized the effects of the "physical" aging on the the T_g peaks obtained by DSC was considered. The results obtained by this method showed that only three blends containing low molecular weight species were compatible. All the others, while incompatible, possessed a certain degree of partial miscibility.

The crystallization kinetics were investigated on the pure PLA-L and the blends. Two separate studies were conducted, the first on the kinetics of the overall crystallization by means of an Avrami analysis, the second on the growth rates of the individual spherulites. The kinetics of crystallization were found to decrease as the molecular weight of the semicrystalline component increased and as the PLA-DL content in the blend increased. In some particular cases, however, a spectacular increase of the growth rates was observed for high DL content blends. Optical microscopy showed that under these conditions, the spherulites grown, contained large inclusions of amorphous material.

Acknowledgements

I would like to thank my advisor, Dr. Wilkes for giving me the opportunity to study in his laboratory. I do greatly appreciate his concern, support and advices in the course of this study. I would also like to thank Dr. Baird and Dr. McGrath for the interest they showed in my work and the effort they spent reviewing my thesis.

I would like to thank Dr. Conger who helped me to come to this university.

Thanks also to Dr. Subramanian for his help in N.M.R. and G.P.C., to L. Lopez and M. Tant for many helpful discussions, to V. Demaret for her help in the typing of this thesis.

Finally, I wish to thank all the group members for their help in the laboratory.

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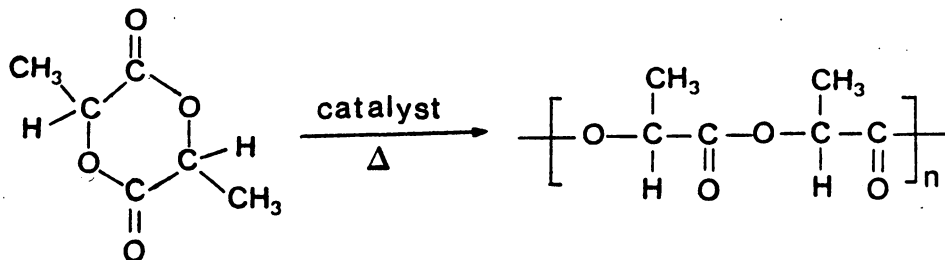
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1.0 INTRODUCTION

1.1 Background Information On Polylactides

The polymerization of lactic acid or its dimer lactide was first achieved in 1932 by Carothers et al (1). Since then, several interesting applications have been found for this material. It is used as a plasticizer and intermediate for preparing elastomers and foams. Its real potential, however, may be as a degradable biomaterial due to its facile hydrolyzability. In that respect, poly-L-lactide (PLA-L) is an important polymer because its controlled biodegradability produces by-products which are non toxic in a physiological system.

The polymer is produced through a ring opening polymerization using organometallic catalyst systems as shown below:



Two different ways have been studied; the polymerization in solution or, in the bulk phase. The former was first investigated by Tsuruta et al (2) under mild reaction conditions. The monomer used was propylene oxide in solution with either dioxane or toluene

at 80°C and 30°C. Later, Kohn et al (3) investigated the mechanism of ring opening polymerization of lactones in solution and the influence of the type of catalyst used. According to their results, the polymerization proceeded either through the formation of a complex between catalyst and monomer or by the addition of strong protonic acids acting as initiators. Moreover, when stannous octoate was used in the reaction, no complex formation was observed and as reported by Brode and Koleske (4), low molecular weight polymer could not be obtained. The last observations support the results found in the bulk phase polymerization by Hostettler (5,7) in which the stannous octoate is described as a pure catalyst and the initiator can be any species containing an active hydrogen like lactic acid or water. The polymerization is initiated by a component containing at least an active hydrogen that is capable, with the aid of a catalyst, of opening the lactone ring and adding it as an open chain without forming water as a condensation by-product. A general method of synthesis often utilized in the literature (8,9) is a bulk phase polymerization performed at about 130°C. The monomer is recrystallized in ethyl acetate before use, stannous octoate is used as a catalyst in a concentration of 10^{-4} mole per mole of monomer and the reaction proceeds under vacuum or inert atmosphere. Following polymerization, the polymer can be recovered and purified from any remaining lactide and catalyst by precipitation in a non solvent as methanol.

Kricheldorf (10,11) investigated the influence of non toxic catalysts as magnesium oxide and other metal derivatives on the polymerization of optically pure L(-) lactide. The temperatures of reaction used were 120°C, 150°C and 180°C respectively. The yields of reaction increased with time and reaction temperature. Moreover, the racemization of the polymer increased for longer time and higher reaction temperatures thereby losing its tacticity and optical purity. This last statement is very important because it is directly related to the potential crystallizability of the polymer.

From the previous discussion, several important parameters emerge with regard to the polymerization of either lactide-L or lactide -DL:

- The monomer must be highly purified before polymerization in order to obtain high molecular weight polymers.
- A good catalyst is stannous octoate in the concentration range of 10^{-4} mole per mole of monomer.
- The molecular weight is controlled by the quantity of initiator present and this species must have at least one active hydrogen.
- The polymerization must proceed under vacuum to avoid traces of water which could react with the monomer to change the concentration of lactic acid or initiator.
- The polymerization is generally done in the bulk phase and the temperature of reaction is 10°C above the melting point of the monomer to minimize racemization.
- The time of reaction at these low temperatures must be of several days to reach a high yield.
- To obtain pure stable polymer, careful purification procedures must be used to separate polymer from residual lactide and catalyst.

All the above points will be discussed further within chapter 2 under the topic of Polymerization.

Poly-L-lactide (PLA-L) is a semicrystalline polymer which can be crystallized from the melt or from solution. According to Kalb and Pennings (12), the equilibrium melting temperature T_m^0 and the dissolution temperature, T_d , in p-xylene are 215°C and 126.5°C respectively. Moreover, a greater understanding of the melting behavior of spherulitic grown films of PLA-L was introduced by Kishore, Vasanthakumari and Pennings (13). Annealing studies at 175°C revealed that there was an increase in melting

temperature and heat of fusion with annealing time, suggesting an increase in lamellar thickness. Moreover, optical microscopy showed that when the periphery of a spherulite melts, the lamellae situated in its central part undergoes thickening, supporting the idea of a highly complex nature of the melting process where melting and recrystallization happen simultaneously. the characteristics of this melting process are not, however, unique to PLA and are common to semicrystalline polymers.

The molecular weight characterization of PLA has been extensively investigated by Schindler et al (8) and the results of this research have been widely quoted in the literature (9,12,13,14). Specifically, Schindler et al first polymerized PLA-L and PLA-DL in the bulk phase according to the general method described above. Then, the polymers were hydrolytically degraded to give materials having a polydispersity of 2.0. The use of an analytical method to determine the content of carboxylic end groups permitted the establishment of a relationship between viscosity and molecular weight and to allow calculation of the Mark-Houwink parameters “ a ” and “ K ” for different solvents at 30°C. These parameters were accurately determined in a range of number average molecular weight higher than 200,000 g/mole. With these constants, the viscosity average molecular weights could, therefore, easily be calculated through the Mark-Houwink equation $[\eta] = K M_v^a$ where $[\eta]$ is the intrinsic viscosity and M_v the viscosity average molecular weight.

1.2 Blends - Their Preparation And Miscibility Determination

The concept of physically blending two or more polymers to obtain new products or to modify certain physical properties of a material is attracting wide interest

both from a fundamental standpoint as well as for potential commercial purposes. the main routes for blend preparation are discussed below.

The preparation of a blend can be achieved according to several methods. The first and more widely used in academic studies consists of dissolving the polymer in a common solvent and casting a film as described by Walsh and Rostani (15). However, for a given molecular weight and blend composition, phase separation can occur depending on the solvent used to dissolve the polymers. When there is a large difference between the two separate polymer-solvent interaction parameters, a two phase zone exists within the polymer/polymer/solvent ternary phase diagram as shown in Fig.1. As the solvent evaporates, the mixture enters, at composition A, a two phase region. When the composition leaves this region, the separated zones are large enough and the viscosity has increased in such a manner that complete remixing is impossible. The resulting blend at composition C is, therefore generally inhomogeneous. Another possibility is that used by Carter (16) where precipitation of a solution of two polymers in a non solvent was carried out. Here again, the compatibility of the final blend is very much dependent on the choices of solvent and coagulant.

The mechanical mixing of two polymers to form a blend is of great practical importance in the industry. However, even if compatible, the polymers must be mixed for long times in order to obtain homogeneity and in some cases, this can induce degradation when the mixing temperature is high. Moreover, many polymer system exhibit a lower critical solution temperature (LCST) on heating which induces phase separation.

The thermodynamics of polymer blends are described by the equation of the free energy of mixing:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad [1]$$

The combinatorial entropy of mixing ΔS_{mix} is always positive but very small per unit volume due to the small number of molecules present for large molecular weight compounds. It is, therefore, generally too small to counterbalance any positive value of the enthalpy of mixing ΔH_{mix} . This is the main reason why most of the high molecular weight polymeric blends are incompatible according to Paul (17). One exception to this general argument is observed for polar or ionic systems where the polymer-polymer interaction gives negative values of ΔH_{mix} which in turn leads to a negative ΔG_{mix} , favoring the change of state.

The Flory-Huggins solution theory (18) provides an approximation to describe the mixing of polymers, and gives for the free energy of mixing polymers A and B:

$$\Delta G_{\text{mix}} = RTV \left[\frac{\phi_A \ln \phi_A}{\bar{V}_A} + \frac{(1 - \phi_A) \ln(1 - \phi_A)}{\bar{V}_B} + \chi_{AB} \phi_A (1 - \phi_A) \right] \quad [2]$$

where ϕ_A is the volume fraction of polymer A, V_i is the molar volume of i and χ_{AB} is an interaction parameter related to the heat of mixing. If the two polymers are of equal molecular weight M , and density ρ , the interaction parameter χ_{AB} can be replaced by $\frac{2\rho}{M_{\text{cr}}}$, where M_{cr} is a critical molecular weight at which the curve ΔG_{mix} versus volume fraction in Fig.2 changes in concavity. Equation [2] can then be rewritten as:

$$\Delta G_{\text{mix}} = \rho TV \left[\frac{M_{\text{cr}}}{M} (\phi_A \ln \phi_A + (1 - \phi_A) \ln(1 - \phi_A)) + 2\phi_A (1 - \phi_A) \right] \quad [3]$$

For non polar and non ionic polymers, where no specific interaction between polymeric chains is assumed, M_{cr} can be estimated as a function of the solubility parameters δ_A and δ_B according to the following equation:

$$M_{\text{cr}} = 2\rho RT(\delta_A - \delta_B)^2 \quad [4]$$

Therefore, the free energy of mixing two polymers can be computed as a function of the volume fraction as shown in Fig.2. This particular case illustrates the two important parameters governing the miscibility of a blend, which are; molecular weight and respective volume or weight fractions. For example in the particular case of $M = 1.5$ Mcr, ΔG_{mix} is negative except in the window $\phi_A = 0.25 - 0.75$. Therefore, any blend with $0.25 < \phi_A < 0.75$ will be immiscible while all the blends with $\phi_A < 0.25$ or $\phi_A > 0.75$ will be miscible.

The Flory-Huggins theory and its latest modifications accounting for free volume effects is commonly used in the literature to predict polymer-polymer miscibility (19,20). Now that the fabrication techniques and the basic theoretical predictions have been reviewed, the next point of interest is how to characterize the miscibility of any polymer blend. Several options are available to test the miscibility of a polymeric blend. A simple one would be optical clarity while a more sophisticated approach might be to determine if there is a frequency shift of interacting functional groups as detected by Fourier transform infrared spectroscopy. These techniques and others have been discussed by Walsh et al (16) and MacKnight, Karasz and Fried (21) and will not be repeated here. The only common technique utilized in this study has been the measurement of the glass transition temperature (T_g). For compatible blends, the unique T_g observed is often closely related to the blend composition through the well known Fox equation:

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}} \quad [5]$$

where w_A and w_B are the weight fractions of polymers A and B, T_{gA} and T_{gB} are the glass transition temperatures of the two pure polymers. For incompatible blends two T_g 's are observed.

Many methods are available to determine the T_g of polymers. Among them are; differential thermal analysis (DTA), dynamic mechanical analysis (DMA), dielectric measurements, dilatometry and differential scanning calorimetry (DSC). In view of the techniques used for this research and presented in Chapter 2, only the latter technique (DSC) is discussed. Moreover, due to its simplicity and straight forwardness, it is widely applied and described in the literature (22-25). The DSC thermograms are plots of the heat capacity (C_p) versus temperature from which T_g can be defined as the intersection point of the projection of the baseline with the tangent to the discontinuity characterizing the glass transition.

The DSC method, however, can be inapplicable or even misleading in certain cases. For example, in a two phase system, if one of the components is present in a very small quantity, its T_g may not be detected leading to the wrong conclusion of compatibility. Another possibility of error, much more important for the following results, is the proximity of the T_g 's of the two components of the blend. When the difference between the two T_g 's is less than 20°C , it becomes very difficult to separate them by DSC particularly if one component is of minor weight fraction. Therefore, it is necessary to use another approach to increase the resolution. A convenient way to do this is to physically age the blend and use the resulting accentuation of the T_g 's (if miscibility or partial immiscibility occurred) to separate them. According to Struik (26), the development of an endothermic peak in the DSC scan is a general feature of the physical process for aging glassy polymers. Moreover, the increase of the peak is a function of the aging time and the annealing temperature T_a . According to Berens (27), the closer T_a is to T_g , the larger the increase of the peak for a given aging time. Furthermore, for a given T_a , the T_g peak increases with storage time as illustrated in Fig.3. This latter approach will be used to characterize blends of PLA-L and PLA-DL and will be described in Chapter 2.

1.3 Bulk Crystallization Of Chain Folding Polymers

The occurrence of spherulitic growth in linear polymers has been widely studied (28-30), since spherulites are one of the most common crystalline superstructure encountered in polymers. Moreover, the knowledge of their rate of growth and the type of crystalline texture existing in them is of major importance for the understanding of the physical properties of these systems. Spherulites in bulk polymers grow outward from a nucleus. Their radial growth is generally the result of the lamellae formation whose longest dimension lies parallel to the radial direction. These bladelike lamellae typically have a thickness in the range of 50 to 250 angstroms and are formed of folded polymeric chains. The overall “ bulk crystallization kinetics” of a macroscopic sample is determined by two parameters - primary nucleation density and rate of growth of the individual spherulites.

- Nucleation can be separated into two phenomena: primary nucleation (which can be homogeneous or heterogeneous) and secondary nucleation which occurs on the surface of a growing crystal.
- The rate of growth is a function of the secondary nucleation (thermodynamic in origin) and the diffusion of the polymeric chains in the bulk.

The overall bulk crystallization kinetics are usually obtained from dilatometry or calorimetry (DSC) as described in the following section.

1.3.1 Crystallization Kinetics - Avrami Analysis

The crystallization kinetics are often analyzed by means of the well known Avrami equation (31). The theory was developed by assuming a randomly nucleated liquid phase where the “ germs ” (as named by Avrami) or nuclei become activated according to a probability function $P(t)$. Then, the growth of the solid phase was assumed to be linear with time and no impingement situation was considered. The resulting equation of this theoretical treatment (Eq.6) describes the volume fraction of material transformed from the melt as a function of time.

$$1 - X_c(t) = \exp(-Kt^n). \quad [6]$$

Assuming that the crystallization leads to three dimensional spherulitic growth, $X_c(t)$ is the volume fraction of crystals occupied by the spherulites at a given time t , n is the Avrami coefficient, which in particular cases can be related to the dimensionality of the growth and the type of nucleation (heterogeneous or homogeneous). The parameter K is a kinetic constant and is a function of the crystallization temperature T_c . For three dimensional growth with heterogeneous nucleation, the value of K is given as:

$$K = \frac{4}{3}\pi\gamma G^3 \quad [7]$$

where γ is the nucleation density and G the radial rate of growth of the spherulites.

The Avrami equation does not perfectly describe the bulk crystallization of polymers (32) because at high conversions the spherulites impinge and the overall rate of growth is decreased. Moreover, the Avrami exponents obtained from experimental measurements are commonly fractional numbers as reported by Pratt and Hobbs (33). These results are explained by Price (34) as coming from a significant fractional com-

ponent of the polymer that undergoes secondary crystallization. This latter term refers usually to the thickening of the lamellae inside a spherulite through a recrystallization process. Another possible explanation obtained from microscopical observation of growth rates is that the nucleation mechanism is often a combination of both heterogeneous and homogeneous mechanisms. Finally, according to Mandelkern (30), the value of the Avrami coefficient n is raised by 0.5 when the growth of a developing crystal is controlled by the diffusion processes occurring in the liquid phase.

The Avrami analysis can be performed in several ways, one of which is through the use of depolarized microscopy (33). The crystalline fraction is then obtained through the following equation:

$$X_c(t) = \frac{I(t) - I_0}{I_\infty - I_0} \quad [8]$$

where I_∞ , I_0 are respectively the final and initial intensities of transmitted polarized light. $I(t)$ is the intensity at a given time. Dilatometry is another method commonly used (35). Here, the weight fraction of a polymer in the crystalline state can be reached according to the following equation:

$$X_c(t) = \frac{V(t) - V_l^0}{V_c^0 - V_l^0} \quad [9]$$

where V_l^0 and V_c^0 represent the specific volumes of liquid and fully crystalline polymer at temperature T_c , and $V(t)$ is the specific volume of the system at temperature T_c and time t . This particular technique permits one to also calculate the final degree of crystallinity. Finally, isothermal crystallization by DSC is another common and very convenient method as described in chapter 2. When compared, dilatometry and DSC methods (36-38) give similar results for the Avrami coefficient n , the kinetic constant K and $t_{1/2}$, or time necessary for the crystallinity to reach half of its final value.

The usual way to perform an Avrami analysis on homopolymers from an isothermal DSC crystallization curve is widely described in the literature (39-44). The Avrami equation becomes:

$$1 - X_c(t) = 1 - \frac{\int_0^t \frac{dQ}{dt} dt}{\int_0^\infty \frac{dQ}{dt} dt} = 1 - \frac{\Delta H(t)}{\Delta H_\infty} \quad [10]$$

or

$$1 - \frac{\Delta H(t)}{\Delta H_\infty} = \exp(-Kt^n) \quad [11]$$

where $\Delta H(t)$ is the enthalpy of crystallization at time t and temperature T_c , and ΔH_∞ is the enthalpy of the complete transformation (maximum crystallinity achievable) at T_c . The time dependent enthalpy values are calculated from the thermogram obtained for each T_c . Then, a plot of $X_c(t)$ versus $\log(\text{time})$ which show the evolution of the crystallization as a function of time, can be constructed. A simple transformation of the Avrami equation gives:

$$\log(1 - X_c(t)) = \log(X_{am}(t)) = -Kt^n \quad [12]$$

and

$$\log(-\log X_{am}(t)) = \log K + n \log t \quad [13]$$

Therefore, a simple plot of $\log(-\log X_{am}(t))$ versus $\log(\text{time})$ gives the values of $\log K$ at the intercept and n from the slope. Another common method used to calculate the Avrami coefficient n is to consider the plot $X_{am}(t)$ versus time and to calculate the slope, S , at $t = t_{1/2}$. Specifically, n is given by the relationship:

$$S = -n(\log 2)^{1/2} = -0.35n. \quad [14]$$

The last parameter of importance is the half time of crystallization, $t_{1/2}$. It can be calculated directly from the plot of $X_c(t)$ versus $\log(\text{time})$. It might be stated that this analysis is also applicable to polymer blends as shown by Martuscelli et al (38).

As we have seen at the beginning of this section, the Avrami equation contains two important parameters in the kinetic expression for the constant K as seen in Eq.(7). The first is γ , the nucleation density while the second is the rate of growth G . Therefore, the determination of G by optical microscopy gives additional information on the crystallization kinetics and allows to separate the relative effect of these two parameters. The fundamental theory describing the growth rate and the techniques used for its determination are discussed in the following section.

1.3.2 Crystallization Growth Rates

The classical nucleation theory of Turnbull and Fisher (45) as described by Hoffman et al (28) and Sanchez (29) expresses the rate of growth of a lamellar crystal according to the following equation:

$$G = G_0 \exp \left(\frac{-\Delta E_a}{kT} \right) \exp \left(\frac{-\Delta F^*}{kT} \right) \quad [15]$$

where ΔE_a is the free energy barrier opposing transport of material across the interface liquid-solid, ΔF^* is the free energy required to create a nucleus of critical size, G_0 is a constant. Assuming that the growth of the lamella occurs by nucleation at the surface of the crystal, ΔF^* can be written as:

$$\Delta F^* = \frac{4\sigma\sigma_e T m^0}{\Delta h \Delta T} \quad [16]$$

where σ and σ_e are respectively the surface free energies of formation of the lateral and end interfaces of the lamella crystal, Δh is the enthalpy of fusion of bulk polymer crystal, T_m^0 is the equilibrium melting point, and ΔT is the undercooling ($T_m^0 - T_c$). The radial growth of polymeric spherulites are the same as those of their constituent lamellar crystals (46) and are commonly described in the actual literature (47) under the revised form of equation [15]:

$$G = G_0 \exp \left(\frac{-U^*}{R(T_c - T_\infty)} \right) \exp \left(\frac{-\beta}{T_c(\Delta T)f} \right) \quad [17]$$

where β is the nucleation constant; f is the factor accounting for the change in the heat of fusion Δh as temperature is decreased below T_m^0 and is given by $f = 2T_c/(T_m^0 - T_c)$; U^* is the activation energy for transport of segments to the site of crystallization, T_∞ is the hypothetical temperature at which all the motion associated with viscous flow ceases and is correlated to T_g .

Vansanthakumari et al (9) have studied the rates of spherulitic growth of PLA-L as a function of T_c and molecular weight on a hot-stage microscope. The PLA-L materials were prepared under vacuum by ring opening polymerization using stannous octoate as initiator. It was found that the radial growth rates of the spherulites were linear for all T_c 's. They increased as molecular weight decreased and showed a maximum at $T_c = 125^\circ\text{C}$. Moreover, for all molecular weights $M_v > 150,000$, the crystallization followed a regime II behavior characteristic of spherulitic growth. For $M_v < 150,000$ and $T_c > 163^\circ\text{C}$, the growth of axiallites was observed which is characteristic of a regime I behavior. The growth rates were in agreement with the theory and verified equation (17). The difference in the growth dimensionality between regime I and II is evaluated in the parameter β

$$\text{regime I} \quad \beta^I = \frac{4b\sigma\sigma_e T_m^0}{\Delta h k} \quad [18]$$

$$\text{regime II} \quad \beta^{II} = \frac{2b\sigma\sigma_e T_m^0}{\Delta h k} \quad [19]$$

where b is the layer thickness and k is the Boltzmann constant , all the other terms having already been defined.

Let us now consider the case of blends containing a crystallizable component and compatible but non crystallizable diluent. The kinetics of crystallization are reduced by dilution of the crystallizable component at the growth surface. Indeed, the diluent is rejected from the growing crystal and forms a buffer zone which reduces both the diffusion of the crystallizable polymer to the crystalline surface and the secondary nucleation. Keith and Padden (48,49) in their classic work on isotactic / atactic polypropylene blends found that the rates of radial spherulitic growth, at the same supercooling, were higher for the blends containing the higher level of impurity. This surprising result was credited to the difference in molecular weight distribution upon fractionation of the atactic polypropylene and is not the expected result if the molecular weights of the diluent matched that of the crystallizable species. In the recent literature (48-50), the spherulitic growth rates in compatible blends of semicrystalline/amorphous polymers have been described by equation [15]. However, in this particular case ΔF^* is more correctly expressed as:

$$\Delta F^* = \frac{4b\sigma\sigma_e}{\Delta F'} - \frac{2\sigma K T_c \ln V_1}{b \Delta F'} \quad [20]$$

where V_1 is the volume fraction of crystallizable polymer, $\Delta F'$ is the free energy difference between the supercooled liquid and the crystal of the blend and can be approximated by:

$$\Delta F' = \frac{\Delta H^0(Tm_B^0 - T_c)}{Tm_B^0} \quad [21]$$

where ΔH^0 is the perfect crystal heat of fusion of the crystallizable polymer. The second term included in equation [20] accounts for the probability of selecting the required number of crystalline sequences from the blend (20). This term which is of entropic origin is always positive and promotes an increase in the value of ΔF^* . According to Martuscelli et al (51), when the T_g of the crystallizable component ($T_{g_{cr}}$) is lower than the T_g of the non crystallizable one ($T_{g_{am}}$), ΔF^* increases. Consequently, the radial growth rates of spherulites grown from compatible semicrystalline/amorphous polymer blends having components of similar molecular weights will always be lower than that of the pure crystallizable component. Moreover, the effect of the diluent is more significant at low T_c and induces larger depressions of growth rate G . On the contrary, if $T_{g_{cr}} > T_{g_{am}}$ one might expect an increase of G due to the presence of diluent.

These statements are supported by the results of Keith et al (49). On isotactic/atactic blends of polypropylene and polystyrene, the spherulitic radial growth rate is decreased for a given T_c when the percentage of diluent increases.

1.4 Objectives And Justifications

The objectives of this research can be divided in three important parts: the polymerization of PLA-L and PLA-DL, the fabrication and characterization of the blends and the crystallization kinetics study. PLA-L and PLA-DL homopolymers were synthesized according to a method derived from the literature. The polymerization

method was modified and completed to allow one a good control of the molecular weight of the final products. After the determination of their molecular weight by intrinsic viscosity, the polymers were used to prepare blends containing PLA-L and PLA-DL. The compatibility of the blends was investigated by determining their T_g with a DSC. However, as seen before, the great proximity of the T_g 's of the two constituents of the blends was a limitation for the use of the method. Another approach was used to solve this problem. The samples were "physically" aged in order to enhance the T_g peaks and to allow their separation by a better resolution whenever a certain degree of incompatibility was present in the blend.

The experiments involved in the crystallization kinetics study apply a certain heat treatment to the samples. According to the literature (10) and to other projects studied in this same laboratory, the heat treatment could induce degradation, racemization and/or transesterification. A small complementary study was, therefore, conducted to be sure that these processes were not taking place in the pure polymers or the blends during the heat treatment.

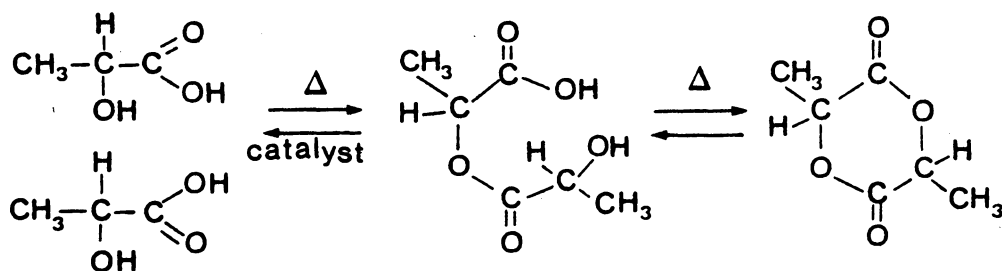
The final step of this research was to study the crystallization of the pure PLA-L and the blends previously prepared. The overall kinetics were studied by isothermally crystallizing the samples within a DSC, while the growth rates were determined by using a hot-stage microscope. The Avrami analysis performed on the overall crystallization data provides information about the crystallinity content of the materials as a function of time and T_c . The information provided by the growth rates and the optical microscopy is more directed on the morphology of the spherulites grown under particular conditions. Finally, the comparison of both the overall kinetics and the growth rates allows the calculation of the nucleation density (N). The combination of all these results could be of potential use to predict the final morphology of these materials when they are processed at a given temperature for a specific amount of time.

2.0 MATERIAL AND EXPERIMENTS

2.1 Polylactides

2.1.1 Materials

The starting monomer for the synthesis of polylactides is a dimer denoted as lactide which is produced from the reaction of two molecules of lactic acid as shown in the following chemical reaction:



Two different lactide monomers are available commercially, the optically pure L(-) and the racemic DL. They can be purchased from Boehinger Ingelheim as a white, free flowing crystalline powder. The purity of the commercial products is greater than 99% and their melting temperatures are:

T_m of L(-) lactide = 96-97°C.

T_m of DL lactide = 124-126°C.

Each melting temperature is very sensitive to the purity of the monomer. After further purification to remove traces of lactic acid, the values of T_m become:

T_m of L(-) lactide = 98°C .

T_m of DL lactide = 127°C .

The polymerization of lactide can be carried out using the pure L(-) monomer to obtain the semicrystalline polymer. Using the DL racemic monomer leads to an amorphous polymer. As expected, the purity of the monomers plays an important role in the polymerization reaction. Therefore, the monomer must be purified by two successive recrystallizations under nitrogen, prior to polymerization as described below.

2.1.2 Monomer Purification

The purification procedure was identical for both the pure L(-) and the DL monomers. The schematic of the apparatus used for the two recrystallizations is shown in Fig.4-a. The device was heated to 45°C and charged successively with ethyl acetate and an excess of monomer. After complete dissolution, the vessel was turned upside down to filter the solution and was then flushed with nitrogen for a few minutes. The recrystallization occurred on slow cooling and after several days under a nitrogen atmosphere. This procedure produced large crystals of lactide which were recovered after filtering off the mother liquor to the other part of the vessel. Then, more monomer was dissolved in the solution to continue the process. The crystals recovered from the first recrystallization were dissolved in fresh ethyl acetate and the same procedure was followed for the second recrystallization. After recovery, the final crystals were washed with

ethyl ether and stored over phosphorous pentoxide in an evacuated desiccator until further use.

2.1.3 Polymerization

The polymerizations were carried out in the bulk phase, but since they were very sensitive to the moisture content and the purity of the monomers, they were performed under vacuum using only sublimed monomers (described below). Moreover, as discussed in chapter.1, Hostettler et al (6,7) had found that an initiator can be any component with one or more active hydrogens e.g., as lactic acid. Therefore, careful control of the quantity of lactic acid in the reactor allowed control of the desired molecular weight. Specifically, the correct quantity of lactic acid was added to the reactor just before the polymerization was started.

2.1.3.1 *Sublimation Procedures*

The monomer sublimation was performed in the polymerization reactor itself. The reactor was charged with 6 g of twice recrystallized monomer and was then connected to a vacuum line providing a vacuum of 0.1 μm of mercury. Then, the monomer was sublimed by heating the bottom of the reactor with an oil bath to a temperature just below its melting point while the upper part of the reactor was cooled with an ice bath as shown in Fig.4-b. With this arrangement, the monomer condensed on the upper part of the reactor. After this occurred, the catalyst and initiator were added in solution form

to the bottom of the reactor and the polymerization started. A general method for the polymerization is discussed in detail in the next section.

2.1.3.2 General Synthesis Methodology

The catalyst used was stannous octoate at a concentration of 10^{-4} mole/mole of monomer. The initiator used was lactic acid and the proper quantity was added to achieve a particular molecular weight. A standardized method was followed for all the polymer batches. The only varying parameters were the type of monomer charged, optically pure L(-) or racemic DL, and the quantity of corresponding lactic acid added to the reactor. Below is given, in listed form, the stepwise procedure used:

- The reactor was charged with 6 g of twice recrystallized monomer and the vacuum was established.
- The monomer was sublimed as described above.
- 1 cc of stannous octoate dissolved in dry pentane was charged and the pentane evaporated under vacuum.
- 1 cc of lactic acid dissolved in ethyl ether was charged and the solvent evaporated under vacuum.
- The reactor was separated from the vacuum line by torch sealing.

- The reactor was placed in an oven for 6 days at a temperature of 10°C above the melting point of the monomer.
- During the first two hours of the reaction, the reactor was shaken by hand every 20 minutes to assure homogeneity.
- After completion of the reaction (conversion > 90%) , the reactor was broken and the polymer dissolved in dry chloroform.
- The polymer was precipitated in dry ethyl ether and dried in a vacuum oven at 75°C for 24 hours.
- Finally, the polymer was stored over phosphorous pentoxide in an evacuated desiccator.

2.1.4 Characterization

2.1.4.1 *Intrinsic Viscosity*

The intrinsic viscosities were measured using a capillary viscosimeter suspended in a water bath at $30^{\circ}\text{C} \pm 0.5$. In each case, mother solutions were prepared by dissolving a very precise amount of polymer in chloroform. The operating method consisted of charging the viscosimeter with 2 ml of polymer solution, waiting to reach a thermal equilibrium and measuring the time needed by the solution to flow between two reference marks. After repeating each measurement three times, other dilutions were

prepared with chloroform. The quantities of solvent added successively and very precisely into the viscosimeter were 2, 4, 8 and 16 ml of chloroform. The flow times were measured under the same conditions as the mother solution. The time used for the calculations was in each case, the average of three measurements made at each concentration. The intrinsic viscosity, $[\eta]$, is related to the concentration and time through the following equations:

$$[\eta] = \lim_{C \rightarrow 0} \left[\frac{\eta - \eta_s}{\eta_s C} \right] \quad [22]$$

where

$$\left[\frac{\eta - \eta_s}{\eta_s C} \right] = \left[\frac{t - t_s}{t_s C} \right] \quad [23]$$

where η and η_s are the viscosities of the solution and the pure solvent respectively, C is the concentration of the solution in g/dl, $[\eta]$ is the intrinsic viscosity of the polymer, t and t_s are the times necessary for the solution and the pure solvent to flow. Therefore, a single plot of $((t-t_s)/C.t_s)$ versus $1/C$ gives $[\eta]$ at the intercept. The value of $[\eta]$ was used to calculate the viscosity average molecular weight M_v by using the Mark-Houwink equation.

$$[\eta] = K M_v^a \quad [24]$$

where K and a are the Mark-Houwink coefficients given by Schindler and Harper (8). They investigated the viscosity-molecular weight relationship on polylactides of $M_w/M_n=2$. The values they found are shown in Table 1 and were obtained from measurements in chloroform solutions at 30°C.

2.1.4.2 N.M.R

The stereochemistry of the polymers synthesized was determined using high resolution C-13 NMR spectroscopy. The 50.13 MHz spectra were obtained at room temperature using a Bruker WP-200 SY spectrometer. The samples were prepared by dissolving the polymer into deuterated chloroform (10 % weight per volume) while TMS was used as the internal reference. The tacticity was determined from the fine structure associated with the carbonyl (C=O) peaks.

The PLA-L isomer was identified by a single peak at 169.2 ppm, whereas the PLA-DL analog had three different peaks at 169.1, 168.8 and 168.5 ppm assigned respectively to the iso, hetero/iso or hetero/syndio and syndio triads.

2.2 *Preparation Of Blends*

2.2.1 Materials And Preparation

Polymer blends were prepared by mixing the optically pure L(-) and racemic DL polylactides (PLA). Their viscosity average molecular weights are given in Table 2-a.

The list of the blends prepared is given in Table 2-b along with their arbitrary denomination, chosen only for simplification reasons. For each blend, four compositions were prepared by weight percentage.

- 90% PLA-L / 10% PLA-DL

- 80% PLA-L / 20% PLA-DL
- 70% PLA-L / 30% PLA-DL
- 50% PLA-L / 50% PLA-DL

The blends were prepared by dissolving 1 g of the corresponding weight percentages of the two polymers in 50 cc of chloroform. After complete dissolution and homogenization, the solutions were poured into Teflon molds and the solvent evaporated at room temperature. Then, the blends were removed from the molds, dried for 24 hours at 70°C under vacuum and stored over phosphorous pentoxide.

2.2.2 Miscibility Considerations

The miscibility of the blends was investigated by studying their T_g behavior on a Perkin Elmer DSC-4 differential scanning calorimeter. All the samples were heated above T_g, at 70°C for 30 seconds and then brought back to room temperature. Depending upon the molecular weight of the PLA's and their relative weight percentages, the blends obtained were found to be compatible or not. In the first case they presented a single T_g while in the second, two were observed. In the present case, however, the problem was complicated by the proximity of the two T_g's: T_g=53°C for PLA-DL, T_g=65°C for PLA-L as discussed in chapter 1. It was, therefore, necessary to let the samples physically age in order to detect a phase separation in an incompatible blend as shown in Fig.5-a and 5-b. Fresh samples of all the blends were, therefore, aged for

14 days and were run at a heating rate of 20°C/ min . The weight of the samples was in the range of 10 mg. In all cases the DSC was first calibrated with an indium sample.

2.3 *Avrami Analysis - Methodology*

2.3.1 Isothermal DSC Study

The crystallization kinetics of the samples were carried out using a Perkin Elmer DSC-4 Differential Scanning Calorimeter. The sample weights were in the range of 10 mg. The DSC was used in the isothermal mode to obtain the crystallization isotherms. For a semi-crystalline polymer, the crystallization window lies between T_g and T_m . In this case, $T_g = 65^\circ\text{C}$ and $T_m = 180^\circ\text{C}$. However, the entire range of crystallization temperatures could not be investigated because of the sensitivity limits of the instrument. At low temperatures, the diffusion of the polymeric chains was too slow and at high temperatures, the nucleation density was too low. Therefore, the temperature range investigated was between 90°C and 140°C . To obtain materials more suitable for DSC analysis, all the PLA-L samples and the blends were pressed at 200°C for 30 seconds and quenched at room temperature between aluminum plates which led to transparent, amorphous thin films. The samples cut from these films were then heated to 200°C at $50^\circ\text{C}/\text{min}$ and held at this temperature for 2 minutes to destroy possible residual nuclei. Then they were cooled at $60^\circ\text{C}/\text{min}$ to the chosen crystallization temperature T_c , at which the isothermal crystallization was recorded versus time as shown in Fig.6.

2.3.2 Analysis Of Calorimetric Data

The extent of crystallization completed at a given time $X_c(t)$, was determined by digitizing the isothermals and calculating the partial areas under the curve as described earlier. The assumption made was that the fractional crystallization at a given time is proportional to the ratio of the isothermal peak area up to that time over the total peak area as stated by Jog et al (43). The digitizing table was connected to a computer and the data collected served to calculate the partial crystallinity as a function of time, the Avrami coefficient, the kinetic constant K and the half-time of crystallization. The same computer programs, shown in Appendix A, calculated the data necessary for the plots $X_c(t)$ versus $\log(\text{time})$ and $\log(-\log X_{am}(t))$ versus $\log(t)$.

An example of the analysis method is developed below and schematized in Fig.7. The starting point is the isothermal curve which is digitized to give a data file containing 20 coordinates points plus the total time in minutes needed to obtain the curve as reported in Fig.8. The time value is used to transform the X-coordinate, originally in inches to a time scale in minutes. Then, the computer program creates 2 files of output as shown in Fig.9-a and 9-b. The Avrami coefficient was calculated by the two usual methods and the logarithm of the kinetic constant K as explained in chapter 1. The second file contains 3 columns of data which are respectively, $\log(\text{time})$ in minutes, the crystalline fraction $X_c(t)$ and the double logarithm of the amorphous fraction. The third column contains only 12 data points because the last point were removed to avoid deviation from the theory due to the spherulitic impingement. The type of graphs obtained from these data are shown in Fig.10-a and 10-b. Finally, another program is used to calculate $t_{1/2}$, the time at which the crystallinity has reached one half of its final value.

This same procedure was repeated for each particular T_c and for each PLA-L sample or blend.

2.4 Crystallization Growth Rates - Methodology

The crystallization of the polylactides or the blends occurs in the spherulitic mode. Therefore, the measurement of the growth rate of the spherulites as a function of the time gives fundamental information about the nucleation of the polymeric chains into the crystal phase. This parameter is a part of the overall kinetics studied by the DSC and it permits one to differentiate the two important phenomena leading to crystallization which are the nucleation density and the spherulitic growth rates. Moreover, the direct visual observation of the spherulites also reveals their possible imperfection due to phase separation.

2.4.1 Optical Microscopy And Growth Rates Determination

The samples used for the microscopic study were cut from the film used from the DSC work. All the observations were made on a Zeiss optical microscope equipped with a 35 mm camera and a Leitz hot-stage. The hot stage was calibrated before use with organic (naphthalene) and mineral (sodium nitrate) crystalline compounds of known melting points (T_m). The samples were placed between microscope glass slides, heated at 200°C for 2 minutes and then cooled down rapidly to the required T_c . The relatively

short time spent at 200°C to erase the previous nuclei was justified by using amorphous films to start with and by the desire to avoid or minimize degradation. All the samples were used only once and the measurements were made in the middle of the samples to avoid any problem of surface nucleation (where hemispheres are grown instead of spherulites) or degradation in the periphery of the sample. The range of T_c's values investigated was 100°C-150°C. Below 100°C the nucleation density was too high to allow differentiation of the spherulites and, above 150°C, their shapes were too irregular and diffuse. Furthermore, when low supercooling temperatures were used, the samples were nucleated at lower temperatures and then returned to the required T_c. This artifact showed no influence in the growth rates measured when compared with samples nucleated at the correct T_c after a very long induction time. It was only used to accelerate the nucleation which is almost nonexistent at temperatures close to 150°C.

In each case a portion of the film was chosen to be photographed. A timer was started when the first picture was taken. Then, a series of 4 to 6 pictures were taken at predetermined intervals of time. After film processing, the series of pictures corresponding to a given T_c were examined. One or more spherulites were chosen and followed through the series of pictures, its diameter carefully measured and reported versus time as shown in Figs.11-a, b, c, d. Several advantages of this method are listed below.

1. Eliminates the need to center a spherulite on the graduated scale printed on the microscope ocular . This procedure always increased the observation time.
2. Several spherulites can be measured on the same picture to increase the accuracy of the results.
3. The pictures can be enlarged at will. That is very useful when using high supercooling temperatures where the nucleation density is very high.

The values of the diameters were plotted versus time which provided straight lines whose slope was the rate of growth (G). The values of these slopes were then used to obtain the curves of growth rates versus Tc. At this stage of the method, the problem remaining is the transformation of the values obtained into appropriate units: microns/minute. A convenient way to do this was to simply take a picture of a 0.5 mm marker on the microscope using the same lens as for the spherulitic observation and to develop it at the same magnification as the other pictures. Then, a simple measurement of the marker on the picture permitted the calculation of the growth rates of the radius of the spherulite in $\mu\text{m}/\text{min}$. The error introduced by this method was determined by calculating the relative error:

$$\Delta E = \Delta S/S \quad [25]$$

where ΔS is the maximum difference in the slope obtained by the measurement of 5 different spherulites on the same picture and S is the average of the 5 slopes. The values obtained showed a relative error no larger than 6%.

3.0 RESULTS AND DISCUSSION

3.1 *Polymerization Results*

3.1.1 Control Of Molecular Weight

As described in chapter 2, the precise control of the quantity of initiator (lactic acid) present in the polymerization reactor allows one to achieve variable yet controllable molecular weights. The total quantity of lactic acid present during the polymerization is, however, from two sources:

- The quantity left into the reactor after sublimation.
- The quantity added directly prior to polymerization.

Since the polymerization reaction was always repeated following the same routine, the quantity of lactic acid remaining in the reactor after sublimation was assumed to be constant and was determined by polymerizing the monomer without adding any extra initiator. This reference sample had an average viscosity molecular weight, $M_v = 935,000$ g/mole and was used to back calculate the concentration, C , of lactic acid

initially present. The details of the calculation are shown in Appendix B and lead to the value of C equal to 2.90×10^{-4} mole/mole of monomer.

Since the goal was to synthesize polymers having a wide range of molecular weights, quantities of initiator to be added in each particular case were calculated consequently. These values are also determined and presented in Appendix B. The viscosity molecular weights intended, M_{in} and obtained, M_{ob} for both PLA-L and PLA-DL are shown in Table 3. From this table, the calculation of the error obtained through polymerization is: $E = \frac{[M_{in} - M_{ob}]}{M_{in}} \times 100$. The error E does not exceed in general 10% , showing a good control and reliability of the method of polymerization. The only exception is observed for the PLA-L sample ($M_v = 290,000$ g/mole) where $E = 16\%$. This fluctuation can be explained by problems encountered with the diffusion vacuum pump at the time of polymerization leaving a vacuum of 0.5 μ m of mercury instead of the usual 0.1 μ m. The quantity of lactic acid left in the reactor was, therefore, larger than planned.

3.1.2 Polymer Characterization

All polymers were characterized before using them for the blend preparation or for the kinetics studies. The molecular weights were determined by intrinsic viscosity measurements as described in chapter 2 and according to the method of Schindler et al (8). The Mark-Houwink coefficients given in Table 1, have been determined and tested only in a range of number average molecular weight higher than 200,000 g/mole. In the present case, however, and based on evidence from GPC measurements collected by

Carter (16), the decision was made to extend the method to lower molecular weight samples.

Another important characteristic with regard to crystallization kinetics, was the stereochemistry of the polymers. According to the experimental conditions (ie: temperature), we do not expect any racemization of the L-lactide to take place during polymerization. However, two samples of PLA-L and PLA-DL were tested using high resolution C-13 N.M.R spectroscopy. The spectra obtained are shown in Fig.12. Figure 12-a clearly exhibits a unique carbonyl peak at 169.2 ppm for PLA-L proving that no racemization had taken place to alter the stereoregularity of the polymeric chains. On the other hand, Fig.12-b shows three different peaks (169.1 ppm, 168.8 ppm, 168.5 ppm) characteristic of the PLA-DL stereochemistry as explained in chapter 2.

3.2 Characterization Of The Blends

In the following sections, the blends are identified as B#-Y/Z, where B# denotes a specific numbered blend as shown in Table 2-b and Y and Z are the weight percentages of PLA-L and PLA-DL respectively.

After fabrication, the blends were characterized with respect to miscibility. The Tg of the different mixtures were studied by DSC on samples "physically" aged for 14 days as explained in chapter 1 and 2. The aging effect which creates an endothermic peak on the Tg transition as displayed in the DSC thermograms, allows one to establish an index of blend compatibility. The state of compatibility for all the blends is summarized in Table 4 and shows that only three blends were found compatible: B1-90/10, B1-80/20

and B1-70/30. Their DSC thermograms are shown in Fig.13-a. The last blend of the series, B1-50/50 is incompatible as shown by the double Tg observed in Fig.13-b.

From Fig.13-a we observe a shifting of the Tg transitions from higher to lower values as the PLA-DL content increases. However, the shifting of the Tg does not follow the equation of Fox (Eq.5) and the Tg appears to be lower for the blend B1-80/20 than for the blend B1-70/30. This surprising result was verified by preparing the blends again with polymers from the same batches. The results obtained with the new samples displayed the same behavior with respect to the shifting of the Tg.

In an attempt to explain the state of compatibility obtained in the blends prepared by casting films from solutions, one might consider the existence of a two phase zone in the ternary diagram PLA-L/PLA-DL/CHCl₃ as given earlier in Fig.1. Although this diagram represents a thermodynamic equilibrium situation, it may be used to follow the concentration of the solutions upon solvent evaporation. Then, a kinetic argument can be developed to explain the compatibility behavior observed in the final state of the blends (no solvent left). Considering that all the blends were prepared following the same procedure (same initial concentration in CHCl₃ and same rate of evaporation of the solvent), a governing factor of the final miscibility state of the blends might be the time necessary to go from A to B and cross the two phase region shown in Fig.1. Another important parameter which controls the kinetics of mixing and demixing when the solution goes through a two phase region, is the viscosity of the mixture. The above concepts can be applied to the blends B1 and their hypothetical equilibrium ternary diagram displayed in Fig.14. In this figure, the lines AB, AC, AD and AE represent the changes in solution concentration as the solvent evaporates. For the compositions 90/10 and 80/20, the lines AB and AC do not cross the phase separated zone. The corresponding blends are therefore completely miscible and their Tg decreases as the PLA-DL content increases. For the 70/30 composition, the line AD crosses the two phase region

but the time necessary to go from “ a ” to “ b ” is relatively short and the phase separated domains ought to be small (far from equilibrium) when the mixture reenters the one phase region. Moreover, the molecular weight of the components of B1 are low enough to favor the kinetics of remixing and allow the achievement of miscibility before the viscosity of the mixture becomes high enough to freeze the molecular motion. From the DSC results, it is assumed that the miscibility is achieved in the final state for B1-70/30. However, its T_g is higher than that of B1-80/20. This might be explained by assuming an imperfect remixing with small inhomogeneous regions within the blend B1-70/30. Finally, B1-50/50 needs a longer time to go from concentration “ c ” to “ d ”. The phase separated domains have more time to grow and approach the thermodynamic equilibrium. When the composition reaches “ d ”, the remixing starts but the viscosity becomes quickly high enough to limit it. The blend is, therefore, inhomogeneous in its final state and shows two T_g values in Fig.13-b. Partial miscibility does, however, exist to some extent since the two T_g peaks corresponding to the L and DL phases do not appear at the same place as those of the corresponding homopolymers PLA-L and PLA-DL. The shifting of the two peaks of the blend B1-50/50 is shown in Fig.15.

In order to support the above proposed concepts, the three compatible blends were examined by Fourier Transform Infrared Spectroscopy (FTIR) to study the possible shifting of the absorption peak of the carbonyl group ($C=O$) bond appearing in the region of 1760 cm^{-1} . However, the spectra obtained from the three different compositions (90/10; 80/20; 70/30) are similar as observed in Fig.16 and do not show any significant displacement of the carbonyl absorption peak from one blend to another.

All the other blends are incompatible and display two T_g values. An example of this behavior is shown in Fig.17 for the blend B2. From Fig.17, we observe that the 90/10 composition shows a shoulder on the T_g peak indicating the phase separation of

the small amount of PLA-DL. For the 80/20 and 70/30 compositions, this shoulder increases to form a real separated peak for the last composition of 50/50. This increase is directly related to the PLA-DL composition content of the blend and does not reflect any change in phase separation. The use of fresh samples, without any "physical" aging effect is illustrated in Fig.18 with samples of the same B2 blends. The figure clearly shows the limitations and the potential to report misleading results of this approach due to the fact that at this early aging times, it is difficult to differentiate the two Tg's of the low DL content blends. The general arguments developed earlier and applied to the blends B1 may be used to explain the final miscibility state of all the blends. Moreover, the different results obtained from one blend to another ought to be accounted for by the differences in Mv of the polymers used. In all cases, the peaks of the double Tg appear to be shifted with respect to the Tg values of their corresponding pure homopolymers. This is shown in Fig.19 where B4-50/50 displays a double Tg at temperatures above the Tg of the pure PLA-DL component and below the Tg of the pure PLA-L component. The latter observation tends to support the existence of partial miscibility, more or less pronounced in all the incompatible blends studied. Finally, one must be aware that each polymer used in the blend fabrication has a polydispersity of 2.0 which implies a distribution of molecular weights rather than a single value. Therefore, one must realize that the phase equilibrium ternary diagrams used above are in reality complicated by the existence of this distribution. In fact, the blends in solution do not behave like a ternary mixture but like a multicomponent mixture containing several PLA-L and PLA-DL species of different molecular weights. The existence of a fraction of small molecules in all the PLA synthesized might be responsible for the partial miscibility present in all the blends.

3.3 Thermal Effects On The Samples

Before studying the crystallization kinetics with either the DSC or the hot-stage microscope, the samples were cut from amorphous films, heated to 200°C for 2 minutes and quenched to room temperature to remove any possible though improbable existing crystalline structure and to obtain completely amorphous samples. This thermal pre-treatment could also affect the samples in three different ways. Specifically, the processes of degradation, racemization of the pure PLA-L and transesterification could influence the results of the crystallization kinetics study if any one of these occurred. Each of these topics will be addressed separately.

3.3.1 Degradation

The process of degradation would be expected to lower the molecular weight of samples and also possibly create cyclic compounds, thereby, disturbing the kinetics of crystallization. It can be avoided or at least minimized by melting the samples at temperatures not far above T_m , by keeping the samples under a nitrogen atmosphere during the heating step and by minimizing the time of fusion.

The present research was carried out fulfilling those three requirements. The samples were never heated above 200°C ($T_m = 180^\circ\text{C}$), all the experiments with DSC or hot-stage microscopy were performed under nitrogen and the time of fusion was in all cases 2 minutes. Under these conditions and according to the results of Carter (16) on the molecular weight of samples before and after thermal treatment, it is assumed that

no significant degradation of the polymers took place during the thermal treatment preceding kinetics studies.

3.3.2 Racemization

According to Kricheldorf et al (10,11), the use of certain organometallic catalysts induces racemization at high temperatures. This phenomenon introduces changes in the stereoregularity of the polymeric chains and, therefore, influences the crystallization. An easy way to detect racemization is to study the melting point of the samples. According to Mandelkern (30), when the inversion of configuration occurs in a linear polymeric chain, even on small percentages of monomer units, the melting point can be depressed by as much as 40°C.

In the present case, the polymers were made free of residual catalyst by precipitation into a non-solvent. However, as a precaution, the variation of the melting point (T_m) of PLA-L ($M_v = 550,000$ g/mole) was investigated after annealing three samples at 200°C for 2, 10 and 20 minutes respectively. The melting points obtained by DSC with a heating rate of 10°C/min are given in Table 5-a and show no change of T_m 's values with annealing time. Therefore, it is assumed that there was no problem of racemization occurring during the heat treatment up to 200°C.

3.3.3 Transesterification

Another project carried out by Subramanian in this laboratory and dealing with PLA blends allows the author to state that transesterification occurs in PLA-L/PLA-DL blends containing stannous octoate when these are annealed at 200°C for several minutes. The possibility of transesterification occurring in the samples used for this research during such thermal pretreatment was investigated on two different blends: B1-80/20 which is a miscible blend where the molecules of PLA-L and PLA-DL are in close contact and B3-50/50 which is immiscible but with a high content in DL. The melting points of these blends were studied by DSC at a heating rate of 10°C/min on samples not annealed, annealed 2 minutes and 10 minutes respectively, at 200°C. The T_m values are reported in Table 5-b and do not show a significant change, supporting the conclusion that transesterification does not take place in the samples when placed under the heat treatments discussed above.

3.4 Overall Crystallization Kinetics

3.4.1 Isothermal DSC Results

The isothermal crystallization of a polymer or a blend, appears on a DSC curve as an exothermic peak. Figure 20 shows an ensemble of curves recorded from the same polymer PLA-L ($M_v = 290,000$ g/mole) at different crystallization temperatures, T_c . From the figure, one sees that the broadness of the peak and the induction times are

function of T_c . Moreover, the ordinate scale being at the maximal possible sensitivity, it clearly appears that T_c values above 140°C and below 90°C cannot be used for the analysis because the crystallization peaks are too broad and low to be accurately detected i.e., it is difficult to specify an accurate baseline.

All the isothermal peaks are not shown because the same type of DSC response curves was observed for all the polymers and blends tested. The limit of the T_c range which could be utilized was also the same in general ($90^{\circ}\text{C} < T_c < 130^{\circ}\text{C}$ or 140°C) with the exception of a few cases: B1-70/30 which gave a flat line at $T_c = 90^{\circ}\text{C}$ and B2-50/50 which gave the same response at $T_c = 100^{\circ}\text{C}$ and $T_c = 90^{\circ}\text{C}$. In both cases, these samples were close to their T_g and hence in a region where crystallization was controlled by the diffusion of the molecules. Furthermore, the two blends have a high PLA-DL content and hence a low diffusion rate which greatly spreads the time scale over which the crystallization occurs thereby making the DSC peak too broad to be accurately determined.

3.4.2 Results Of The Avrami Analysis

The Avrami plots ($X_c(t)$ versus $\log(t)$ and $\log(-\log X_{\infty})$ versus $\log(t)$) for PLA-L ($M_v = 290,000$ g/mole) are given in Fig.21. Each curve corresponds to a particular T_c and is obtained through the digitalization of the crystallization peaks shown in Fig.20 and the use of a computer program (Appendix A). Again, the curves are not presented because the main features of these graphs are the same for all the polymers and blends studied. Figure 21-a shows an ensemble of sigmoids which describe the evolution of the crystallinity content as a function of time. The lower part of the curves characterizes the

induction time or time necessary to form the primary nuclei which will start the crystallization. Figure 21-b exhibits straight lines and, thereby, proves that the crystallization follows the Avrami equation (Eq.6, 13) given in chapter 1. The interesting feature of this graph is the change observed in the slopes of the lines which become steeper as T_c moves from 90°C to 140°C and, suggests that the nucleation mechanism is evolving from heterogeneous to homogeneous. This suggestion is supported by Fig.22 where two optical micrographs of PLA-L ($M_v = 65,000$ g/mole) taken at $T_c = 110^{\circ}\text{C}$ and 140°C respectively, are shown. The figure clearly shows spherulites of uniform sizes at $T_c = 110^{\circ}\text{C}$ versus mixed sizes at $T_c = 140^{\circ}\text{C}$. This is a general tendency of all the materials tested and is better seen in Table 6 where all the values obtained for the Avrami coefficient are reported. Those values are not integer as predicted by the classical theory (Chapter 1). Moreover, they are lower than expected from the classical theory which predicts values of the Avrami coefficient of 3 and 4 for the three dimensional growth of spherulites with pure heterogeneous and homogeneous nucleation respectively. Even if one considers diffusion controlled crystallization at high supercoolings as seen in chapter 1, the values of the Avrami coefficient are still below the theoretical expectations. According to Price (53), the major difficulty arises because equation [9] applies only to a constant volume situation. The common approximation of replacing volume by weight into the equation can be responsible for an error up to 0.3 in the Avrami coefficient. Other sources of error can arise from the deviation from the assumptions made in the initial theory as discussed by Hillier (54). In particular, constant growth rates, no impingement of spherulites and random nucleation.

From optical microscopy applied to these systems and described in the following sections, the growth rates were proven to be constant with time. The two other factors are related because an oriented nucleation creates impingement even at the beginning of the crystallization. In this case, the last part of the crystallization DSC isotherm is

not considered in the calculations of n to avoid impingement problems. The small thickness of the samples can, however, reduce the value of n by increasing the probability of nucleation at the surface and, therefore, the truncation of spherulites. The last problem detected by optical microscopy is the presence of residual orientation of nucleation in the samples, even after the thermal pretreatment. This phenomenon arises from the way the samples are pressed (low temperature, short time) to avoid degradation. It is observed at high supercoolings and disappears as T_c increases contributing thereby, to the general increase of n with T_c observed in Table 6. This last argument along with the considerations on the thickness of the sample can explain why the values of the Avrami coefficient n are lower than predicted by theory.

The values of the kinetic constant, K calculated from the double logarithmic plots are displayed in Table 7. These values were used to create graphs ($\log K$ versus T_c) as shown in Fig.23 for the B4 blends. The general shape of the curves is parabolic with the maximum at $T_c = 110^\circ\text{C}$. These curves are characteristic of the expected crystallization kinetics and their shape is directly related to the curves of $t_{1/2}$ versus T_c , described in the following pages. When observed in more detail, the three curves corresponding to 90/10, 80/20 and 70/30 compositions appear almost identical. This can be explained by the existence of phase separation in the mixtures. Indeed, when more PLA-DL is present, the zones rich in DL may simply become larger without perturbing the kinetics of the L regions. The 50/50 composition shows a decrease in the kinetics, especially in the nucleation controlled area of the curve (close to T_m). A satisfactory explanation can be provided by the mechanism of phase separation described earlier and illustrated in Fig.14 which holds here. However, due to the high molecular weight of the DL species, the two phase region of the equilibrium phase ternary diagram ought to be larger and the viscosity of the mixtures is higher for a given concentration than for the B1 blends. These two factors may be responsible for the phase separation observed at

all compositions, even for the B4-90/10 blend. For the 50/50 composition, the partial mixing is less pronounced and some small domains of L material may stay enclosed within the bulk of DL material. Since these small domains are isolated from the bulk of the L material, the average value of the diffusion is reduced and consequently, the overall kinetics decreases more than expected when going from 30% to 50% DL.

The most interesting result with respect to practical applications is the variation of the half-time of crystallization, $t_{1/2}$ with T_c . The results for the pure PLA-L polymers are shown in Fig.24. All the curves are parabolic with a minimum near 100°C for higher molecular weights and 110°C for the lower ones. The parabolas tend to open-up when going from low to high molecular weights, especially in the nucleation controlled zone. That suggests there may be a higher nucleation density at $T_c > 120^\circ\text{C}$ for higher molecular weight species, which increases the overall bulk conversion kinetics.

The crystallization half-times for the blends B1, B2, B3 and B4 are given in Figs.25-28 respectively. Figure 25, for the series B1, shows a major difference of the curves in the nucleation controlled part of the curves. A decrease in the kinetics is observed for the three miscible blends as the DL content increases and there is a very wide gap between the 80/20 and the 70/30 compositions for high supercooling temperatures. This may result from the diluent effect of the DL component into the blend combined with a sharp decrease of the nucleation density at low supercoolings. The 50/50 blend shows a behavior similar to the 70/30 at low supercoolings suggesting no change with respect to nucleation density. However, the kinetics are accelerated for high supercoolings because the phase separation occurring in the B1-50/50 blend leaves regions of pure PLA-L where the diffusion of the L-chains to the surface of the growing crystals is easier.

The blends B2 and B3 are incompatible for all compositions and the diluent effect of PLA-DL is not very pronounced for the first three curves as seen in Figs.26-27. The

wide gap observed between the 70/30 and 50/50 compositions in those two blends and especially for B2, is explained by the kinetics arguments discussed earlier which describe the phase separation upon solvent evaporation. For the 50/50 composition, PLA-DL is believed to form an almost continuous separated phase with inclusions of PLA-L domains of different sizes which should be related to the molecular weights of the two components. If the PLA-L domains are small, the probability to form nuclei decreases and the consequence on the overall kinetics appears as a considerable decrease, especially in the region of low supercoolings. On the contrary, the B4 blends with the larger difference in molecular weight of their components are not expected to form any inclusion of PLA-L within the PLA-DL bulk material (mainly because of the high mobility of the "small" PLA-L molecules). Only well defined zones of PLA-L and PLA-DL are present, both of them containing small inclusions of the other polymer as explained before. Therefore, no major decrease of the kinetics is observed from B4-70/30 to B4-50/50 as shown in Fig.28.

All the above results are explained by phase separation considerations but again, one must remember from DSC that the determination of the Tg's indicated that all the blends possess a certain degree of partial miscibility. This limited miscibility most probably occurs at the contact zones of the L and DL regions. Therefore, it is suspected that the sharpness of the interfacial regions is directly related to the extent of partial miscibility in the particular blend considered.

Up until now, the results discussed emphasize the effect of the blend composition with respect to the overall kinetics of crystallization. Another approach of the problem is to discuss the influence of the molecular weight of both L and DL components by comparing the results exhibited in the different figures.

The effect of PLA-DL molecular weight is observed when directly comparing the two blends B1 and B4 having the same PLA-DL content but where B1 contains PLA-DL

of $M_v = 60,000$ g/mole and B4 contains PLA-DL of $M_v = 530,000$ g/mole - see Fig.29. The most obvious difference comes from the different degree of miscibility of the respective components of the two blends which increases the diluent effect of PLA-DL and reduces the overall kinetics of all the compositions investigated in the particular case of the B1 blend. Therefore, the influence of the DL content is very important for the B1 blends while it is quite minimal for the B4 blends. Indeed, for the B4 blend, due to the great difference in molecular weight of the two species, the interfacial regions are likely well defined and hence an increase in DL content does not increase the specific contact area between the two species. The kinetics are, therefore, not sensitive to the DL content and the curves in Fig.28 are almost identical. For the B1 blend, any addition of PLA-DL is crucial because it increases the interaction region of the two species and reduces the kinetics, at least until phase separation occurs.

The effect of the PLA-L molecular weight is deduced by comparing B3 and B4 respectively in Fig.30. In both cases, the systems are phase separated but the presence of PLA-L of lower molecular weight for B4, increases the overall kinetics. The main difference obtained for the two sets of curves comes from the difference in the crystallization behavior observed between the two pure PLA-L polymers. This explains the lowering of the right hand part of the curves for B3 compared to B4. The other important difference between these two figures is the wider gap separating the 50/50 curve from the others for the B3 systems. That can be explained by molecular weight considerations. In the B3 blends, the molecular weights of the two species are similar and very high, possibly creating larger boundary regions with more L-DL interactions than in the B4 blend. This last statement is, however, only a speculation which could explain the behavior of the blend but which is not verified by any experimental result.

3.5 Spherulitic Growth Rates

3.5.1 Growth Rates Determination

The growth rates were determined by measurements from the series of optical micrographs obtained during crystallization as explained in Chapter 2. The diameter of spherulites grown from PLA-L ($M_v = 25,000$ g/mole) is reported as a function of time for different T_c 's in Fig.31. For each T_c a straight line is obtained, showing the linearity of the growth rate with time. Moreover, the slope of these lines increases up to a maximum obtained at $T_c = 120^\circ\text{C}$ and then decreases as T_c continues to increase. The accuracy of the method is determined by measuring the evolution of several spherulites in the same picture. The results obtained for five of them grown from PLA-L ($M_v = 65,000$ g/mole) at $T_c = 130^\circ\text{C}$ are shown in Table 8. This example of the relative error calculation due to the method is given by eq [25] (chapter 2) which gives in this particular case:

$$E = \frac{(G_1 - G_4)}{(G_1 + G_2 + G_3 + G_4 + G_5) / 5} \times 100 \quad [26]$$

and

$$E = \frac{0.1}{4.90} \times 100 = 2\text{p.c.} \quad [27]$$

The same process was followed for all the samples studied. The graphs of G versus T_c , which characterize the final results of these calculations are reported in the next section.

3.5.2 Growth Rates Plots

The radial growth rates (G) of spherulites grown from PLA-L having different molecular weights are reported in Fig.32. All the curves display a parabolic shape with a maximum at $T_c = 120^\circ\text{C}$ (different than the half-time maximum: 110°C). For a given T_c , G decreases drastically from $M_v = 25,000$ to $65,000$ g/mole and continues to decrease but more slowly as the molecular weight increases. The viscosity of the polymers through the free energy of transport (term U^* in Eq.[17]) is believed to be mainly responsible for the great changes in G for the low molecular weight materials. The results of the growth rate studies for the blends B1, B2, B3 and B4 are shown in Figs.33-36 respectively which display in all cases the same general behavior.

Figure 33 exhibits some unusual features. As expected from the earlier discussion regarding blend miscibility and T_g shifting, the mixture B1-80/20 displays the lower values of G well below B1-70/30 and even B1-50/50. This unique effect is explained as before by considering that the best miscibility is achieved for the 80/20 composition. The other three compositions show a decrease of G as the content in DL and its diluent effect increases.

The results for the B2 blend are shown in Fig.34 and are quite difficult to interpret. In this case, one deals with incompatible blends and the argument of diluent effect coming from the presence of PLA-DL material does not apply. On the contrary, from the figure, G increases with DL content at low supercoolings. This behavior could result from the inclusions of PLA-DL into the spherulites and from the continuation of growth around these zones. The inclusions of PLA-DL are apparent in Fig.37 where two

spherulites of B2-70/30 and B2-50/50 grown at $T_c = 140^\circ\text{C}$ show a very irregular and diffuse shape with black spots of what the author believes to be amorphous material.

At high supercoolings, the curves come very close together because at these low temperatures, the controlling step is diffusion. The higher viscosity of the blends reduces the diffusion and increases the selectivity of the crystallization which forms spherulites containing no DL domains and displaying a well defined maltese cross between crossed polarizers as seen in Fig.38.

The central part of the curves in Fig.34 shows abnormally high values of G for B2-70/30 and B2-50/50. The measurements were repeated on several samples and no consistent values were obtained for $T_c = 120^\circ\text{C}$ and 130°C . The values reproduced in Fig.32 are the average obtained from measurements made on three different samples. The degree of the variation in the G values at these crystallization temperatures, reached 50% for B2-70/30 and 30% for B2-50/50. This inconsistency in the results, may reflect the non homogeneity of the blends with large zones rich in DL containing more or less inclusions of L, varying in size and number from sample to sample. For these T_c values, the growth rates are a maximum by combination of secondary nucleation and diffusion effects and depending on the composition of the particular sample tested, more or less DL material is included into the spherulites. This is shown by Fig.39 and may help explain the disparity and inconsistency of these specific results.

The blends B3 displays a more rational behavior in Fig.35 with a decrease in G as the PLA-DL content increases. The decrease is, however, greater for lower contents in DL, where the diluent effect of the amorphous component is enhanced. Then, the curves become almost identical as the DL content increases because for a phase separated system, the diluent effect due to the presence of DL material applies only at the interfacial zones where partial miscibility exists. Indeed, only 10% of PLA-DL creates contact zones with PLA-L but as the percentage increases to 20, 30 and 50, the DL do-

mains become larger and the corresponding increase in the specific contact area between L and DL materials becomes less.

The results obtained for the B4 blend are displayed in Fig.36 and show similar values of G for the compositions 90/10, 80/20 and 70/30, supporting again the assumption of phase separation well achieved in these particular blends. On the other hand, B4-50/50 gives slightly lower values of G for all crystallization temperatures, showing some kind of diluent effect due to the high content of PLA-DL. This behavior can be explained by the same argument developed for the $\log(K)$ versus T_c plots. The relatively high value of G for B4-50/50 at $T_c = 140^\circ\text{C}$ corresponds to the formation of "fuzzy" spherulites containing DL material as seen in Fig.40.

3.6 Comparison Between Overall Kinetics And Growth Rates

The comparison of the overall kinetics and growth rates results gives a complement of information to better understand and interpret the behavior of these materials. The major difference observed when comparing the $t_{1/2}$ versus T_c curves to the growth rates is the gap of approximately 15°C between the respective maximum rates curves. In the growth rate case, the kinetics are controlled by the diffusion of chains to the growing crystals, while in the overall kinetics, the contribution of the primary nucleation parameter is added. This parameter, predominant at high supercoolings, shifts the curves to lower T_c values.

The influence of molecular weight on PLA-L crystallization kinetics is very different when comparing Fig.26 and Fig.32. It is much more pronounced for the growth rates, suggesting an increase in nucleation density as molecular weight goes up which

reduces the differences for the overall kinetics. Indeed, the knowledge of G and $t_{1/2}$ allows one to calculate the nucleation density, N , according to the relationship given by Icenogle (39):

$$N = (3 \log 2) / 4\pi G^3 t_{1/2}^3 \quad [28]$$

For the PLA systems, however, N can be calculated only between T_c equal 110°C and 130°C. The limits of N calculation are fixed by the intersection of the T_c ranges utilized for both the determination of G and $t_{1/2}$. The calculation of N at T_c equal 120°C was performed for pure PLA-L. The results are given in Table 9 and confirm that N increases as the molecular weight increases.

This particular case illustrates the importance of both results, growth rates and overall kinetics. Their combination allows one to determine the nucleation density which is of great importance when it comes to achieve a particular set of physical properties. Indeed, the mechanical properties (Young's modulus, ultimate strain) of a material are not only a function of its level of crystallinity but also of the size and specific number of the crystalline superstructures.

When considering the blend B1, the slowest kinetics correspond to B1-70/30 for the $t_{1/2}$ versus T_c curves and B1-80/20 for the G versus T_c curves. This inversion is only explainable if the nucleation density is a function of the composition and reaches a minimum for 70/30 which overcompensates the diffusion problems encountered in the 80/20 blend.

The results obtained for the blends B2 and B3 support the earlier assumption of large phase separated regions of PLA-DL with inclusions of PLA-L for the high compositions in DL. Indeed, an enormous decrease in nucleation density for these compositions is deduced by comparing Figs.28-29 and Figs.34-35 respectively which is responsible alone for the decrease in the overall kinetics. The blend B4 does not exhibit

such a drop in nucleation density because of its more pronounced phase separation as explained before. Therefore, the small increase in $t_{1/2}$ observed for B4-50/50 in Fig.30 is only due to the corresponding decrease observed for G and shown in Fig.36.

4.0 CONCLUSIONS AND FUTURE RECOMMENDATIONS

The polymerization of PLA-L and PLA-DL was achieved by using a reliable polymerization method which allows a quite good control of molecular weight. Moreover, the stereochemistry of the final products was well defined and only a function of the starting monomer. As a future work, one may recommend to study the effect of a hydroxyl initiator (alcohol) on the polymerization. The replacement of the carboxylic group of the lactic acid by a hydroxyl will probably increase the thermal stability of the resulting polymers.

Blends of PLA-L and PLA-DL of different molecular weights and compositions were prepared by casting films from chloroform solutions. A method to test the compatibility of the blends was developed. The approach was to use the physical aging effect on the T_g blends to differentiate the two peaks of an incompatible blend. Even though, it was possible to establish the relative compatibility of the blends, the technique is not sensitive enough to follow the degree of phase separation. More work is necessary in the solid state NMR field to understand and verify the mechanism of amorphous phase separation that has been described in chapter 3. Another interesting area of future studies is the determination of the phase equilibrium ternary diagrams for different molecular weights of PLA-L and PLA-DL. This knowledge would perhaps allow the production of compatible blends of higher molecular weights.

The overall crystallization kinetics of the pure PLA-L and its blends with PLA-DL were studied by means of an Avrami analysis while the growth rates were investigated by studying the growth of individual spherulites. The results obtained show that growth rates are primarily influenced by molecular weight, while half-times of crystallization are more composition dependent. The diluent of PLA-DL is much more effective for the compatible blends. However, it also appears in the half-times of crystallization for the incompatible blends with high contents of PLA-DL. The morphology of the spherulites was studied by optical microscopy. For some high DL content blends, inclusions of PLA-DL into the PLA-L spherulites were detected through the presence of black spots (non crystalline regions). The change in spherulitic morphology with blend composition and crystallization temperature should be investigated by developing an etching technique and using scanning electron microscopy. Moreover, the simultaneous comparison of spherulitic morphology, physical properties (modulus) and hydrolysis under mild conditions (ambient atmosphere) is an interesting area which may permit one to investigate possibilities of new potential applications.

The overall crystallization kinetics mainly reflected by the results of crystallization half-times provide useful information with regard to polymer processing applications. Therefore, given a particular set of conditions relative to the material processed (molecular weight, composition of the blend, temperature and processing time) one may be able to predict the crystallinity content of the final material. On the other hand, the growth rates provide information on the morphology of the samples, (i.e: perfection of the crystalline superstructures grown). The use of both results may, therefore, be useful to optimize a set of processing parameters in order to achieve a particular morphology and the corresponding physical properties.

5.0 Tables And Figures

Table 1: Mark-Houwink coefficients K and a for PLA-L and PLA-DL in chloroform at 30°C. From Schindler and Harper (8).

Polymer	PLA-L	PLA-DL
a	0.73	0.77
K (10 ⁴)	5.45	2.21

Table 2-a: Viscosity average molecular weight of PLA-L and PLA-DL samples.

PLA-L	65,000	290,000	550,000
PLA-DL	60,000	240,000	530,000

Table 2-b: Sample labelling and molecular weight data of the blends used.

Denomination	PLA-L : Mv	PLA-DL : Mv
B1	65,000	60,000
B2	290,000	240,000
B3	550,000	530,000
B4	65,000	530,000

Table 3: Viscosity average molecular weight of PLA-L and PLA-DL
synthesyzed.

Polymer	Mv intended	Mv obtained
PLA-L	20,000	25,000
	60,000	65,000
	250,000	290,000
	500,000	550,000
PLA-DL	60,000	60,000
	250,000	240,000
	500,000	530,000

Table 4: State of compatibility of the blends prepared. Y denotes compatible while N denotes incompatible blends.

Blend Composition	B1	B2	B3	B4
90/10	Y	N	N	N
80/20	Y	N	N	N
70/30	Y	N	N	N
50/50	N	N	N	N

Table 5: Melting points after different annealing times at 200°C.

a) PLA-L(Mv= 550,000), b) blends B1-80/20 and B3-50/50.

Annealing time	2 min	10 min	20 min
Tm°C	178	178	178

Annealing time	2 min	10 min	20 min
B1-80/20	178	178	177
B3-50/50	178	178	177

Table 6: Avrami coefficient n obtained from DSC isothermals for pure PLA-L and blends B1, B2, B3, B4 as a function of T_c .

Sample	$T_c^{\circ}\text{C}$					
	90	100	110	120	130	140
PLA $M_v = 25,000$	2.1	2.4	2.4	2.4	2.6	-
PLA $M_v = 65,000$	2.6	2.5	2.8	3.0	3.0	-
PLA $M_v = 290,000$	2.8	2.7	2.7	3.3	3.2	3.3
PLA $M_v = 550,000$	3.5	2.5	2.7	3.1	3.5	3.5
B1-90/10	2.7	2.3	3.0	3.5	3.6	3.6
B1-80/20	3.1	2.9	3.4	3.4	3.7	-
B1-70/30	-	-	3.5	3.5	3.6	-
B1-50/50	3.1	3.0	3.3	3.0	-	-
B2-90/10	2.5	2.2	2.6	3.2	3.2	3.8
B2-80/20	3.1	3.1	3.3	3.5	3.2	2.9
B2-70/30	2.4	2.6	2.7	3.3	3.2	-
B2-50/50	-	-	2.9	2.8	3.2	-
B3-90/10	2.4	2.3	2.9	3.0	3.1	-
B3-80/20	3.1	2.6	2.8	3.0	3.0	2.9
B3-70/30	3.0	3.0	2.8	3.2	3.3	3.0
B3-50/50	2.9	3.0	2.6	3.0	-	-
B4-90/10	-	2.3	2.7	2.5	3.4	3.5
B4-80/20	2.4	2.4	2.2	3.3	3.1	-
B4-70/30	2.3	2.2	2.3	2.9	2.9	-
B4-50/50	2.8	3.0	3.1	3.5	3.5	-

Table 7: Kinetic constant ($-\log K$) obtained from DSC isothermals for pure PLA-L and blends B1, B2, B3, B4 as a function of T_c .

Sample	$T_c^{\circ}\text{C}$					
	90	100	110	120	130	140
PLA $M_v=25,000$	3.97	1.75	0.88	3.33	7.18	-
PLA $M_v=65,000$	4.95	2.73	1.90	5.93	8.38	-
PLA $M_v=290,000$	7.75	4.16	3.85	7.05	8.04	10.50
PLA $M_v=550,000$	9.06	3.33	3.51	5.73	8.08	10.07
B1-90/10	7.02	3.25	4.26	6.61	10.10	11.01
B1-80/20	8.02	4.32	6.39	7.98	9.21	-
B1-70/30	-	-	7.45	8.89	12.34	-
B1-50/50	9.13	5.92	6.97	7.77	-	-
B2-90/10	7.25	3.99	5.12	5.59	8.81	11.71
B2-80/20	9.42	5.60	6.38	8.49	8.37	8.65
B2-70/30	7.05	5.66	5.59	8.79	8.60	-
B2-50/50	-	-	9.00	7.62	8.20	-
B3-90/10	6.03	3.20	4.46	5.94	7.93	-
B3-80/20	8.79	3.91	4.73	6.26	7.11	7.24
B3-70/30	7.57	5.12	5.22	7.26	8.96	9.27
B3-50/50	7.03	6.50	6.42	7.91	-	-
B4-90/10	-	2.87	2.16	4.65	9.77	12.65
B4-80/20	5.54	2.71	1.56	6.39	7.80	-
B4-70/30	5.24	2.62	2.50	5.54	7.65	-
B4-50/50	6.18	4.42	4.39	7.99	10.51	-

Table 8: PLA-L ($M_v = 65,000$ g/mole) crystallized at 130°C :

a) diameter of 5 different spherulites (mm) versus time (s).

time	D_1	D_2	D_3	D_4	D_5
0	14	12	11.5	13	15
60	20	17.5	17	19.5	21
150	29	27	26	29	30
300	43	41	41	43	44
450	57	55.5	55	57	58.5

b) radial growth rates (microns/min) for the 5 previous spherulites.

G_1	G_2	G_3	G_4	G_5
4.83	4.92	4.93	4.93	4.88

Table 9: Nucleation density, N, of PLA-L crystallized at 120°C.

PLA-L : Mv(g/mole)	N (#/mm ³)
25,000	5,500
65,000	10,300
290,000	11,400
550,000	24,400

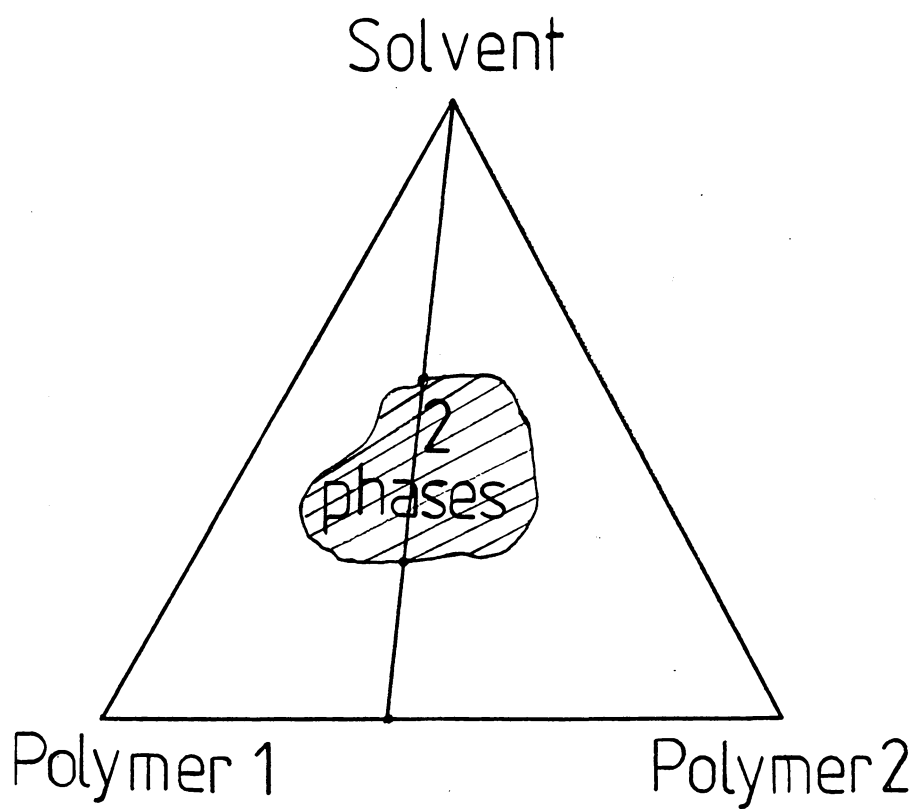


Figure 1. Hypothetical ternary diagram: System containing two polymers in a common solvent and displaying a two-phase region.

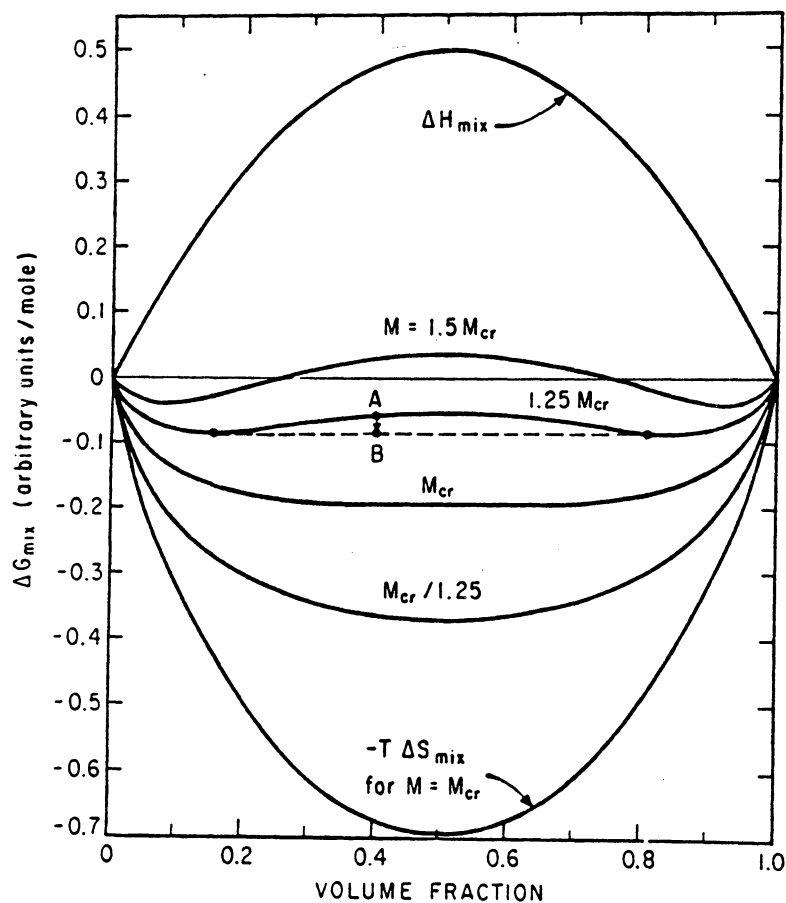


Figure 2. Free energy of mixing and component terms of polymers A and B with the same molecular weight M .: The curves were computed from equation (3). From Paul (17).

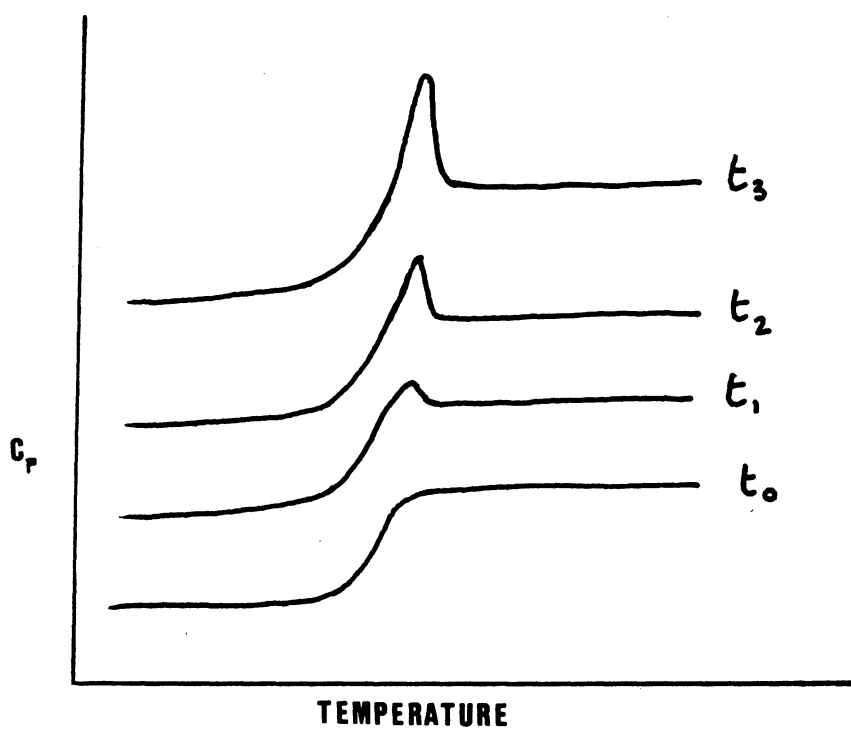


Figure 3. DSC thermograms showing the physical aging effect on the Tg: Influence of the time at a given storage temperature, $t_0 < t_1 < t_2 < t_3$

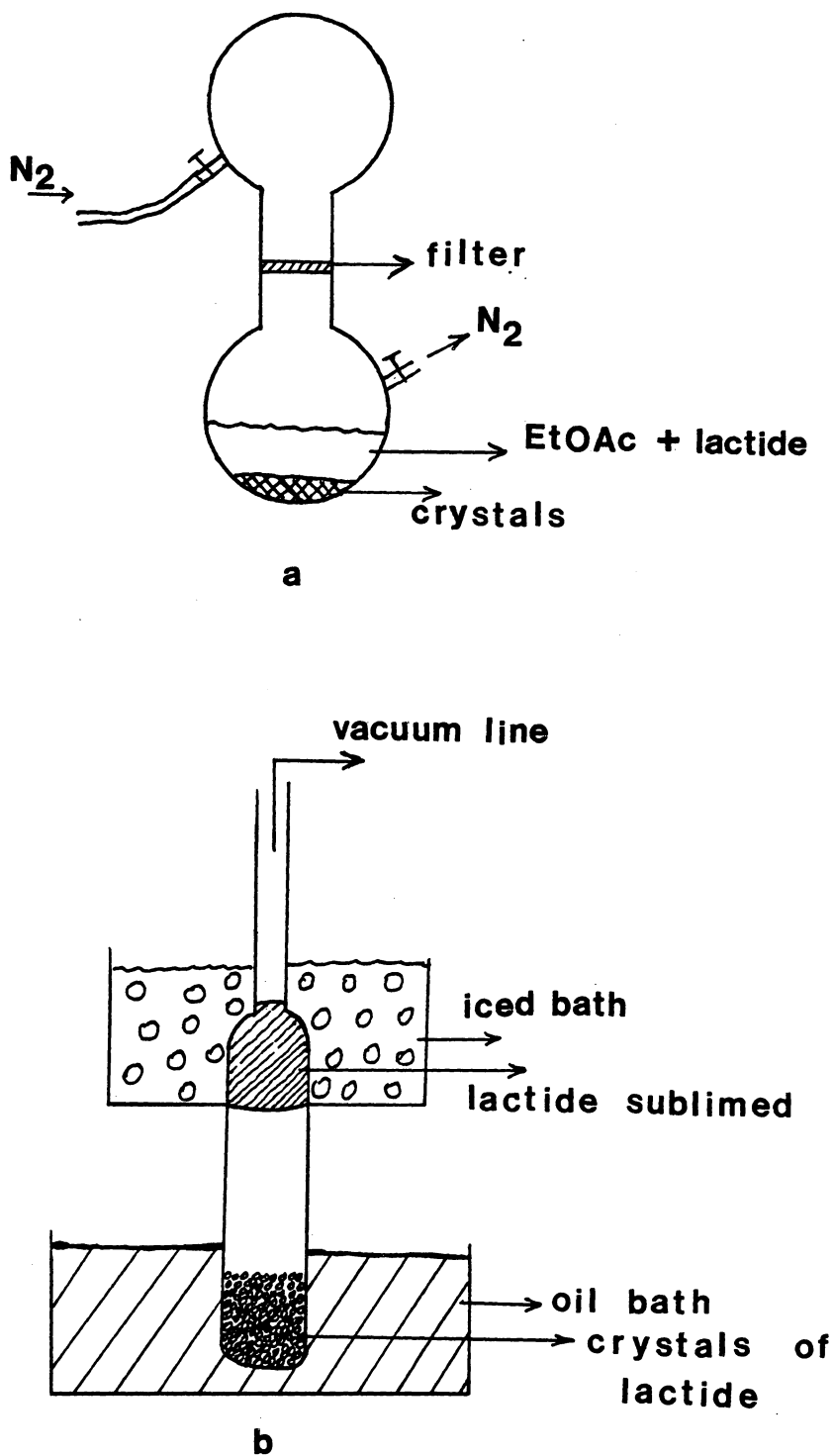


Figure 4. a) Recrystallization vessel; b) Sublimation of the monomer.

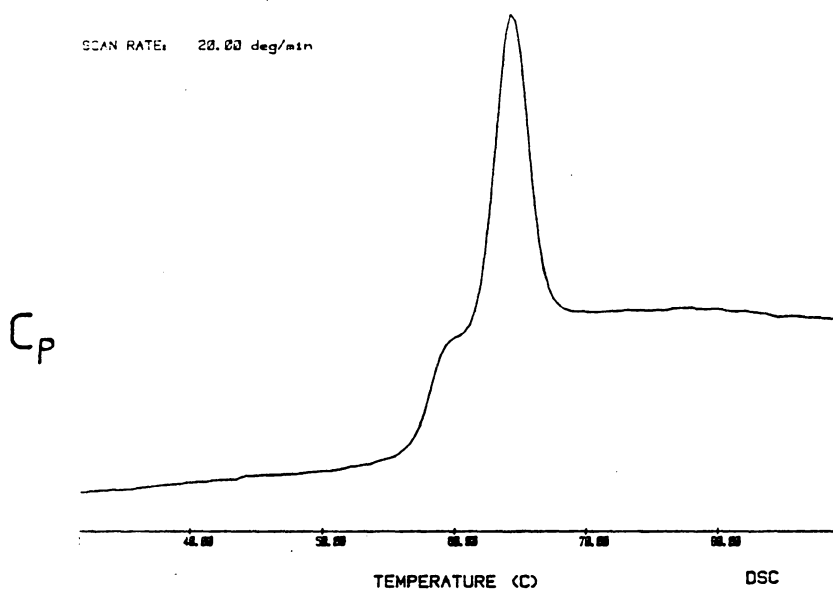
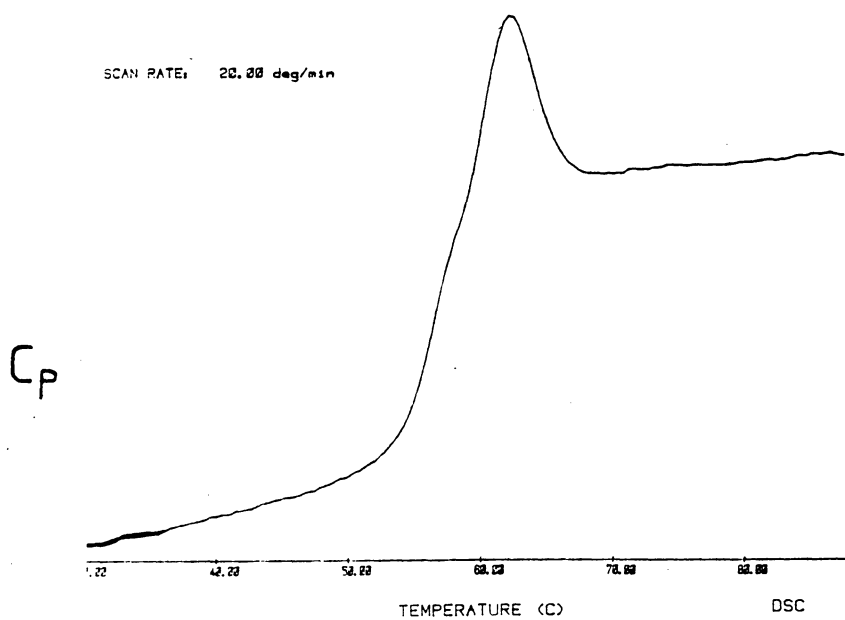


Figure 5. DSC thermogram showing the T_g of a blend containing 80% of PLA-L($M_v = 135,000$) and 20% of PLA-DL($M_v = 135,000$): a) sample aged 2 days; b) sample aged 14 days.

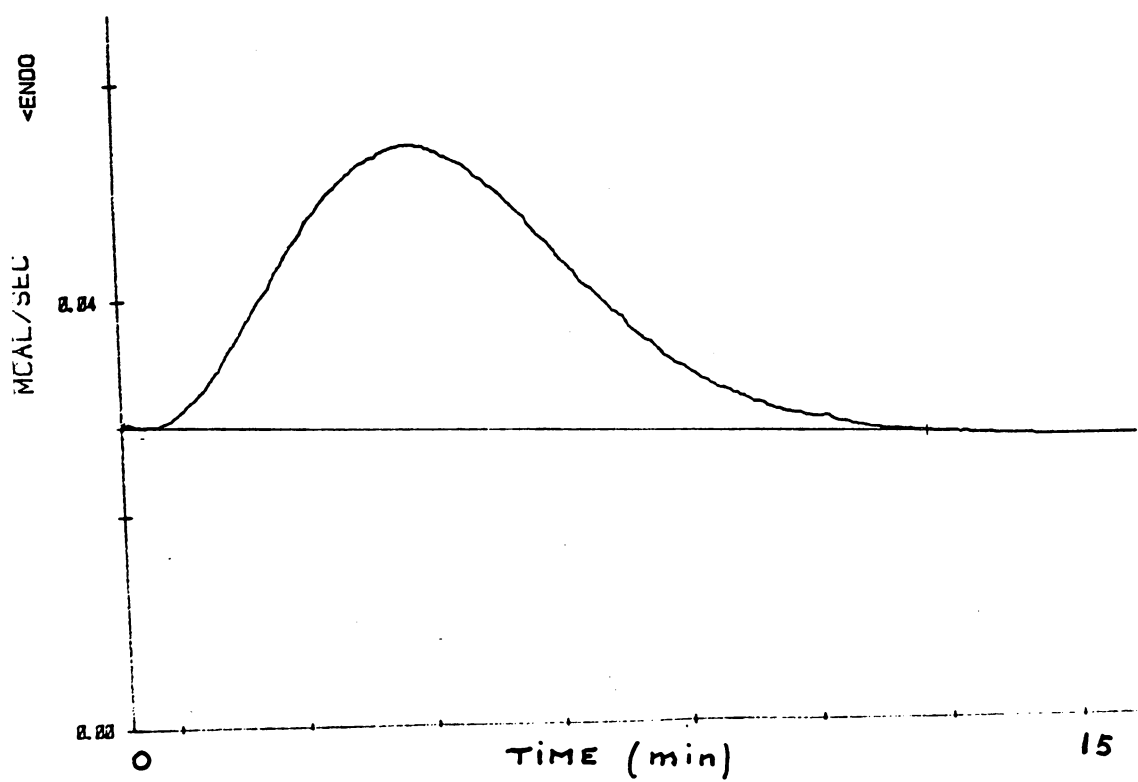


Figure 6. DSC curve showing the isothermal crystallization of the B4-80/20 for a T_c of 120°C

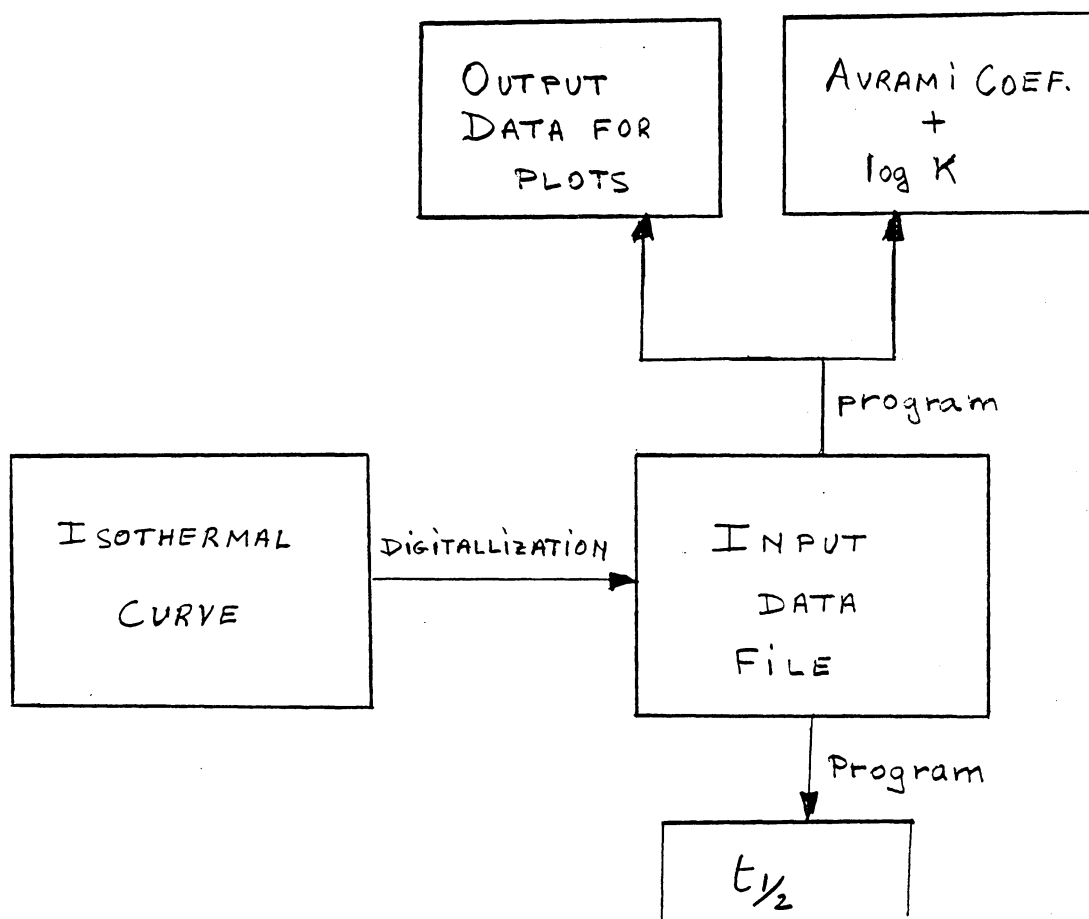


Figure 7. Scheme of the analysis method.

38.8	
0.0000	0.0000
0.2700	0.1200
0.4700	0.2700
0.7600	0.4000
1.0000	0.5100
1.2500	0.6300
1.5200	0.6800
1.7000	0.7300
1.9000	0.7400
2.0900	0.7500
2.3200	0.7200
2.5100	0.6900
2.7300	0.6300
2.9900	0.5300
3.2800	0.4400
3.5500	0.3000
3.8300	0.2000
4.1100	0.1100
4.4400	0.0400
4.7300	0.0000

Figure 8. Digitized data from an isothermal DSC curve used as an input file for the Avrami analysis

TEMPERATURE : 90°C
 AVRAMI = 2.18
 BVRAMI = 2.14
 LOG(K) = -4.95
 FINAL AVRAMI = 2.2

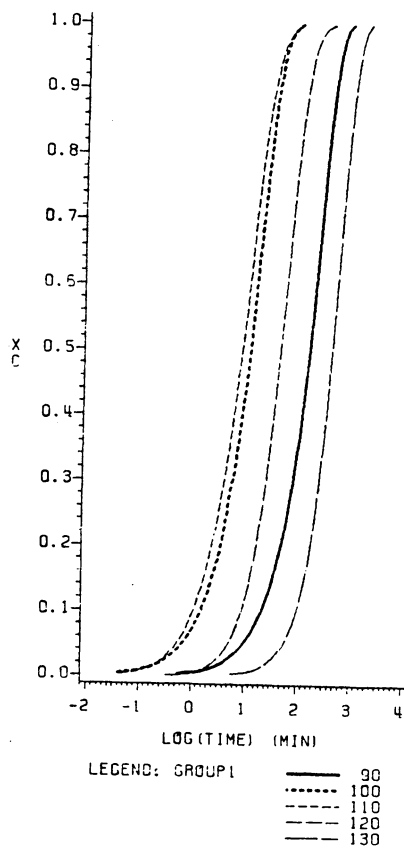
a

log(t)	Xc	log(-log(Xam))
0.065429449	0.008182436	-4.801663400
0.619739711	0.027880888	-3.565710070
1.100325580	0.076950312	-2.524826050
1.374762540	0.132106006	-1.954144480
1.597906110	0.204081178	-1.477277760
1.793473240	0.293406308	-1.057567600
1.905390740	0.357501924	-0.815560162
2.016616820	0.431749880	-0.570586920
2.111927030	0.503245413	-0.357161880
2.216329570	0.588630557	-0.118486702
2.295045850	0.656287313	0.065739334
2.379064560	0.729626000	0.268460333
2.470036510	0.805793583	
2.562605860	0.876834393	
2.641710280	0.927292824	
2.717627530	0.962649047	
2.788186070	0.984569728	
2.865416530	0.997070432	
2.928688050	1.000000000	

b

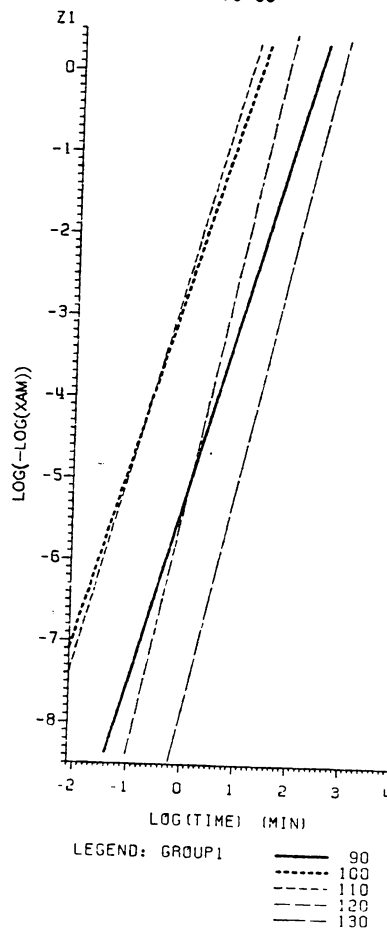
Figure 9. Output data from the Avrami analysis of an isothermal DSC curve: a) results for the Avrami coefficient n and the logarithm of the kinetic constant K ; b) data for the X_c versus $\log(\text{time})$ (min) and $\log(-\log(X_{am}))$ versus $\log(\text{time})$.

BLEND 65K (L)/ 530K (DL)
70-30



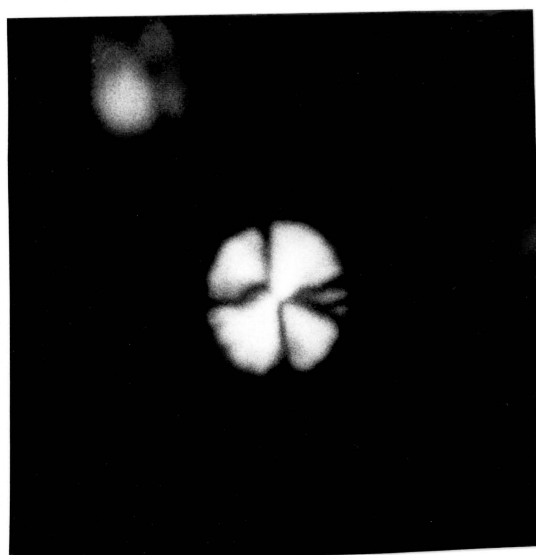
a

BLEND 65K (L)/ 530K (DL)
70-30



b

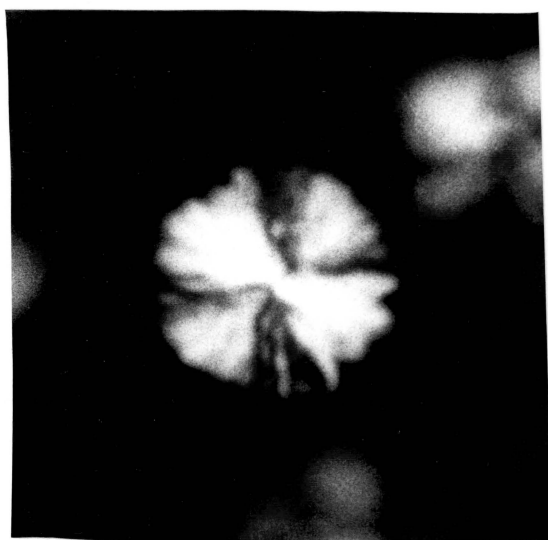
Figure 10. Avrami plots of the blend B4-70/30 for several T_c 's as listed under each plot: a) X_c versus $\log(\text{time})$ (min); b) $\log(-\log X_{am})$ versus $\log(\text{time})$ (min).



a



b

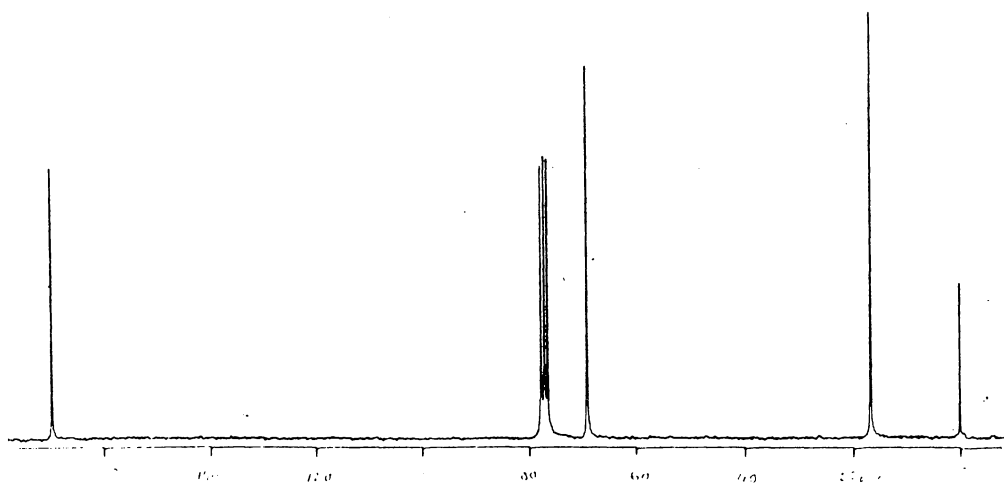


c

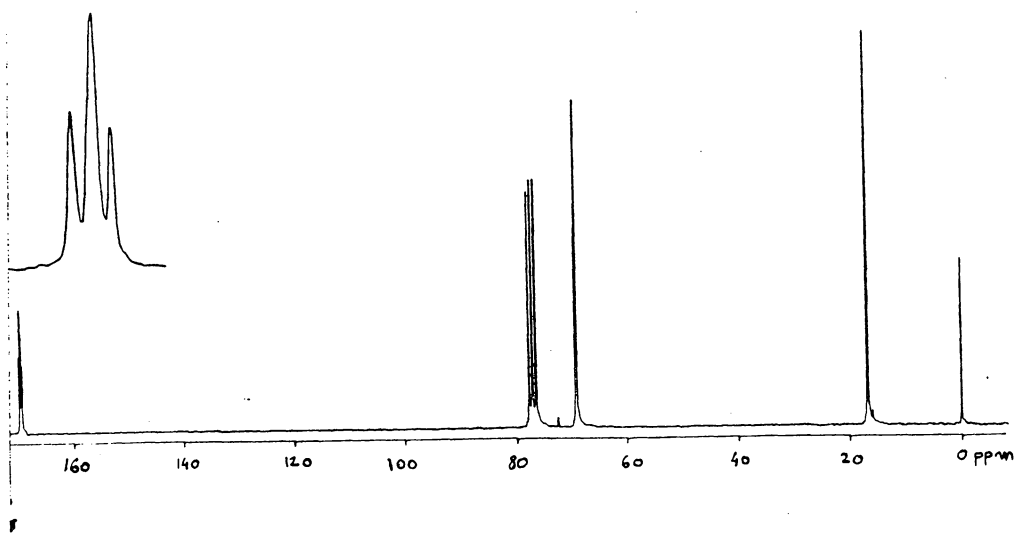


d

Figure 11. Optical micrographs of spherulites from the blend B2-50/50 at $T_c = 120^\circ\text{C}$ and for times: a) $t = 0\text{s}$; b) $t = 60\text{s}$; c) $t = 120\text{s}$; d) $t = 180\text{s}$.

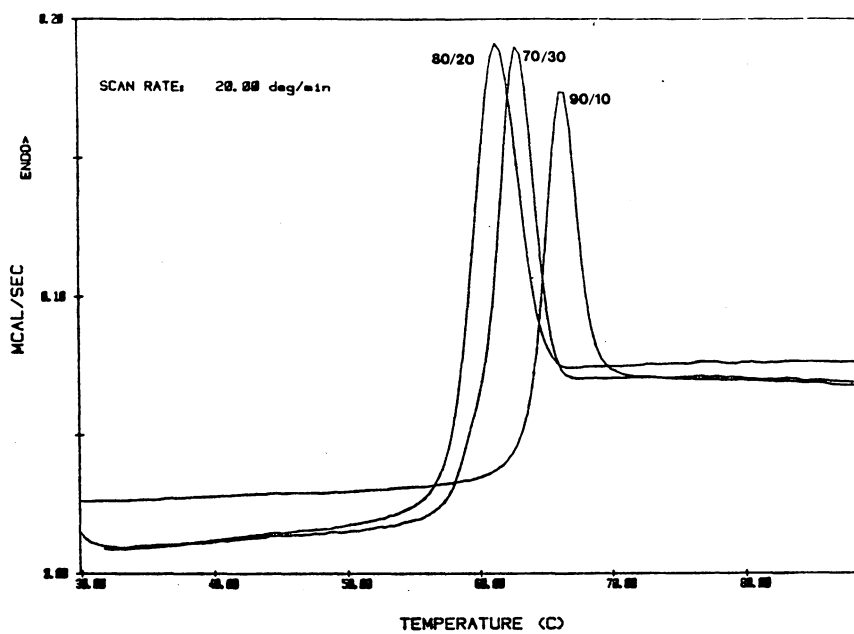


a

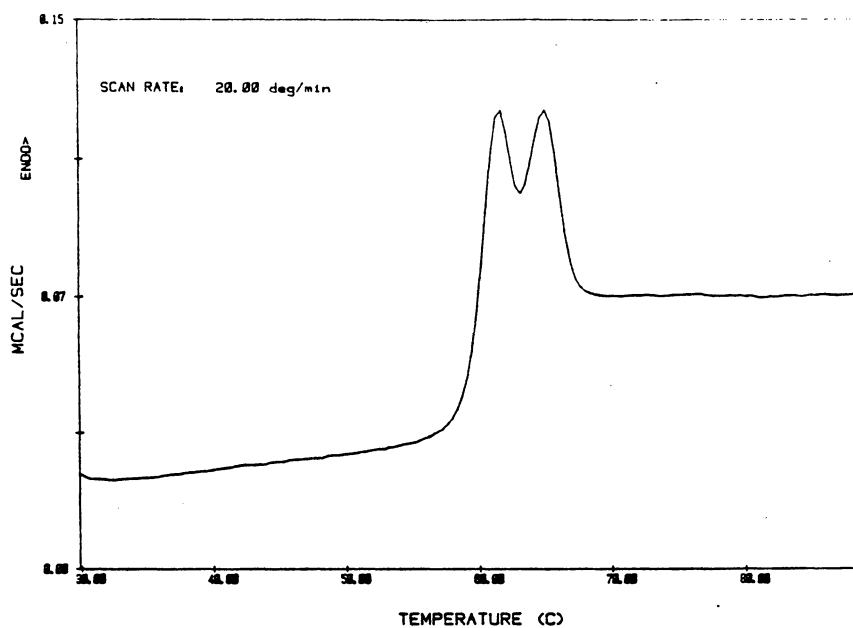


b

Figure 12. ^{13}C -NMR spectra of PLA-L and PLA-DL: a) The carbonyl peak of PLA-L appears as a singlet at 169.2 ppm ; b) The carbonyl peak of PLA-DL appears as a triplet at 169.1, 168.8 and 168.5 ppm.



a



b

Figure 13. DSC thermograms of aged B1 blends: a) B1-90/10, B1-80/20 and B1-70/30 show a single Tg. b) B1-50/50 shows two distinct Tg's.

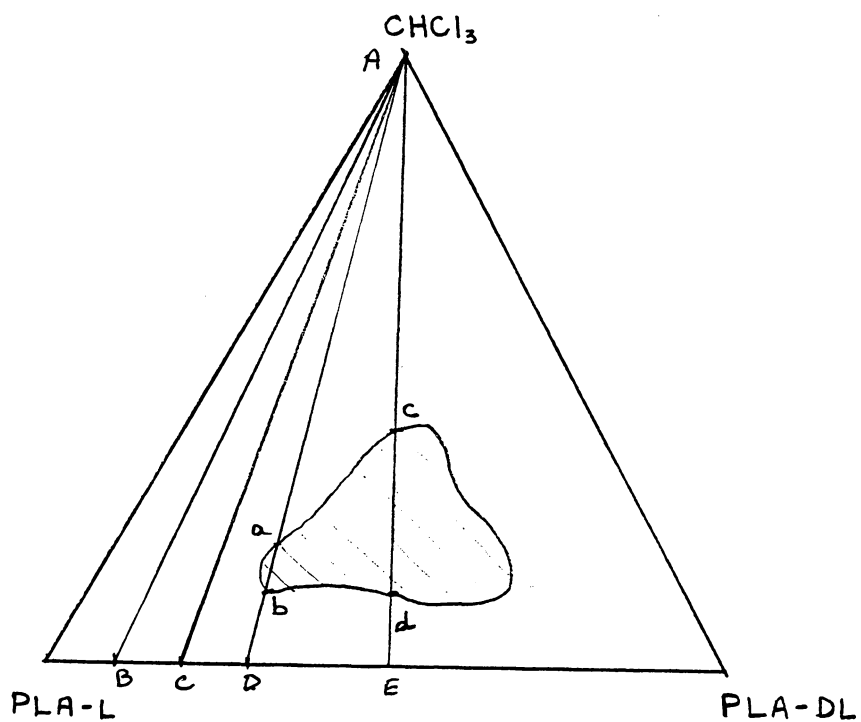


Figure 14. Hypothetical ternary phase diagram for the blends B1: The diagram shows a two phase region. The lines AB, AC, AD and AE represent the paths followed by the concentrations of solutions of B1-90/10, B1-80/20, B1-70/30 and B1-50/50 respectively as the solvent evaporates.

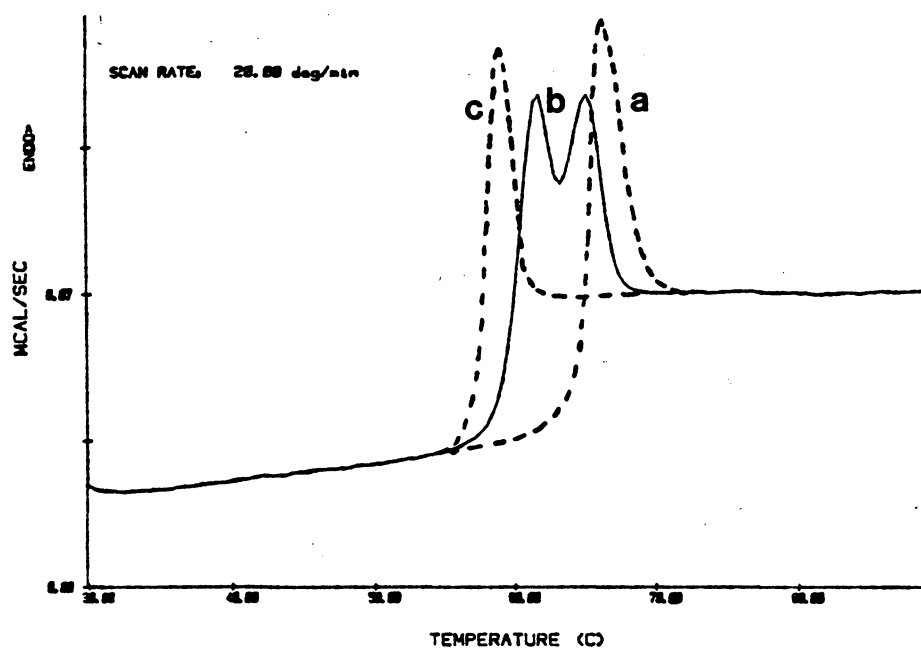
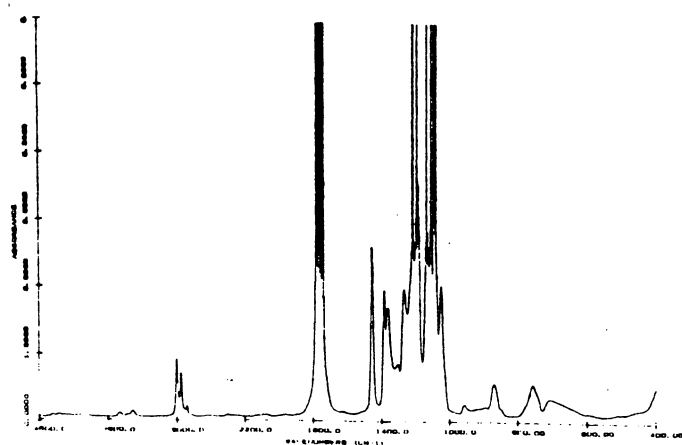
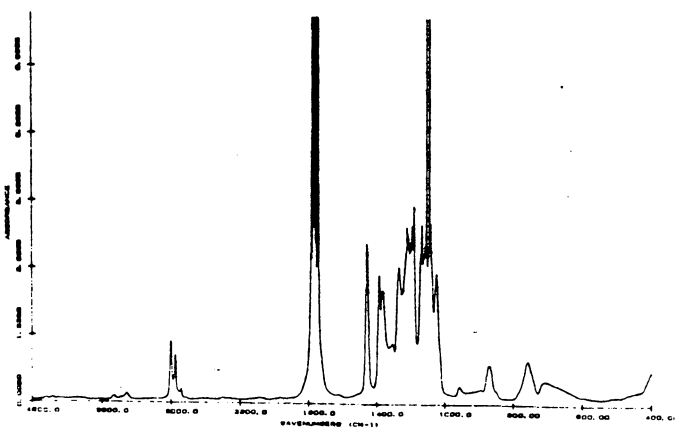


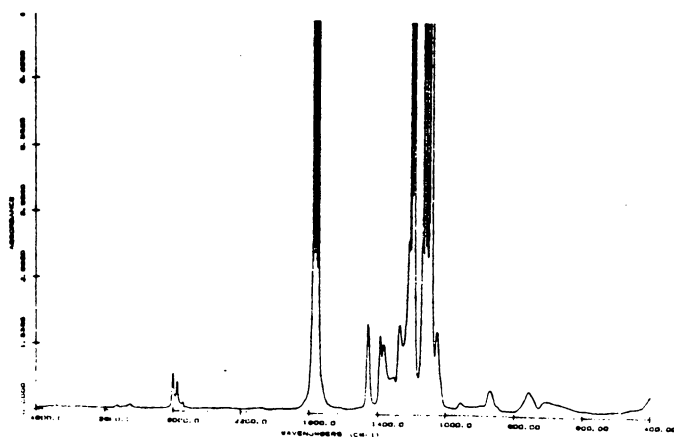
Figure 15. DSC thermogram comparing the Tg's of pure PLA-DL ($M_v=60,000$), B1-50/50 and pure PLA-L ($M_v=65,000$): a) PLA-L b) B1-50/50 c) PLA-DL.



a



b



c

Figure 16. Fourier Transform Infrared spectra of the B1 blends: a) B1-90/10 b) B1-80/20 c) B1-70/30.

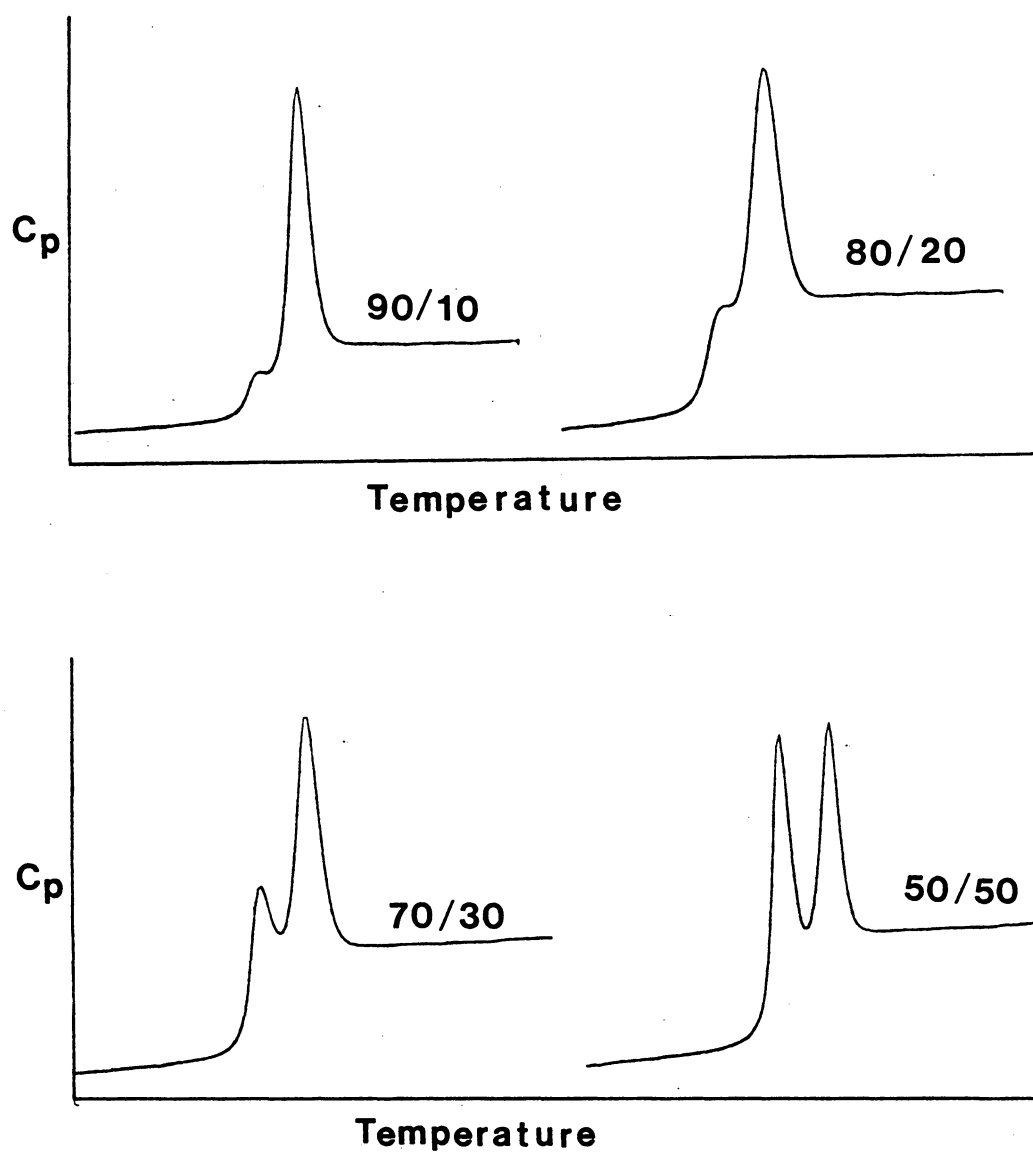


Figure 17. DSC thermograms of B2 samples aged 14 days: All the compositions are incompatible and exhibit a double T_g.

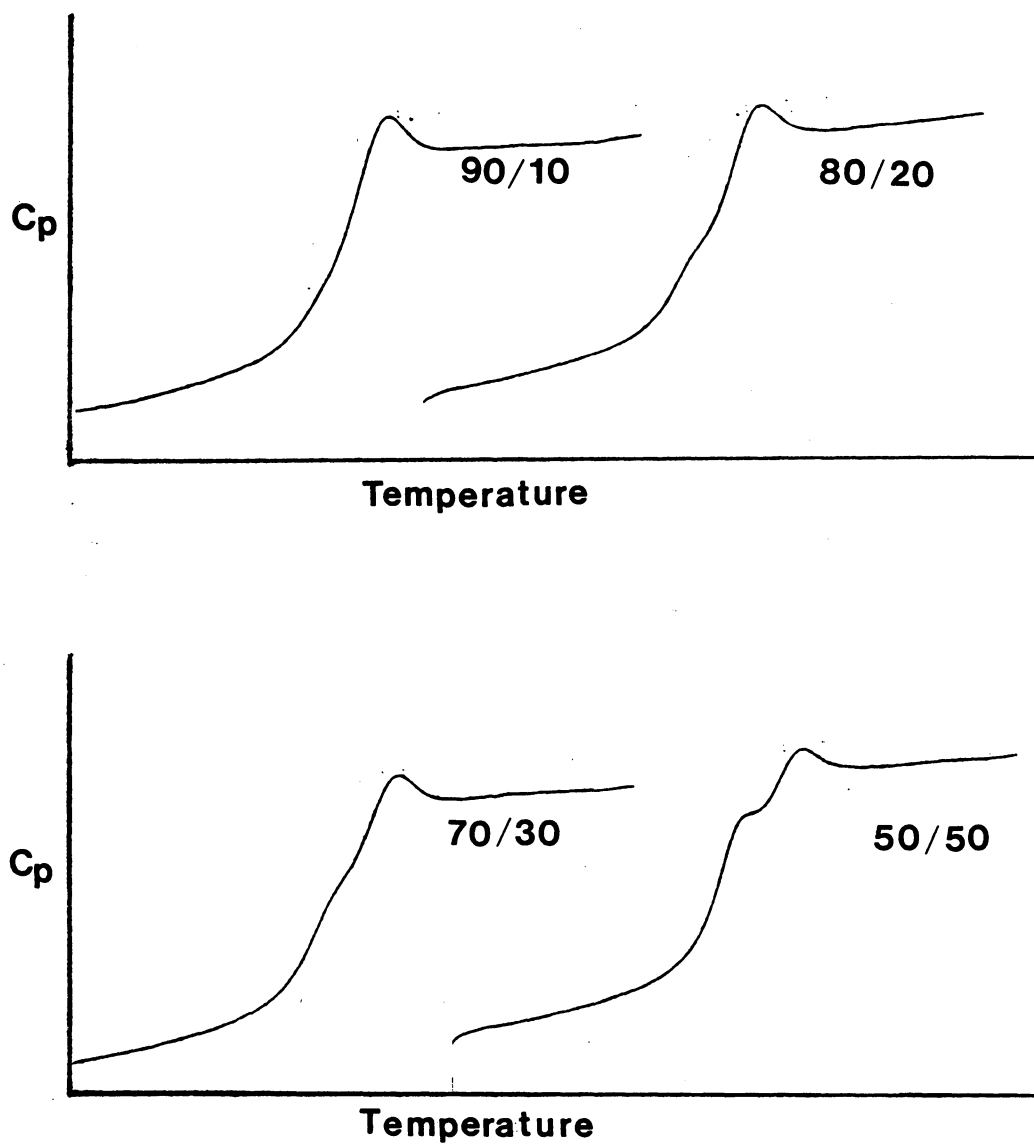


Figure 18. DSC thermograms of B2 fresh samples: The incompatibility of the blends is not detectable in this case because the Tg's are too close to be separated. B2-90/10 shows a single Tg, B2-80/20 and B2-70/30 display a small shoulder on the Tg transition, B2-50/50 is the only one displaying two Tg's.

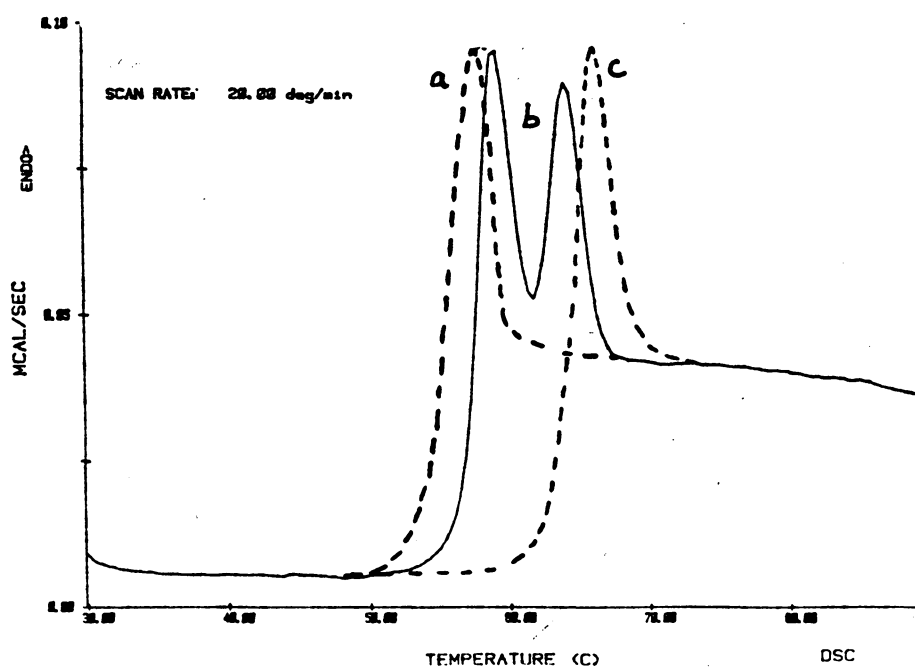


Figure 19. DSC thermogram comparing the Tg's of pure PLA-DL ($M_v = 65,000$), B4-50/50 and pure PLA-L ($M_v = 530,000$): a) PLA-DL, b) B4-50/50, c) PLA-L.

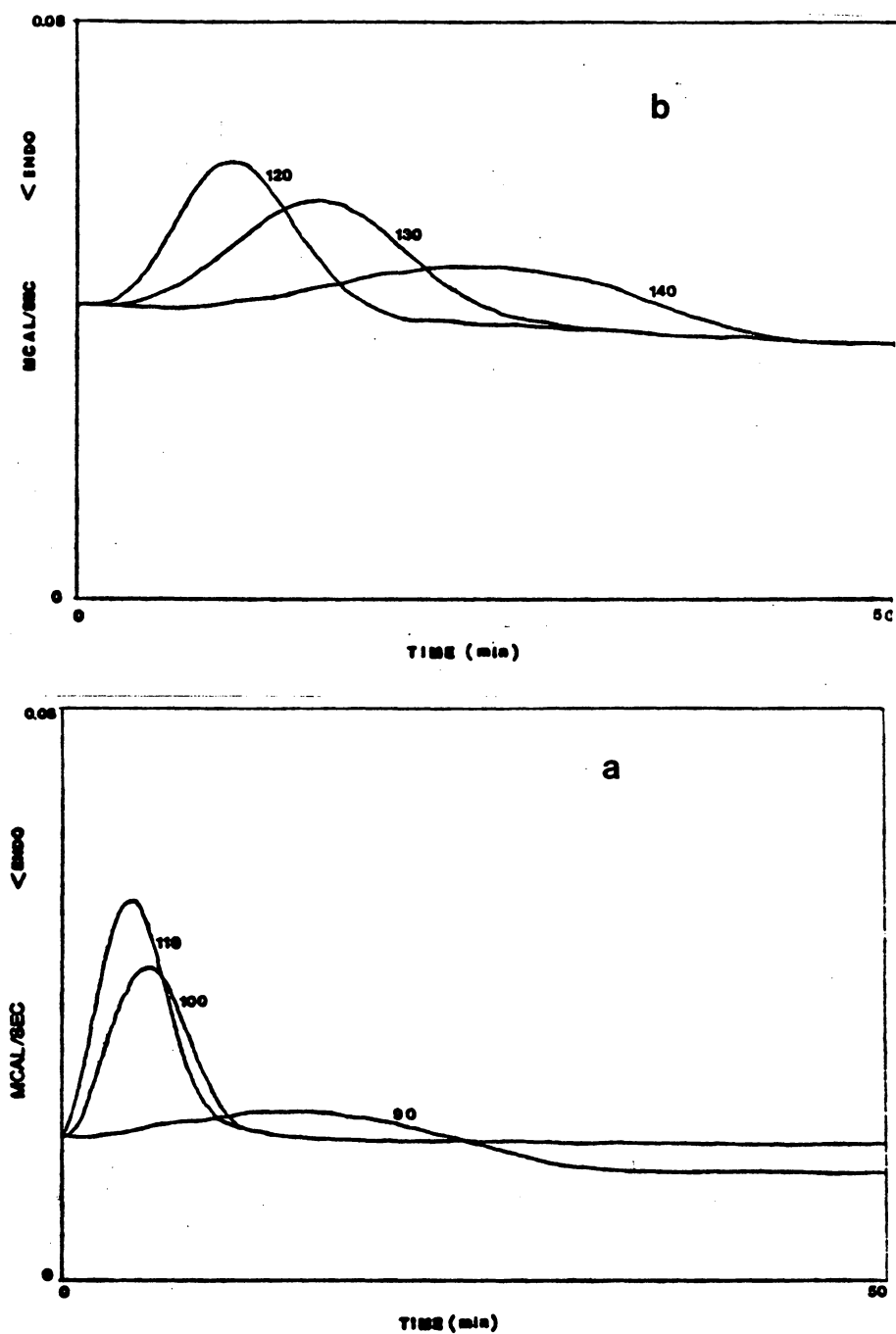


Figure 20. DSC crystallization isotherms of PLA-L($M_v=290,000$) at different crystallization temperatures: a) $T_c=90^\circ\text{C}$; $T_c=100^\circ\text{C}$. b) $T_c=110^\circ\text{C}$; $T_c=120^\circ\text{C}$; $T_c=130^\circ\text{C}$; $T_c=140^\circ\text{C}$

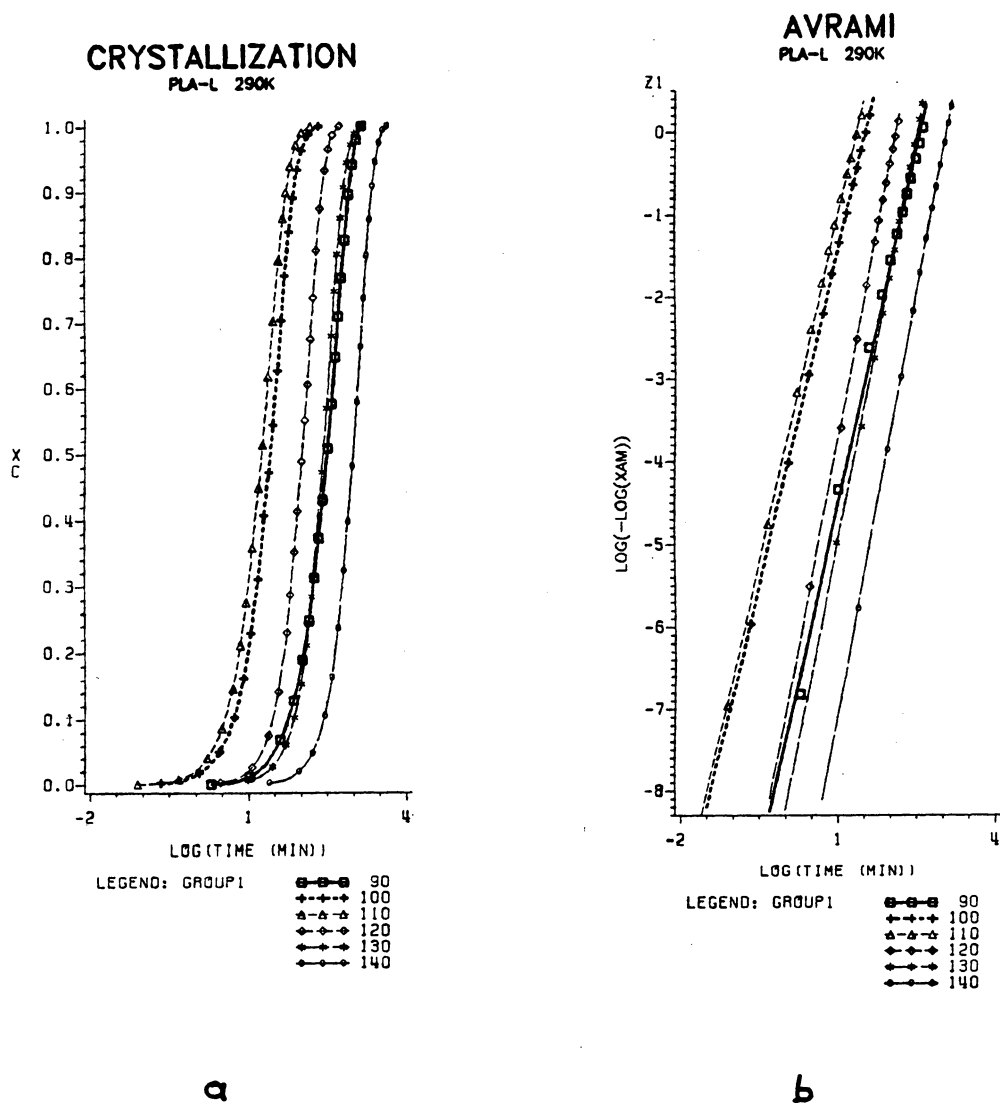
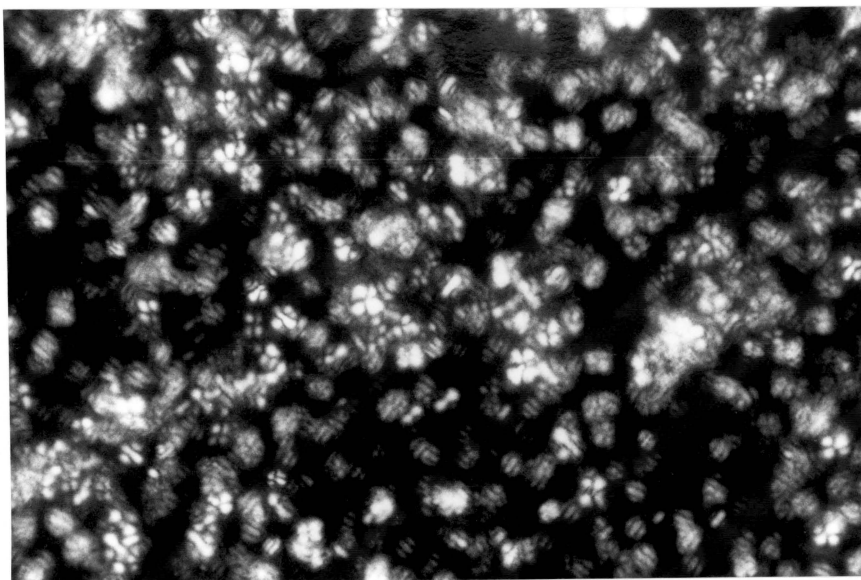
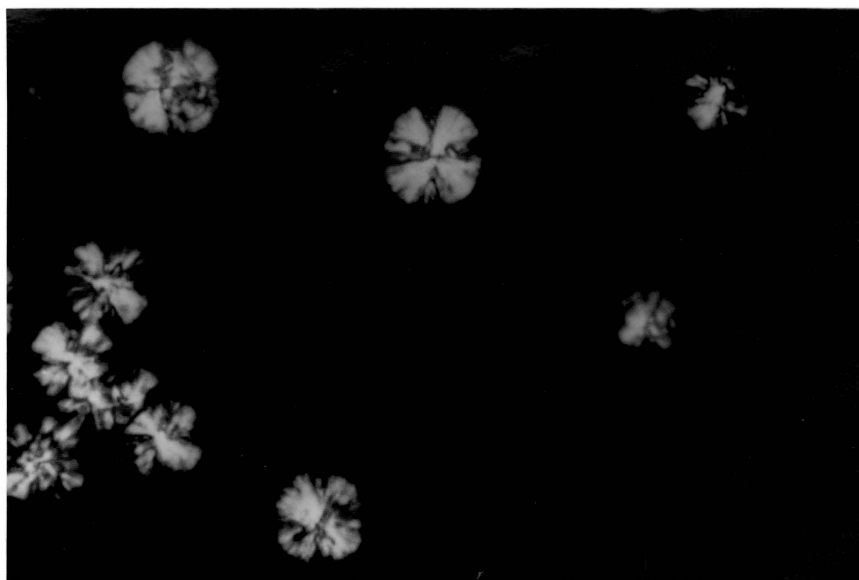


Figure 21. Avrami plots of PLA-L($M_v = 290,000$) at different crystallization temperatures: a) X_c versus $\log(\text{time})$. b) $\log(-\log(X_{am}))$ versus $\log(\text{time})$



a



b

Figure 22. Optical micrographs of PLA-L ($M_v=65,000$): a) At $T_c = 110^\circ\text{C}$, the spherulites display a uniform size; b) at $T_c = 140^\circ\text{C}$, the spherulites are of different sizes.

BLEND 65K (L)/ 530K (DL)

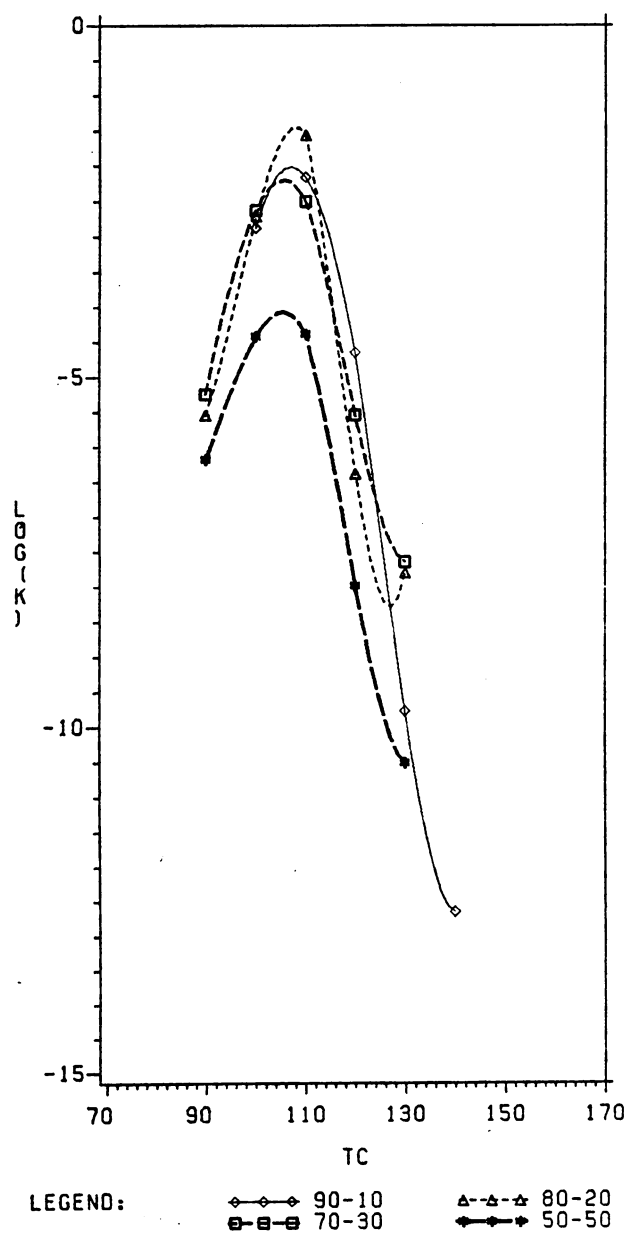


Figure 23. Kinetic constant $\log(K)$ versus T_c for B4 blends.

OVERALL CRYSTALLIZATION

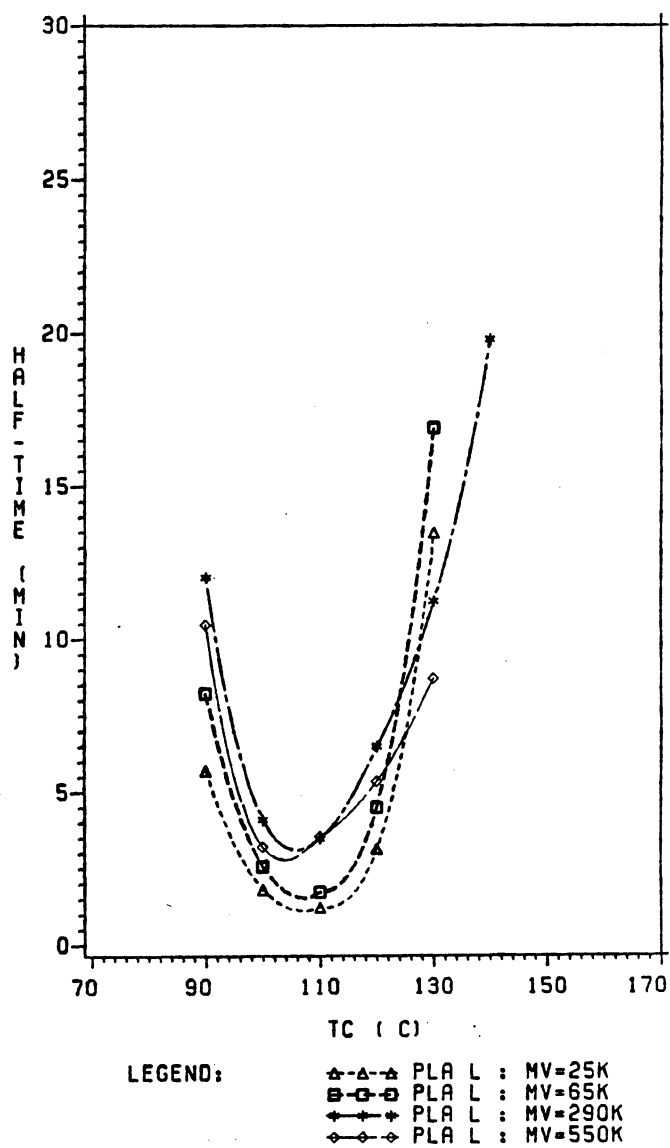


Figure 24. Crystallization half-times versus T_c of PLA-L.

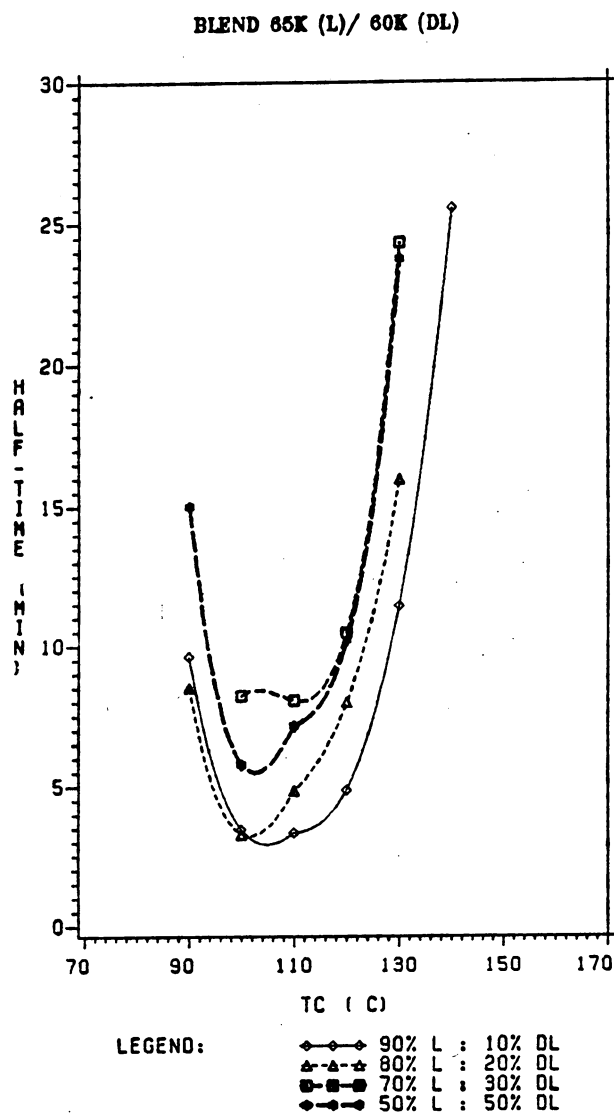


Figure 25. Crystallization half-times versus Tc of the B1 blends.

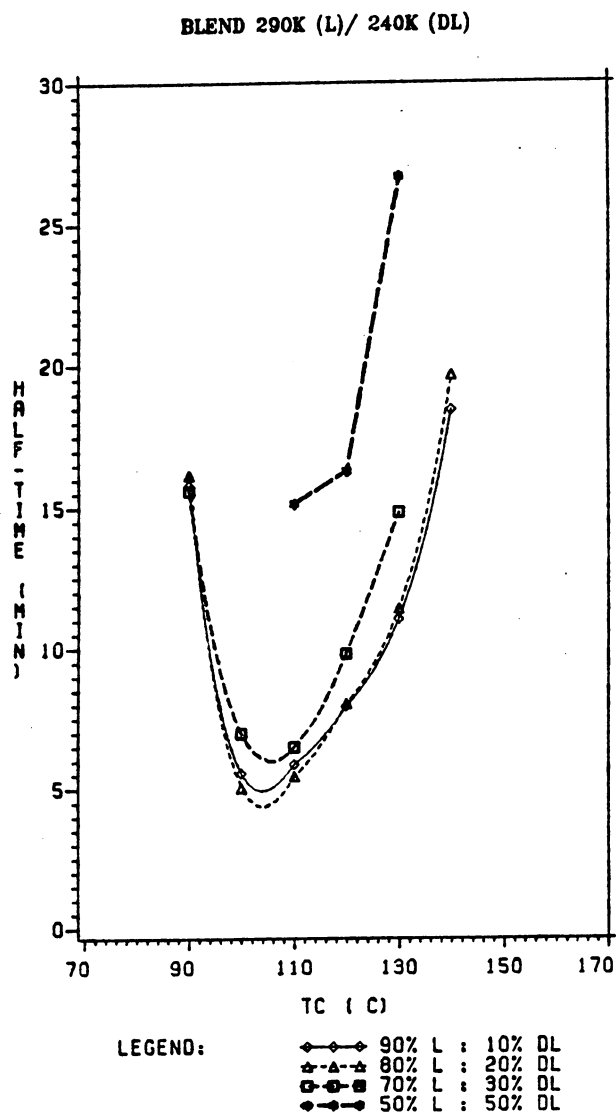


Figure 26. Crystallization half-times versus T_c of the B2 blends.

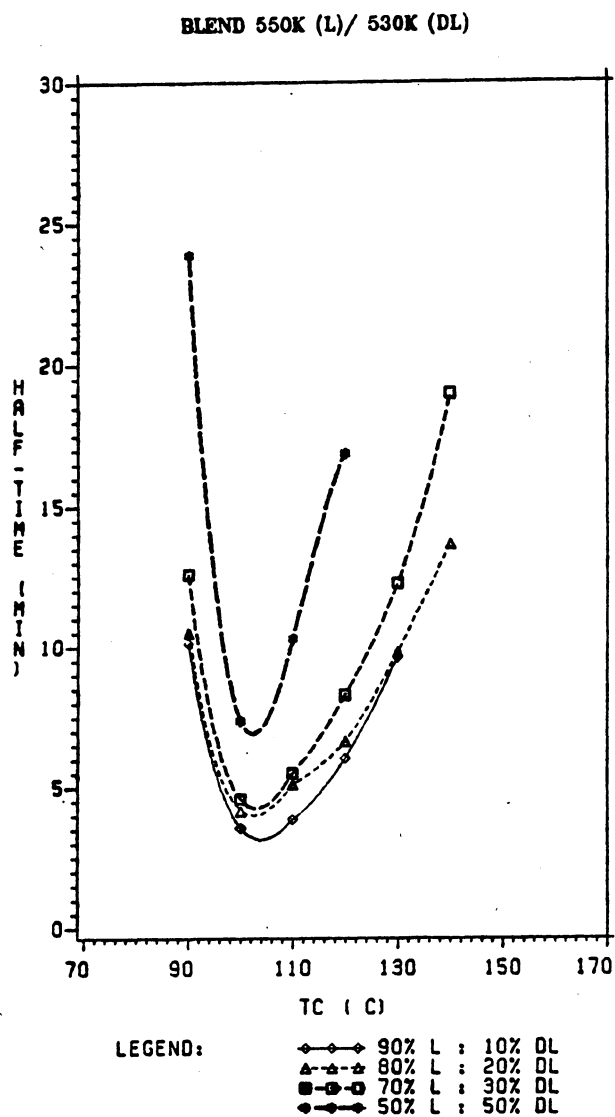


Figure 27. Crystallization half-times versus T_c of the B3 blends.

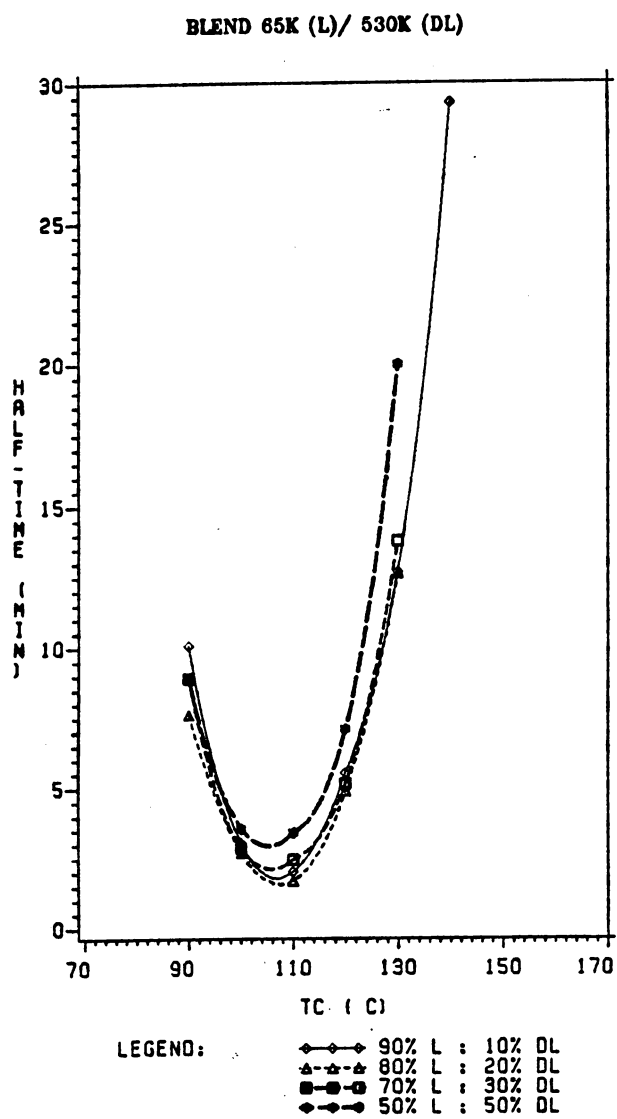


Figure 28. Crystallization half-times versus Tc of the B4 blends.

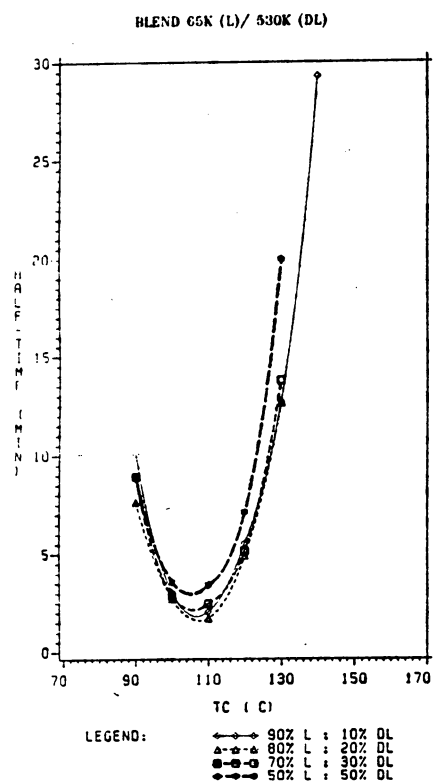
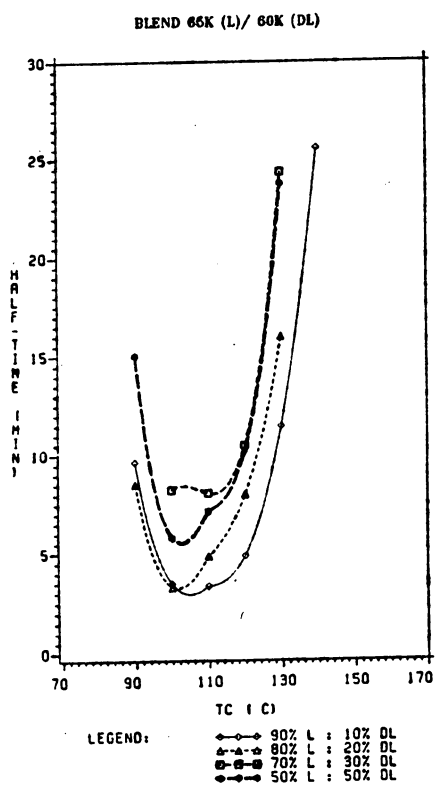


Figure 29. Effect of the PLA-DL molecular weight on the crystallization half-times: a) blends B1, b) blends B4.

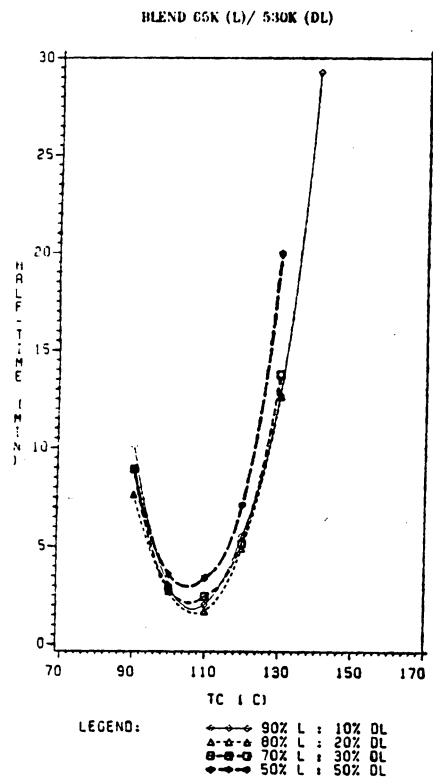
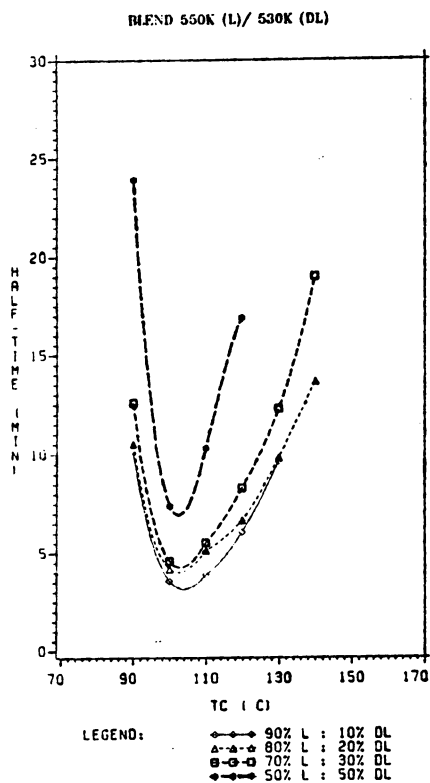


Figure 30. Effect of the PLA-L molecular weight on the crystallization half-times: a) blends B3, b) blends B4.

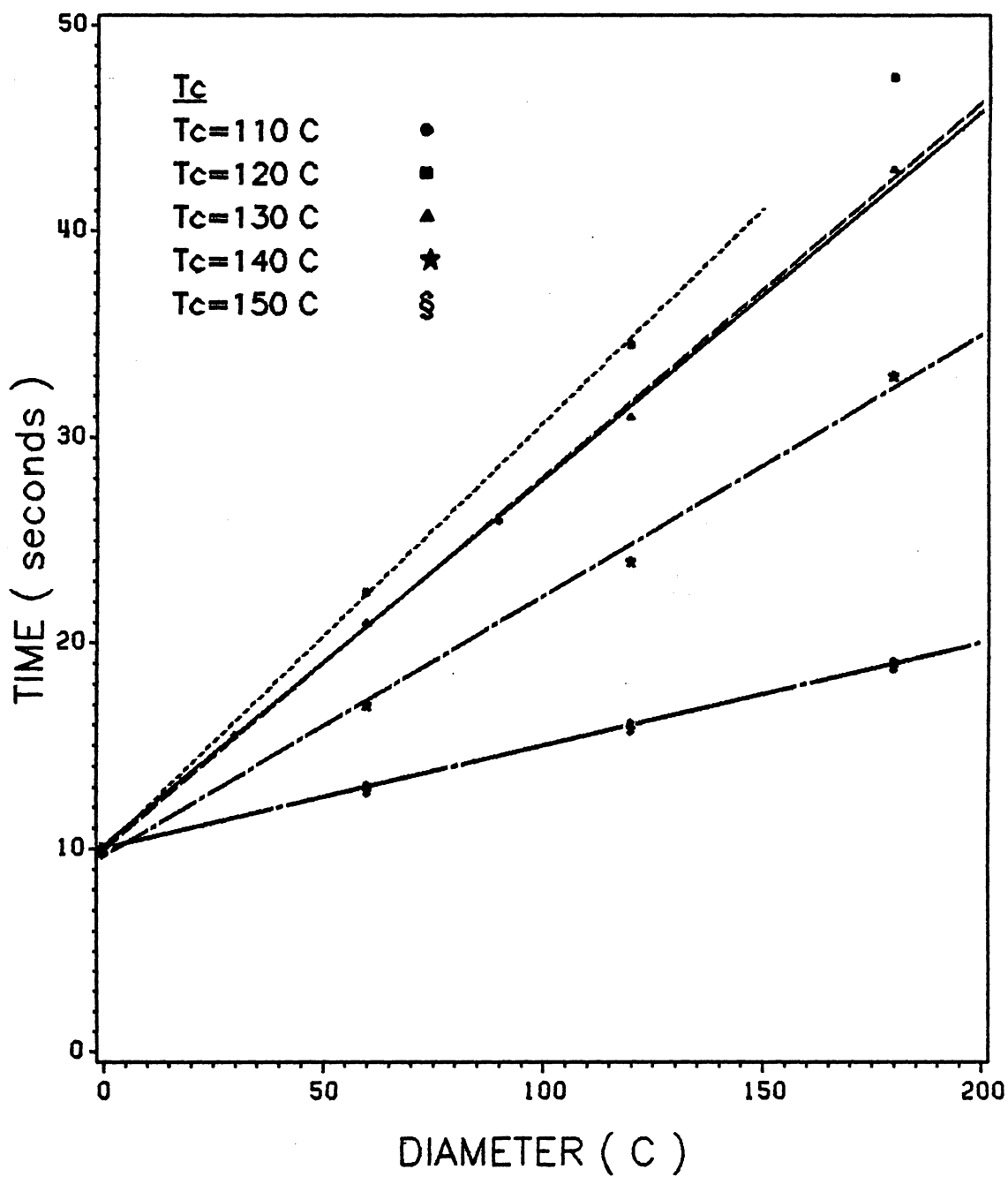


Figure 31. Spherulite diameter against time of PLA-L ($M_v = 25,000$) at different T_c s

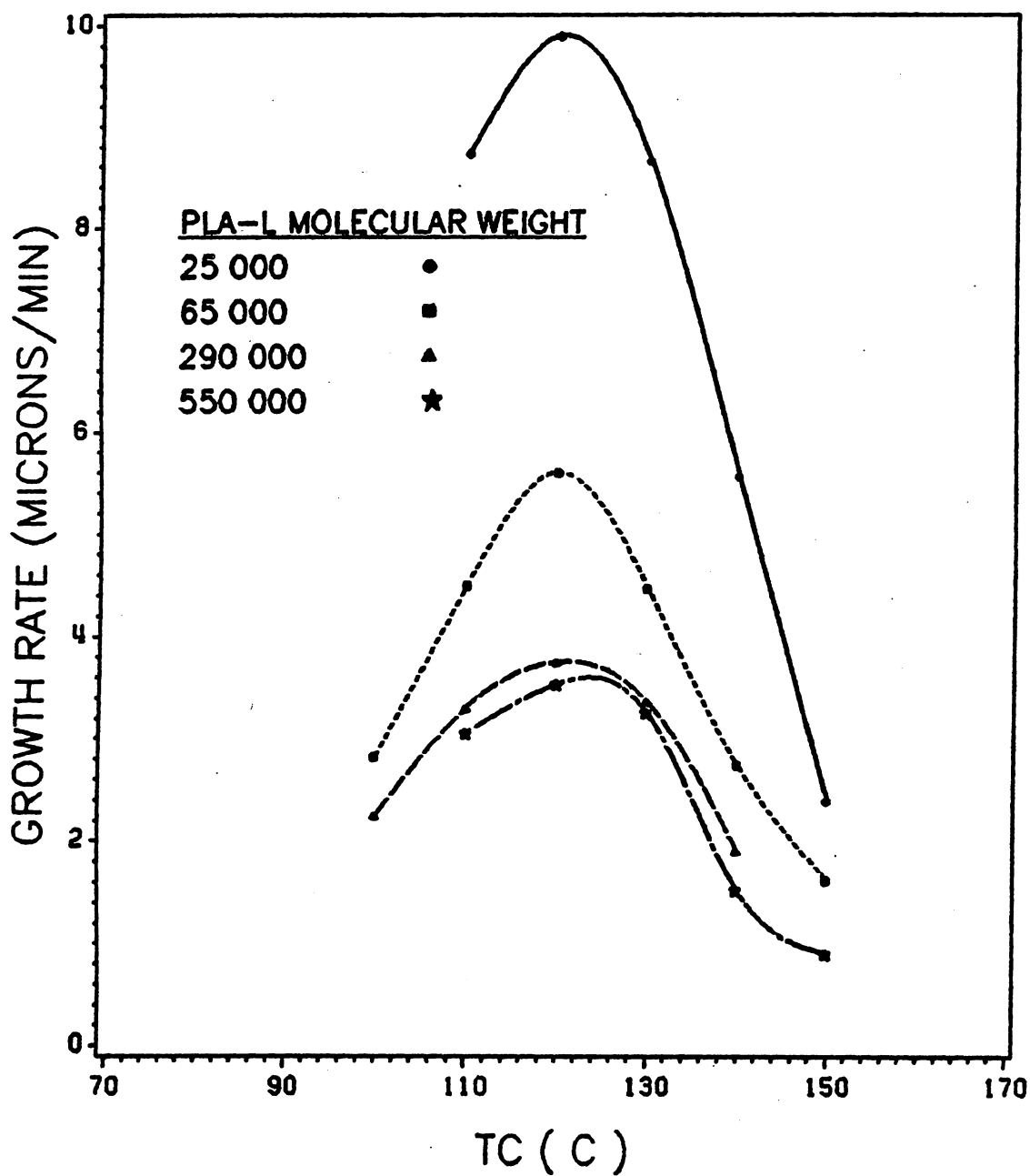


Figure 32. Radial spherulitic growth rates against crystallization temperature of PLA-L

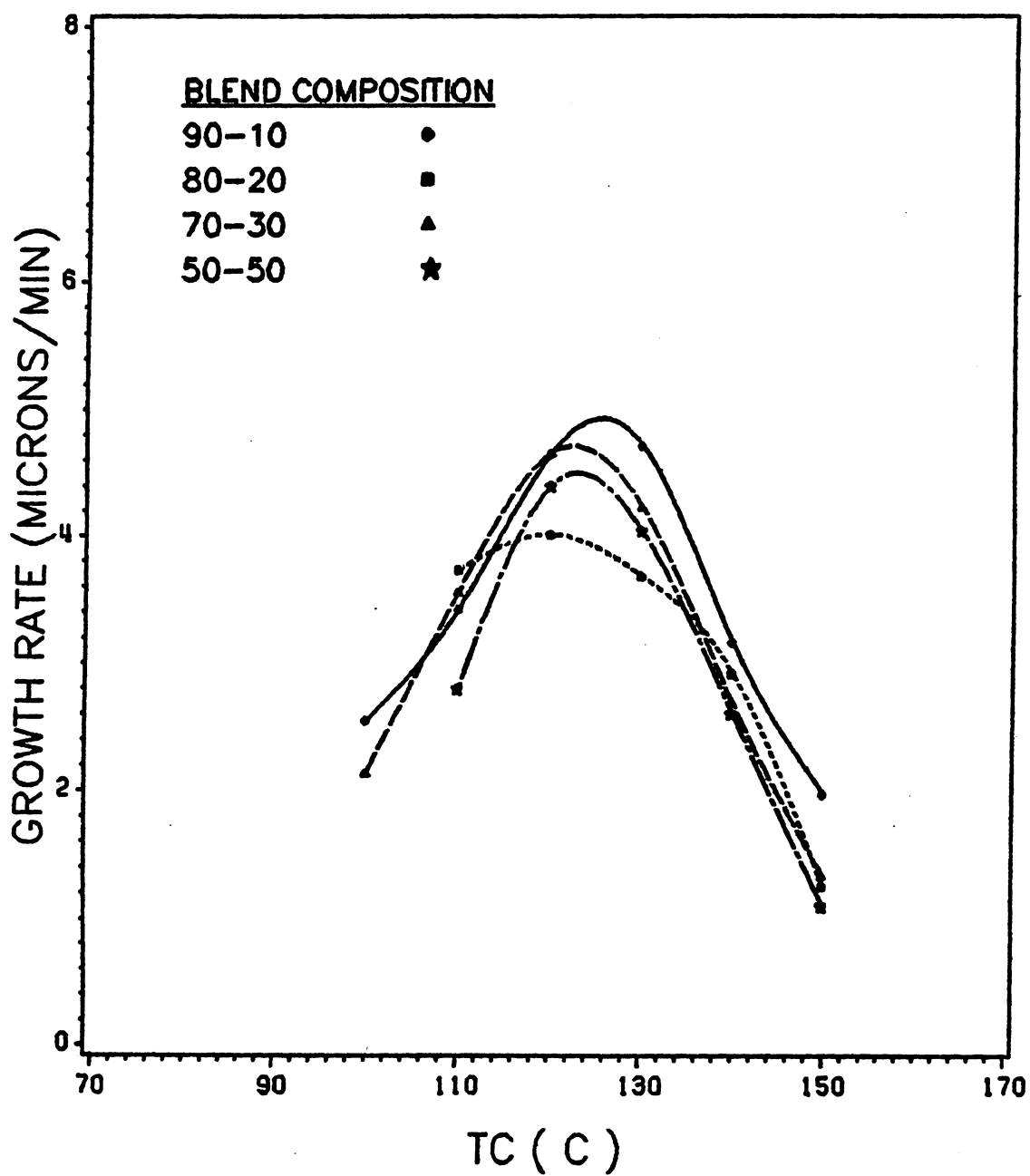


Figure 33. Radial spherulitic growth rates against crystallization temperature of the B1 blends

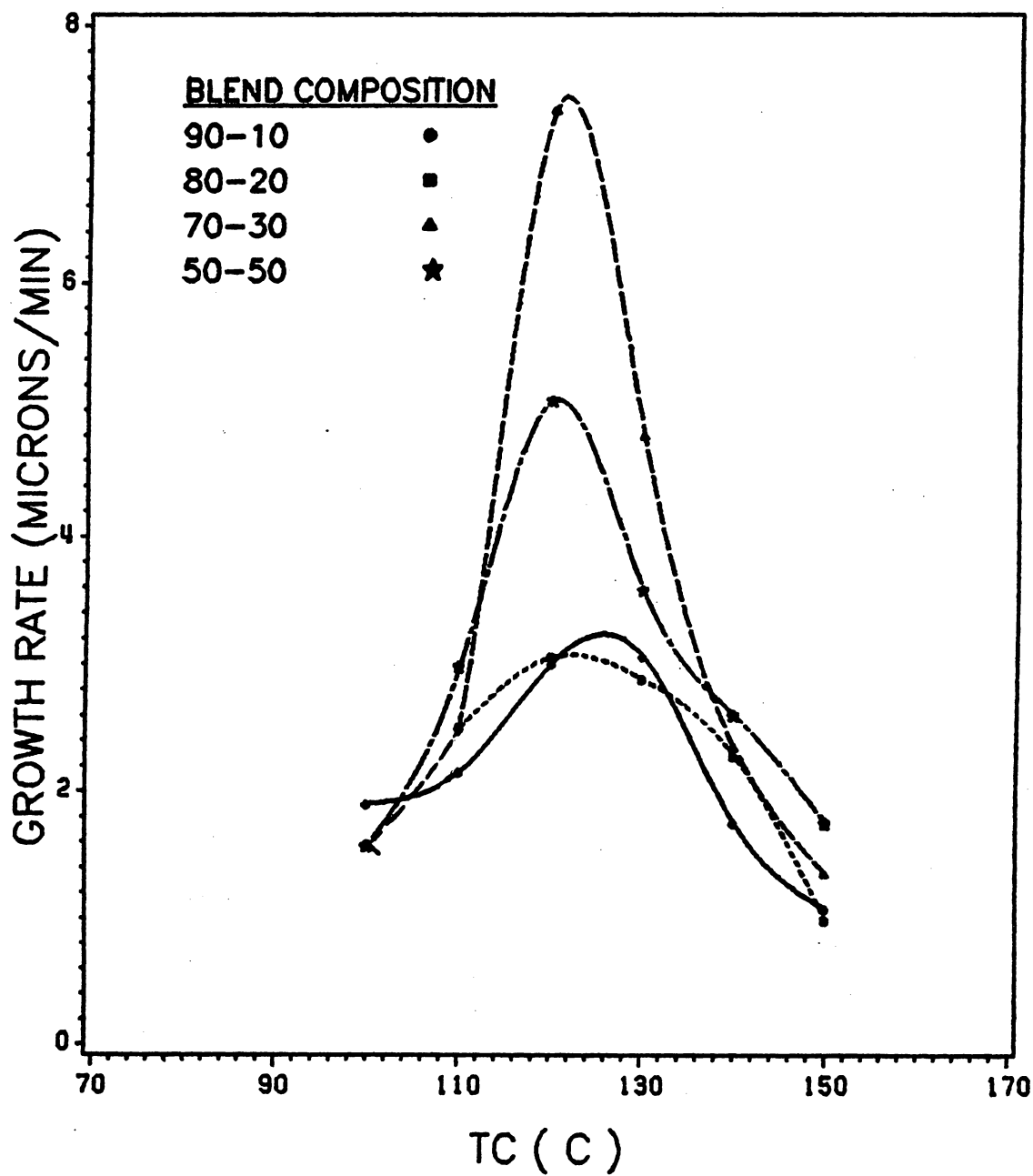


Figure 34. Radial spherulitic growth rates against crystallization temperature of the B2 blends

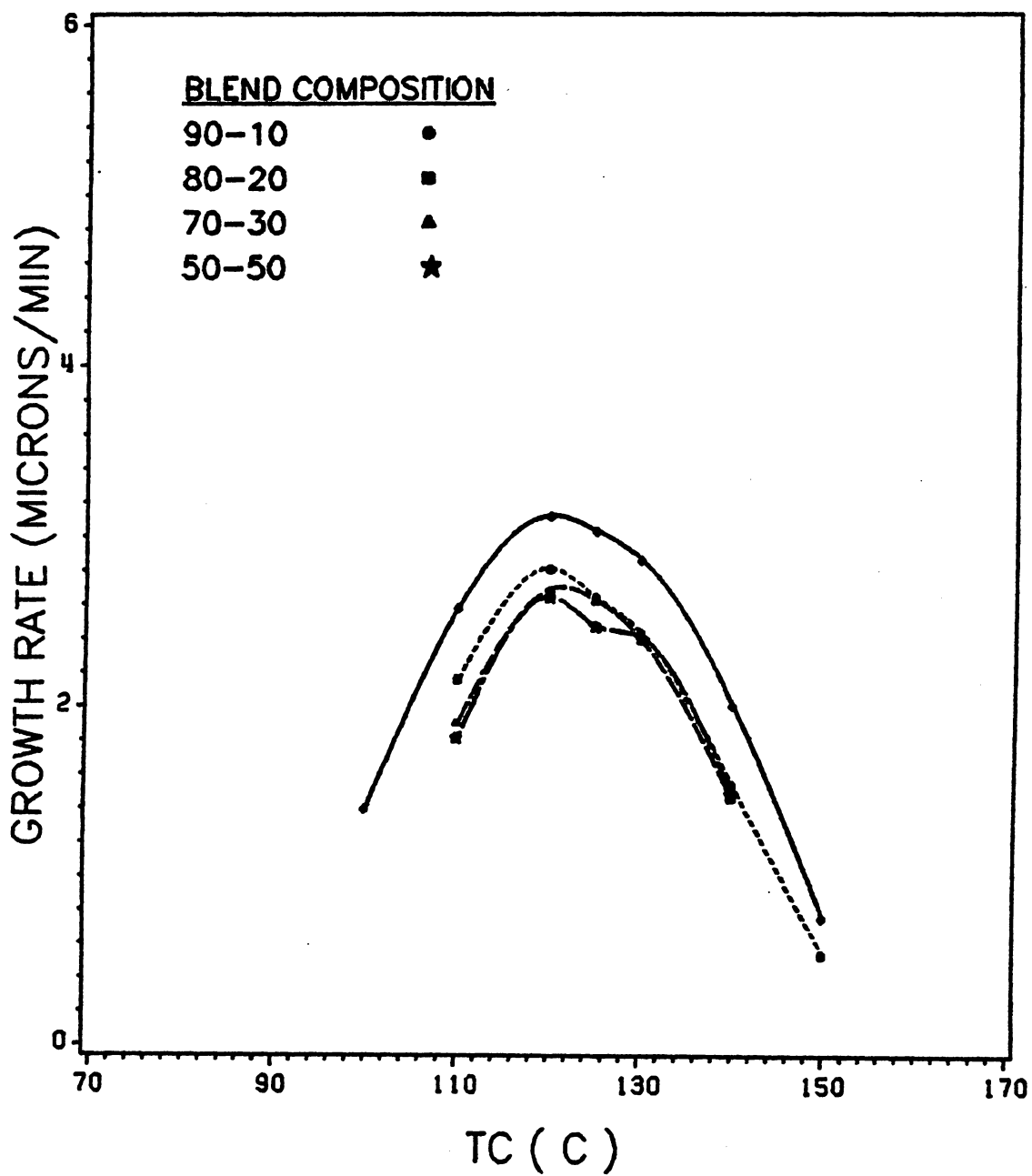


Figure 35. Radial spherulitic growth rates against crystallization temperature of the B3 blends

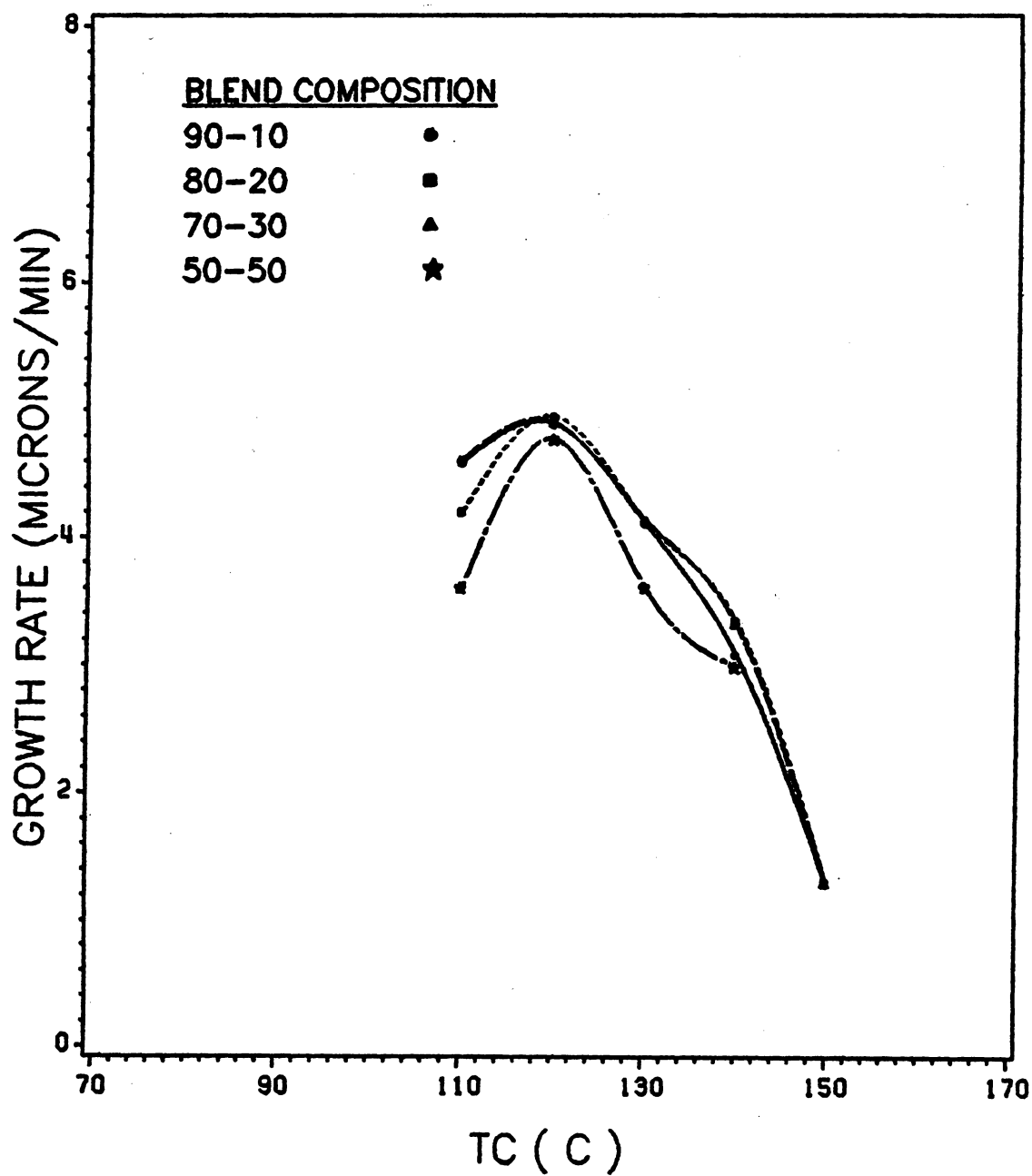
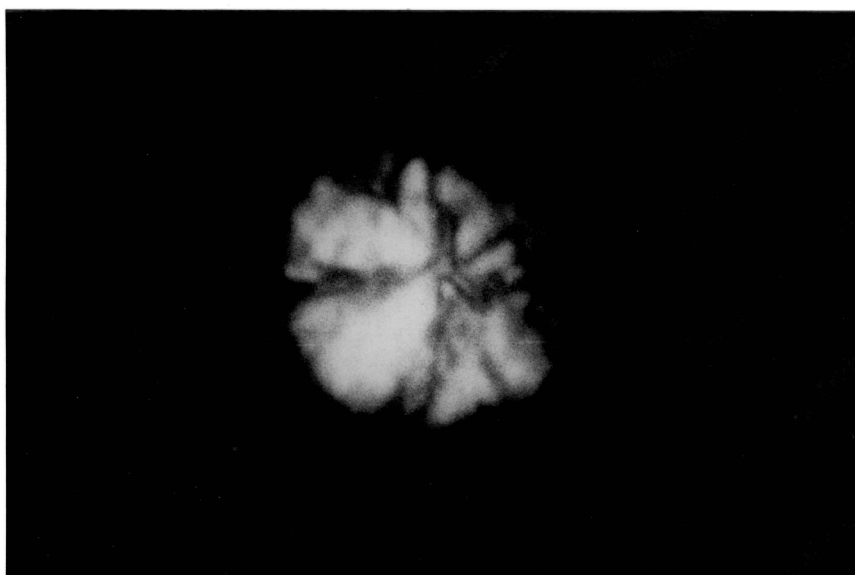


Figure 36. Radial spherulitic growth rates against crystallization temperature of the B4 blends



70/30



50/50

Figure 37. Optical micrograph of spherulites of B2-70/30 and B2-50/50 grown at $T_c = 140^\circ\text{C}$: Diffuse shape with black spots of amorphous DL inclusions.

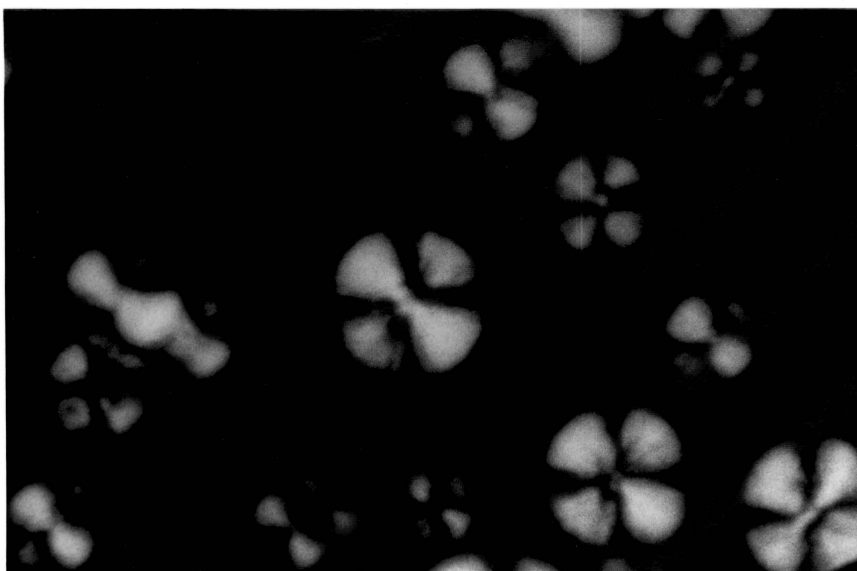
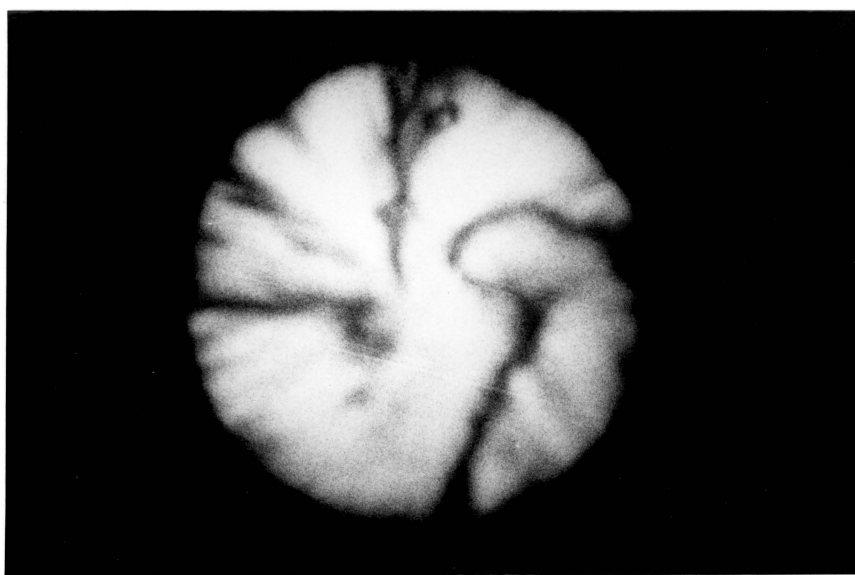


Figure 38. Optical micrograph of spherulites of B2-80/20 grown at $T_c = 110^\circ\text{C}$: Regular shape and characteristic maltese cross.



120 °C



130 °C

Figure 39. Optical micrograph of spherulites of B2-70/30 grown at $T_c = 120^\circ\text{C}$ and $T_c = 130^\circ\text{C}$: More or less black spots or DL material are included according to the starting sample.

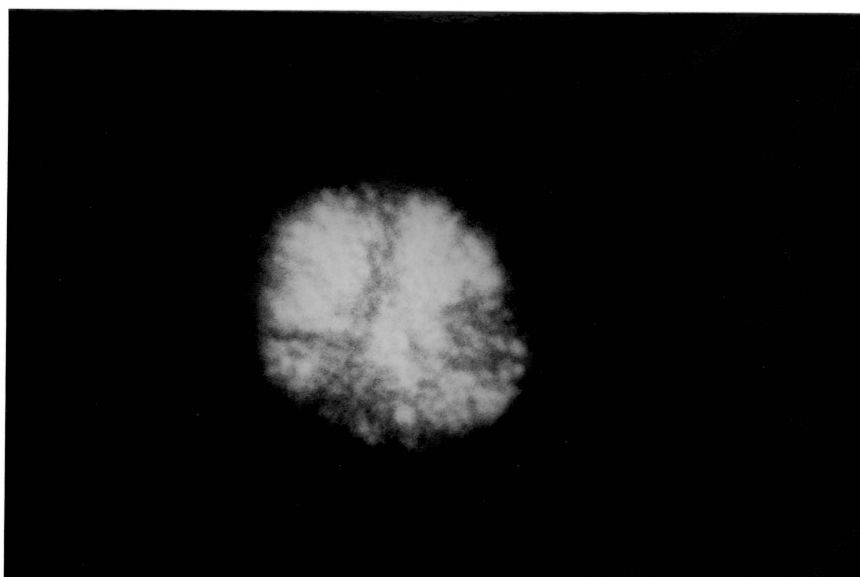


Figure 40. Optical micrograph of a spherulite of B4-50/50 grown at $T_c = 140^\circ\text{C}$: Irregular shape and no distinct fibrillar morphology apparent.

Appendix A. Computer Programs

A.1 Avrami-log(K)-Data For The Double log Plots

```
C  
C  
C CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC  
C C THIS IS A PROGRAM TO PERFORM A STUDY OF KINETICS OF C  
C C CRYSTALLIZATION BY AN AVRAMI APPROACH, USING TWO C  
C C METHODS THE LOG(-LOG(XAM)) PLOT AND THE SLOPE AT 1/2 C  
C C TIME FOR CRYSTALLIZATION METHOD. C  
C CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC  
C  
C CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC  
C  
C VARIABLE DEFINITION.  
C  
C X(30)=INPUT DATA (X COORDINATE)  
C Y(30)=INPUT DATA (Y COORDINATE)  
C T(30)=X(30) CORRECTED TO TIME SCALE  
C S(30), AREA(30) USED TO CALCULATE THE PARTIAL AREAS  
C XAMOR(30),P(30) USED TO CALCULATE THE AVRAMI EXPONENT  
C AR(30) USED TO CALCULATE N IN THE SECOND METHOD  
C  
C CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC  
C  
C REAL AR(30),X1(30),Y1(30),T(30),S(30),AREA(30),XAMOR(30),P(30)  
C REAL Z(30),Y(30)  
C  
C READ(2,*)KO  
C  
C CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC  
C  
C TRANSFORMING X VARIABLE INTO A TIME VARIABLE  
C  
C CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
```

```

      K=1
      READ(3,*) X1(K)
      K=K+1
10    IF(K.GT.21) GOTO20
      READ(3,*) X1(K), Y1(K)
      T(K-1)=X1(1)*X1(K)/9.8125
      Y(K-1)=Y1(K)
      K=K+1
      GOTO10
20    CONTINUE
C
C    CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C    CALCULATING PARTIAL AREAS
C
C    CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
      AREA(1)=0.
      I=2
30    IF(I.GT.20) GOTO40
      S(I)=(T(I)-T(I-1))*(Y(I)+Y(I-1))/2.
      AREA(I)=AREA(I-1)+S(I)
      I=I+1
      GOTO30
40    CONTINUE
C
C    CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C    WRITING THE OUTPUT FOR THE LOG(XAM) VS LOG(TIME) PLOT AND FOR
      THE DOUBLE LOG PLOT.
C
C    CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
      DO45 M= 2,19
      XAMOR(M)=ALOG(-ALOG(1-AREA(M)/AREA(20)))
45    CONTINUE
      DO60 J=2,13
      WRITE(5,800) K0, ALOG(T(J)), AREA(J)/AREA(20), XAMOR(J)
60    CONTINUE
      DO70 L=14,20
      WRITE(5,900) K0, ALOG(T(L)), AREA(L)/AREA(20)
70    CONTINUE
C
C    CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C    CALCULATING THE AVRAMI EXPONENT N.
C
C    CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

```


A.2 Crystallization Half-Times

```
C
C  VARIABLE DEFINITION.
C
C  X1(30)=INPUT DATA  (X COORDINATE)
C  Y1(30)=INPUT DATA  (Y COORDINATE)
C  T(30)=X(30) CORRECTED TO TIME SCALE
C  Y(30)=Y1(30) CORRECTED TO THE RIGHT INDICE
C  S(30), AREA(30) USED TO CALCULATE THE PARTIAL AREAS
C  XC(30) USED TO CALCULATE THE HALF-TIME
C  XF(30) FINAL VALUE OF THE AREA AFTER ITERATIONS
C
C  CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C  REAL X1(30),Y1(30),T(30),S(30),AREA(30),XC(30),Y(30),XF(30)
C
C  CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C  TRANSFORMING X1 VARIABLE INTO A TIME VARIABLE
C
C  CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C  K=1
C  READ(2,*)L0
C  READ(3,*)X1(K)
C  K=K+1
10  IF(K.GT.21)GOTO20
C  READ(3,*)X1(K),Y1(K)
C  T(K-1)=X1(1)*X1(K)/9.8125
C  Y(K-1)=Y1(K)
C  K=K+1
C  GOTO10
20  CONTINUE
C
C  CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C  CALCULATING PARTIAL AREAS
C
C  CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
```

```

AREA(1)=0.
I=2
30 IF(I.GT.20)GOTO40
S(I)=(T(I)-T(I-1))*(Y(I)+Y(I-1))/2.
AREA(I)=AREA(I-1)+S(I)
I=I+1
GOTO30
40 CONTINUE
C
C CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C FINDING T1/2 FOR CRYSTALLIZATION : THE HALF FOR WHICH
C XC EQUALS 1/2
C
C CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C J=2
50 XC(J)=AREA(J)/AREA(20)
CRIST=XC(J-1)
SLOPE=(XC(J)-XC(J-1))/(T(J)-T(J-1))
TF=T(J-1)
IF(XC(J).GE.0.5) GOTO60
J=J+1
GOTO50
60 CONTINUE
L=1
70 XF(L)=CRIST+SLOPE*0.01*L
TIME=TF+0.01*L
IF(XF(L).GE.0.5) GOTO80
L=L+1
GOTO70
80 CONTINUE
WRITE(4,100)L0,TIME
STOP
100 FORMAT(1X,I4,10X,F6.3)
END
```

Appendix B. Calculations Of Initiator Amount

The intrinsic viscosity obtained for the PLA-L reference sample was $[\eta] = 12.44$ dl/g. Using the Mark-Houwink equation and the corresponding parameters, one obtains:

$$12.44 = 5.45 \times 10^{-4} M_v^{0.73} \quad [B - 1]$$

and

$$M_v = 935,000 \text{g/mole} \quad [B - 2]$$

According to Schindler et al (8), for PLA-L samples having a polydispersity of 2.0 (which is verified when using the present polymerization method), the relationship between number average and viscosity average molecular weights is:

$$\frac{M_v}{M_n} = 1.88 \quad [B - 3]$$

Therefore, one obtains $M_n = 497,000$ g/mole and the degree of polymerization, DP_n , equal to 3449. The concentration of initiator present in the polymerization reactor is deduced from the inverse value of DP_n .

$$C = \frac{1}{DP_n} = 2.90 \times 10^{-4} \text{mole/mole} \quad [B - 4]$$

The corresponding weight of lactic acid for the polymerization of 6g of lactide monomer is calculated below.

$$M (\text{lactide}) = 144.1 \text{ g}$$

$$M (\text{lactic acid}) = 90.1 \text{ g}$$

- Moles of monomer

$$M_m = \frac{6}{144.1} = 0.0416 \text{ mole} \quad [\text{B} - 5]$$

- Moles of lactic acid present

$$M_l = 0.0416 \times 2.9 \times 10^{-4} = 1.21 \times 10^{-5} \text{ mole} \quad [\text{B} - 6]$$

- Weight of lactic acid present

$$W_l = 1.21 \times 10^{-5} \times 90.1 = 1.1 \times 10^{-3} \text{ g} \quad [\text{B} - 7]$$

The following results present an example of the calculation of the quantity of lactic acid being added in the reactor to achieve PLA-L ($M_v = 60,000 \text{ g/mol}$). Knowing that $M_v = 1.88M_n$, M_n is equal to $32,000 \text{ g/mole}$. Moreover, neglecting the end groups influence of the lactic acid, one obtains $DP_n = 222$ and the concentration necessary of lactic acid becomes: $C = 45.05 \times 10^{-4} \text{ mole/mole}$. The weight of lactic acid necessary to polymerize 6g of lactide is then:

$$0.0416 \times 45.05 \times 10^{-4} = 1.87 \times 10^{-4} \text{ mole} \quad [\text{B} - 8]$$

and

$$1.87 \times 10^{-4} \times 90.1 = 16.9 \times 10^{-3} \text{ g} \quad [\text{B} - 9]$$

Since the weight of lactic acid left after sublimation is 1.1×10^{-3} g (from the reference sample above), the weight to be added in the reactor is 15.8 mg.

The calculations corresponding to the other molecular weights are similar. The results are listed below.

Mv intended	Lactic acid added (mg)
20,000	49.5
60,000	15.8
250,000	3.0
500,000	0.9

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