

Crystallization Kinetics of Poly- ϵ -caprolactone from Poly- ϵ -caprolactone/Poly(vinyl Chloride) Solutions

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Synopsis

The polymer-polymer solution of poly(vinyl chloride) and poly- ϵ -caprolactone yields an excellent system for studying the crystallization kinetics of a crystallizable component from a polymer-polymer solution. Unlike previous studies of isotactic-atactic polystyrene solutions for which the glass transition temperature is invariant with composition, this system exhibits a marked dependence of T_g on the composition. The experimental data $dE^{1/2}/dt$ (psi^{1/2}/min) were obtained over a composition range of 40 to 70 wt-% poly- ϵ -caprolactone. With the appropriate modification of the spherulitic growth rate equation, the expression

$$\frac{dE^{1/2}}{dt} = k'(1 - C_d) \frac{-\Delta F_{WLF}}{RT}, \quad \left(\Delta F_{WLF} = \frac{4120T}{51.6 + T - T_g} \right)$$

approximated a reasonable fit of the experimental data. This demonstrates a marked dependence of the crystallization rate on concentration. Secondary observations of this investigation show a slower crystallization rate for high molecular weight poly- ϵ -caprolactone and a slow secondary crystallization step. Both homopolymer poly- ϵ -caprolactone and poly- ϵ -caprolactone in the poly- ϵ -caprolactone/poly(vinyl chloride) solution show a slow (relative to the nucleation-controlled step) crystallization stage considered to involve a slow diffusion mechanism.

INTRODUCTION

Crystallization kinetics of undiluted pure polymers have been investigated in detail for the more common homopolymers (i.e., polyethylene,¹ polypropylene,² and poly(ethylene terephthalate)³). Several studies relating to the crystallization of isotactic polystyrene from solutions of isotactic and atactic polystyrene have been reported.^{4,5} In this case, the T_g of the atactic/isotactic polystyrene solution is invariant with composition. The experimental situation described in this paper concerns a polymer-polymer solution in which the T_g is variant with composition.

With homopolymers, crystallization kinetics are determined as a function of temperature (T , remaining constant). With the system investigated in this paper, the T_g becomes the variable and the crystallization kinetics are determined at constant temperature.

Poly- ϵ -caprolactone and poly(vinyl chloride) represent the uncharacteristic feature of polymer-polymer blends in that they result in a true solution.⁶

The glass transition temperature of these blends has been previously shown⁶ to follow the Fox equation

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}}$$

as well as the Gordon-Taylor expression

$$T_g = T_{gA} + [kw_B(T_{gB} - T_{gA})/w_A]$$

where T_g is the glass transition of the blend, W_A and W_B are the weight fractions of the homopolymer constituents of the blends, and k is the ratio of thermal expansion coefficients between the rubber and glass states of the homopolymers. The disappearance of the characteristic glass transition temperatures of the homopolymers with the emergence of a single T_g is the most accepted method of defining polymer-polymer solubility.

Poly- ϵ -caprolactone is a crystalline polymer with a melting point of 60°C. It is, therefore, not unexpected that poly- ϵ -caprolactone (PCL) can crystallize out of the solution of poly- ϵ -caprolactone and poly(vinyl chloride) (PVC), particularly in the case where the T_g of the blend is lower than the annealing temperature. Indeed, this was found to be the case for blends at high PCL levels subjected to dynamic mechanical measurements over a broad temperature spectrum.⁶

In isotactic/atactic polystyrene blends, the spherulite growth rate, G , is depressed linearly with atactic polystyrene concentration.⁴ The isotactic/atactic polystyrene solution presents a constant T_g over the entire concentration range. The poly- ϵ -caprolactone ($T_g = -71^\circ\text{C}$ [amorphous])/poly(vinyl chloride) ($T_g = 82^\circ\text{C}$) solution, however, exhibits a marked change in T_g with composition, and, therefore, a spherulite growth rate would not be expected to follow a linear depression with increasing poly(vinyl chloride) concentration.

The experimental investigation described in this paper deals with data obtained from modulus measurements as a function of time. While this procedure is less common than direct spherulite growth rate determination or specific volume measurements,⁷ a direct analogy to the results obtained from these measurements is possible and represents an accurate, facile method for ascertaining the crystallization rates of the experimental system chosen here for studies at constant temperature.

The crystal structure, the thermodynamics of fusion, and the crystallization kinetics of poly- ϵ -caprolactone have been the subject of several papers.⁸⁻¹⁰ The melting point of 60°C (birefringence)⁶ and 63°C (differential scanning calorimeter)⁹ for PCL have been reported. Independent studies on the degree of PCL crystallinity yields good agreement, with values of 50%⁶ and 48%⁹ reported. Similar studies of poly- ϵ -caprolactone/poly(vinyl chloride) solutions, however, have not appeared in the open literature.

EXPERIMENTAL

The poly- ϵ -caprolactone (PCL) used in this investigation was PCL-700 (Union Carbide Corporation, reduced viscosity = 0.7, 0.2 g/100 ml benzene at 30°C, which corresponds to $\sim 40,000$ weight average molecular weight). The poly(vinyl chloride) (PVC) used was QYSA (Union Carbide Corporation, inherent viscosity = 0.63 as per ASTM D-1243 Method A). All blends contained 2% TM-210 (based on PVC weight) for thermal stabilization. TM-210, a liquid stabilizer, was chosen to eliminate any chance of nucleation which might occur with the use of a solid stabilizer. Solutions of PCL/PVC (70/30, 60/40, 55/45, 50/50, 45/55, 40/60) were prepared in tetrahydrofuran. After devolatilization of tetrahydrofuran at 100°C for 8 hr under vacuum, the samples were fluxed on a two roll mill at 150–160°C to assure homogeneity. These samples were then compression molded into 20-mil films at 160–170°C. From these films, $1/8$ -in.-wide strips were cut for modulus-time studies at 25°C. Before testing, these samples were placed in boiling water for 2 min to melt the PCL and allow the crystallized PCL to redissolve in the PVC/PCL amorphous phase. The samples were then placed in the grips on an Instron where load-extension data to obtain tensile modulus were taken. The Instron was situated in a constant-temperature (25°C), constant-humidity (50% R.H.) room where the maximum temperature variation during the course of these experiments was $\pm 2^\circ\text{C}$.

EXPERIMENTAL RESULTS

To assure that the 2-min immersion in boiling water resulted in redissolving the crystallized PCL in the amorphous PCL/PVC solution to an equilibrated position, the induction time for crystallization (experimental determination described later) was determined under two conditions for the 50/50 wt-% PCL/PVC blend. The condition of measurement for a sample taken directly after compression molding a sample off the two-roll mill yielded an induction time of 134 min. The condition where the sample was allowed to fully crystallize followed by immersion in boiling water for 2 min yielded an induction time of 162 min. This demonstrates that the PCL spherulites melt and redissolve to a reasonably equilibrated state under the conditions described above. The faster nucleation rate for the first-described condition is hypothesized to be the result of residual stresses in the unannealed sample resulting in stress-induced crystallization.

The induction time for crystallization was determined by plotting tensile modulus versus log time, and the intercept of the linear portion of the curve with the zero-time modulus yields the induction time. The zero-time modulus ranged between 70 and 230 psi for the concentration range covered in this investigation. The induction time data for the PCL-700/PVC blends are shown in Figure 1, with the data tabulated in Table I. The plot of tensile modulus versus log time should correspond to degree of crystallization isotherms commonly referred to as the Avrami¹¹ isotherm.

TABLE I
Tabulation of Experimental Results^a

Composition, wt-%	Induction time, min	$\frac{dE^{1/2}}{dt}$, psi ^{1/2} /min ^b	T_g , °C ^c
70% PCL (RV = 0.7) 30% PVC	4.3	5.1	-44.0
60% PCL (RV = 0.7) 40% PVC	26	.80	-35.0
55% PCL (RV = 0.7) 45% PVC	55	.46	-28.5
50% PCL (RV = 0.15) 50% PVC	142	.13	—
50% PCL (RV = 0.7) 50% PVC	162	.12	-20.5
50% PCL (RV = 1.5) 50% PVC	220	.066	—
45% PCL (RV = 0.7) 55% PVC	880	.023	-16.0
40% PCL (RV = 0.7) 60% PVC	4,900	.00051	-5.0

^a PVC used for all samples was QYSA poly(vinyl chloride) homopolymer, Union Carbide Corporation.

^b Modulus data obtained at a strain rate of 0.2 in./min. (2-in. gauge length).

^c Average of three determinations of G'' (loss modulus) peak.

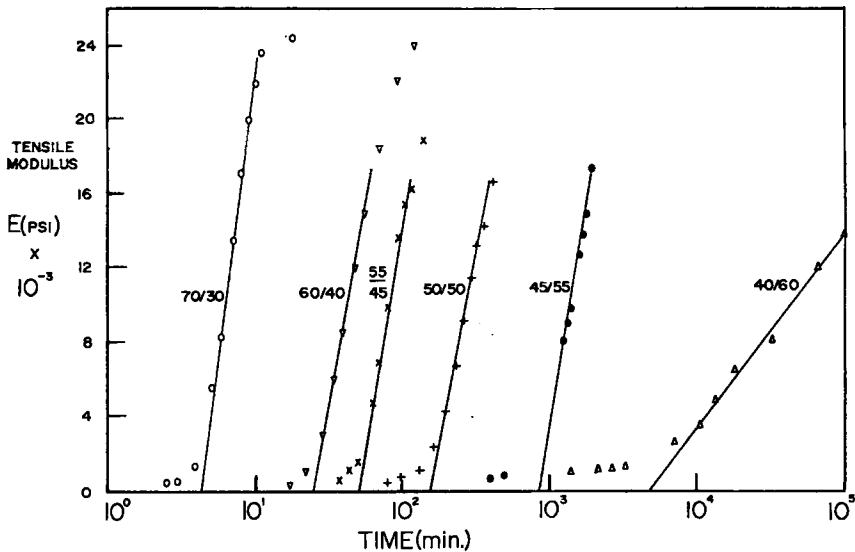


Fig. 1. Crystallization of PCL/PVC blends as determined by modulus-time measurements (temperature = 25°C).

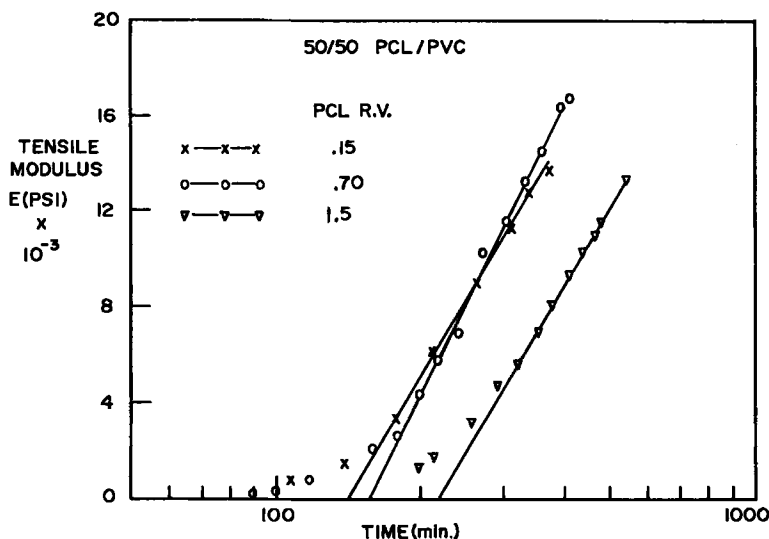


Fig. 2. Crystallization of PCL from a 50/50 PCL/PVC blend: effect of PCL molecular weight.

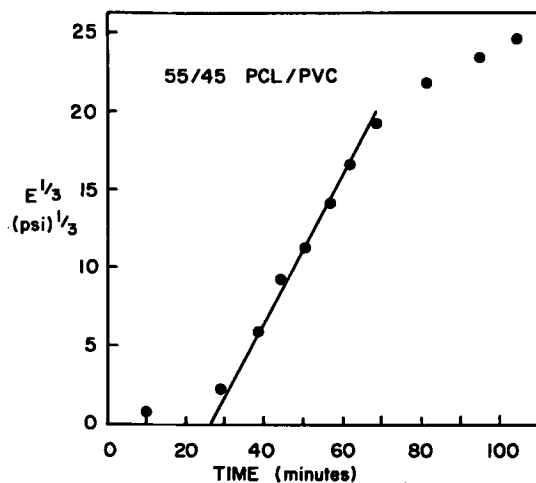


Fig. 3. Modulus^{1/3}-time data for PCL crystallization from the 55/45 PCL/PVC blend.

This would be expected, as the modulus should be proportional to the volume fraction of PCL spherulites.

The data of 50/50 PCL/PVC blends based on two different molecular weight poly- ϵ -caprolactones with reduced viscosities of 0.15 and 1.5 bracketing the data of PCL-700 are listed in Table I. The tensile modulus-log time plots of the three different molecular weight PCL's are shown in Figure 2. While the data corresponding to PCL reduced viscosities of 0.15 and 0.7 are fairly similar, the higher molecular weight PCL (RV = 1.5) exhibits a decreased crystallization rate.

As crystallization kinetics are generally reported as spherulitic growth rates (cm/sec), the increase in modulus^{1/2} with time (psi^{1/2}/min) should correspond to the spherulitic growth rate. The plot of modulus^{2/3} versus time has a linear portion of the curve occurring at a lower modulus than the corresponding modulus-log time curves. A typical plot for the 55/45 (PCL/PVC) concentration is given in Figure 3 and the linear slopes (psi^{1/2}/min) are tabulated in Table I for all samples.

ANALYSIS AND DISCUSSION OF RESULTS

The induction time for crystallization and the rate of modulus^{1/2} change with time shows a marked dependence on concentration, as shown in Figures 4 and 5. As this case represents a varying glass transition temperature with concentration, it is of interest to see if the spherulitic growth rate theory adequately predicts the observed dependence of concentration on the rate of modulus^{1/2} change with time.

The general form of the spherulitic growth rate equation¹² is

$$G = G_0 e \left(- \frac{\Delta F^*}{RT} \right) e \left(- \frac{4b_0 \sigma \sigma_e T_m^0}{\Delta h_f (\Delta T) kT} \right) \quad (1)$$

where ΔF^* represents the barrier restricting movement to the crystallizing surface and has been suggested by Hoffman and Weeks⁷ to be satisfied by the Williams, Landel and Ferry equation¹³

$$\Delta F^* = \frac{4120T}{(51.6 + T - T_g)} \quad (2)$$

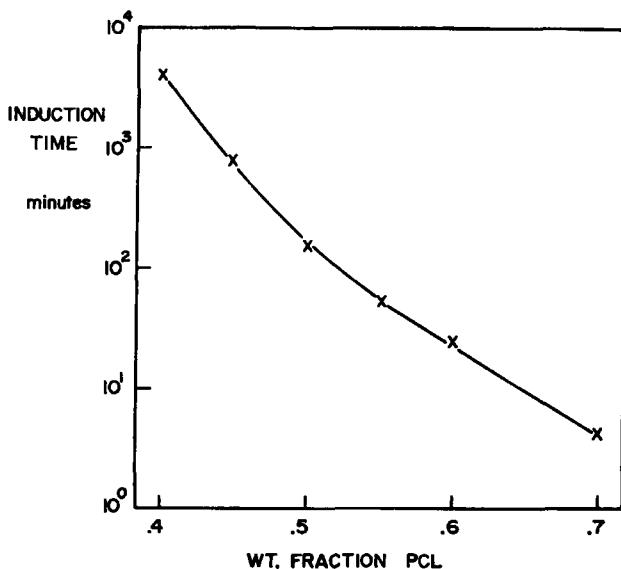


Fig. 4. Induction time for crystallization of PCL from PCL/PVC blends.

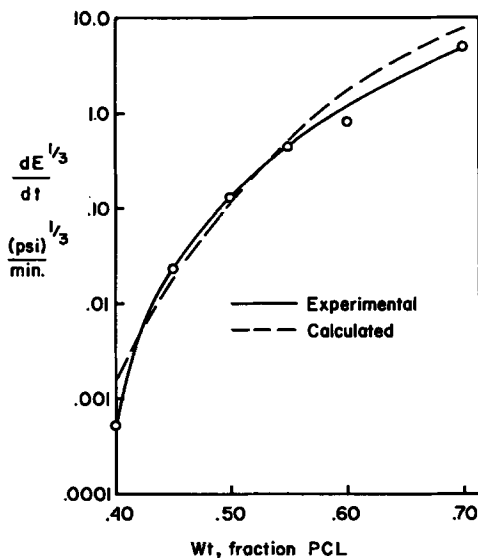


Fig. 5. Crystallization rate as a function of PCL concentration in PCL/PVC blends.

If we assume b_0 (monolayer thickness), σ (lateral interfacial free energy), σ_e (interfacial free energy of chain folded surface), T_m° (equilibrium melting point), and Δh_f (heat of fusion) to be constant, which for approximation purposes should be reasonably valid assumptions, eq. (1) will reduce to

$$G = k_1 e \left(- \frac{4120}{(51.6 + T - T_g)R} \right). \quad (3)$$

As the concentration of poly- ϵ -caprolactone) is a variable, we must revise eq. (3) to yield

$$G = k_1(1 - C_d) e \left(- \frac{4120}{(51.6 + T - T_g)R} \right) \quad (4)$$

where C_d = wt-diluent (PVC).

The linear assumption was chosen based on the results of a previous investigation of isotactic/atactic polystyrene blends⁴ where the spherulite growth rate was shown to be linear with isotactic polystyrene concentration.

The modulus will be proportional to the volume fraction of the spherulites, that is,

$$E = k_2 \frac{4}{3} \pi r^3 \quad E^{1/3} = (k_2 \frac{4}{3} \pi)^{1/3} r \quad (5)$$

$$\frac{dE^{1/3}}{dt} = \left(k_2 \frac{4}{3} \pi \right)^{1/3} \frac{dr}{dt} \quad \text{where } \frac{dr}{dt} = G \quad (6)$$

$$\frac{dE^{1/3}}{dt} = k'(1 - C_d) e \left(- \frac{4120}{(51.6 + T - T_g)R} \right) \quad (7)$$

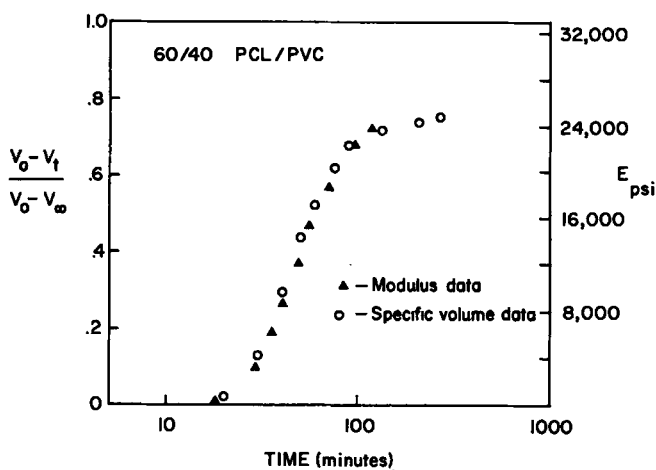


Fig. 6. Comparison of specific volume and modulus data (60/40 PCL/PVC).

where

$$k' = \left(k_2 \frac{4}{3} \pi \right)^{1/3} G_0 e \left(- \frac{4b_0 \sigma \sigma_e T_m^0}{\Delta h_f (\Delta T) kT} \right). \quad (8)$$

The assumption of proportionality of modulus with volume fraction of spherulites was checked on the 60/40 PCL/PVC blend by comparison of modulus-time data with specific volume data. The specific volume of a crystalline sample held at 25°C for four months was initially measured. The sample was held in boiling water for 2 min and then measured as a function of time as per the procedure designated by ASTM D-1505-57T. The plot of $V_0 - V_t / V_0 - V_\infty$ versus log time is shown in Figure 6, where V_∞ , V_t , and V_0 are the specific volumes of the sample fully crystallized, at time = t and time = 0. The modulus-log time data are superimposed in Figure 6 with the modulus axis chosen to provide a comparable slope. As the data fall on the same curve, the assumption of proportionality of modulus with volume fraction appears quite good.

Using eq. (7), if we establish k' from the center position of the experimental data (55 wt-% PCL), the calculated $dE^{1/3}/dt$ curve is shown in Figure 5. The glass transition data used in eq. (7) was determined from G'' (loss modulus) data on quenched specimens using the same procedure as reported by Koleske and Lundberg.⁶ The values of T_g were slightly lower presumably due to lower molecular weight PVC and plasticization by the liquid stabilizer. Although the calculated slope exhibits a slightly different curvature than the experimental data, reasonable agreement within the context of the assumptions made can be claimed.

Several assumptions need to be discussed here, namely, the assumption of constant T_m versus composition and the assumption of constant T_g as crystallization time proceeds. As a melting point depression occurs with

polymer-low molecular weight diluent solutions it would be expected that the same situation is observed with polymer-polymer solutions. Preliminary data have shown a melting point depression in these blends.¹⁴ Correction of the calculated curve would, however, not yield a better fit as the term $T_m/(T - T_m)$, eq. (1), would result in a slightly greater deviation of the calculated curve from the experimental data.

Another assumption which is made is that the T_g remains constant (WLF equation). As PCL crystallizes out of the PVC/PCL solution, the ratio of PVC/PCL increases in the amorphous phase, therefore resulting in a T_g increase. As the $dE^{1/2}/dt$ data were linear in the same modulus range, the $dE^{1/2}/dt$ results were, therefore, obtained within the same range of PCL crystallinity ($E \sim V_f[\text{crystalline PCL}]$). This would have the effect of an equivalent T_g shift for all compositions, thereby minimizing the general curvature of the data (Fig. 5). Also note that the deviation from linearity of $E^{1/2}$ -versus-time data occurs at $E \simeq 8000$ psi, which corresponds to 25% of the ultimate crystallinity for the 60/40 PCL/PVC blend (see Fig. 6). T_g determinations on the 60/40 PCL/PVC blend (annealed versus quenched) show that 25% of ultimate crystallinity corresponds to a T_g shift of 9°C. Many homopolymers show a shift in T_g with crystallization⁶ but not of the magnitude which would be expected with this particular case.

On most of the samples, experimental modulus data were only obtained to the time where the crystallization was nearly complete, namely, where deviation from linearity of modulus versus log time occurred. The data on 60/40 PCL/PVC were obtained at times much greater than the position where deviation from linearity occurred on the log time-modulus plot. Interestingly, a new slope results showing a slow rise in modulus as time proceeds. The same result was also observed for PCL-700 homopolymer. The data were obtained via a different procedure than the data described previously. Samples were placed between the grips in a torsion pendulum (similar to the design of Nielsen).¹⁵ An angular deflection was applied, and the frequency was determined for this free vibration experiment. The shear modulus can then be determined from frequency (cycles/sec) squared, sample dimensions, and system inertia. The plot of shear modulus versus log time is illustrated in Figure 7, for the 60/40 PCL/PVC blend and for PCL-700. The initial modulus-log time slope for PCL-700 could not be determined owing to the rapid crystallization of PCL-700. Both samples illustrate a secondary crystallization process with a crystallization rate much lower than the initial crystallization step.

Similar results were obtained by Hoffman and Weeks⁷ for poly(chlorotrifluoroethylene). The initial linear slope (stage 1) is a nucleation-controlled step. The second linear slope (stage 2) has been considered to involve a slow diffusion mechanism. Several explanations for this process have been offered, of which conversion of the residual amorphous phase into a crystalline phase or trapped amorphous phase in the spherulites crystallizing is a distinct possibility. Further work is in progress to ascertain if a pure PCL amorphous phase exists in the spherulitic structure.

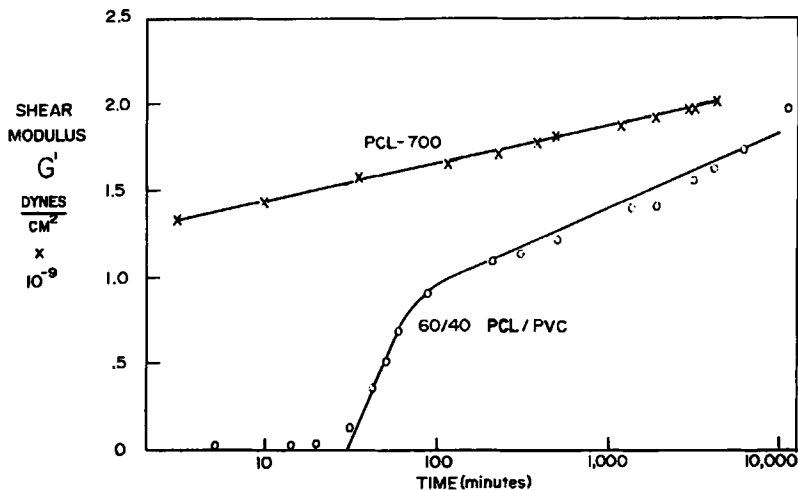


Fig. 7. Long-term crystallization characteristics of PCL for homopolymer PCL and a 60/40 PCL/PVC blend.

Although more detailed studies would be required to further define the effect of molecular weight on the rate of crystallization, the initial data presented here illustrate the expected trend as the highest molecular weight PCL exhibits the slowest crystallization rate as is generally observed in homopolymers.¹⁶ The almost identical results for PCL's with reduced viscosities of 0.15 and 0.70 may be due to the overriding contribution of PVC until the molecular weight of PCL reaches a point in controlling the diffusion of PCL to the amorphous phase-crystal interface where its contribution becomes significant. This would, of course, require further studies with variations in both PVC and PCL molecular weight. One would expect that at constant composition and constant PCL molecular weight an increase in PVC molecular weight would result in a decrease in PCL crystallization rate as observed by Yeh and Lambert⁴ where a slow decrease in crystallization rate (above a critical molecular weight) was observed for atactic/isotactic polystyrene blends.

CONCLUSIONS

The crystallization rate and induction time for crystallization of poly- ϵ -caprolactone out of the poly- ϵ -caprolactone/poly(vinyl chloride) polymer-polymer solution is critically affected by the concentration of the components. The crystallization rate is adequately predicted by the WLF equation substituted into a modified version of the standard spherulitic growth rate equation. Two stages of crystallization are observed not only in the blends but in homopolymer poly- ϵ -caprolactone. The nucleation-controlled stage has a linear region for modulus versus log time, with a slope much greater than the diffusion-controlled stage which also exhibits linearity for modulus versus log time. Based on initial data, increasing the

molecular weight of poly- ϵ -caprolactone results in slower crystallization rate in PVC blends. This result corresponds to that previously observed in homopolymers. Using modulus-time data to correlate crystallization kinetics appears to be an excellent facile method yielding results similar to the direct spherulitic growth rate data or density data which yields the relative crystalline volume fraction change.

References

1. P. Lindemeyer and V. F. Holland, *J. Polym. Sci.*, **57**, 589 (1962).
2. B. V. Falkai, *Makromol. Chem.*, **41**, 86 (1960).
3. K. G. Mayhan, W. J. James, and W. Bosch, *J. Appl. Polym. Sci.*, **9**, 3605 (1965).
4. G. S. Y. Yeh and S. L. Lambert, *J. Polym. Sci. A-2*, **10**, 1183 (1972).
5. H. D. Keith and F. J. Padden, Jr., *J. Appl. Phys.*, **35**, 1286 (1964).
6. J. V. Koleske and R. D. Lundberg, *J. Polym. Sci. A-2*, **7**, 795 (1969).
7. J. D. Hoffman and J. J. Weeks, *J. Chem. Phys.*, **37**, 1723 (1962).
8. H. Bittiger, R. H. Marchessault, and W. D. Niegisch, *Acta Crystallogr.*, **B26**, 1923 (1970).
9. V. Crescenzi, G. Manzini, G. Calzolari, and C. Borri, *Eur. Polym. J.*, **8**, 449 (1972).
10. R. Perret and A. Skoalios, *Makromol. Chem.*, **156**, 157 (1972).
11. M. Avrami, *J. Chem. Phys.*, **8**, 212 (1940).
12. F. Gornich and J. D. Hoffman, in *Nucleation Phenomena*, A. S. Michaels, Ed., ACS, Washington, D.C., 1966.
13. M. W. Williams, R. F. Landel, and J. D. Ferry, *J. Amer. Chem. Soc.*, **77**, 3701 (1955).
14. L. M. Robeson and B. L. Joesten, unpublished observations.
15. L. E. Nielsen, *Rev. Sci. Instr.*, **22**, 690 (1951).
16. C. Devoy and L. Mandelkern, *J. Polym. Sci. A-2*, **7**, 1883 (1969).

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