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A Dynamic Study of Crystallization of Poly(ε-caprolactone) and Poly(ε-caprolactone)/Poly(vinyl chloride) Blend

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ABSTRACT: The crystallization of poly(ε-caprolactone) (PCL) and a compatible blend of PCL with poly(vinyl chloride) were studied by a small angle X-ray scattering (SAXS) method with synchrotron radiation and by microscopic observation. By the SAXS method, the peak of the scattering intensity, arising from the long period in the sample, was observed during crystallization. The maximum intensity of the peak, I_m, increased with crystallization time t_c and reached a constant value $I_m(\infty)$ at time $2\tau^*_{1/2}$ ($\tau^*_{1/2}$ is the time necessary for I_m to reach $I_m(\infty)/2$). The value of $\tau^*_{1/2}$ increased abruptly with an elevation of the crystallization temperature T_c for both pure PCL and the blend, and $\tau^*_{1/2}$ for the blend was larger than that for pure PCL at the same T_c. The change of I_m against t_c was analysed by the Avrami equation, the exponent n being about 2 for the blend at every T_c and pure PCL at higher T_c. For pure PCL at lower T_c, n increased with the decrease of T_c. In the microscopic observation of both pure PCL and the blend, the spherulite radius increased linearly with t_c, and the linear growth rate G of spherulite decreased with T_c. A correspondence was found between T_c dependence of $\tau^*_{1/2}$ and that of $1/G$.

KEY WORDS Crystallization / Microscopic Observation / Polymer Blend / Samll Angle X-Ray Scattering / Synchrotron Radiation /

In compatible polymer blends, the crystallization of components, together with the liquid-liquid phase separation, control the morphology organized and hence the various properties of polymer blends.[1,2] The dynamics of the phase separation has extensively been studied by a laser light scattering technique and the mechanism has been elucidated for many systems.[3-6] The dynamics of crystallization, on the other hand, has been studied mainly by an optical microscope, a dilatometry, and a differential scanning calorimetry (DSC).[2,7,8] These methods are based on the macroscopic or overall change during crystallization, and the change of finer morphology, for example, lamella thickness, could not be measured. Recently, the small angle X-ray scattering (SAXS) technique with a strong source such as synchrotron radiation has become available.[9-16] The strong sources have made possible the observation of the change of the fine morphology at the initial stage of crystallization against crystallization time. Schultz *et al.*[17,18] studied the crystallization of a linear polyethylene at various temperatures T_c, and found that the crystallization behavior at higher T_c was different from that at lower T_c. At higher T_c, the long period and the lamella thickness were nearly invariable during crystallization; but at lower T_c, the long period decreased with time because of the appearance of new lamellae in the amorphous regions between lamellae. Elsner *et al.*[11,12] studied the crystallization process of oriented and unoriented poly(ethylene terephthalate) (PET) with synchrotron radiation and found that the long period decreased at the initial stage of crystallization and reached a constant value. They also reported that the decrease in the long period was largely dependent on the quench depth and the molecular weight of polymers.

To understand the morphology organized in polymer blends by crystallization, it is necessary to know the morphology with respect to both lamella thickness and spherulite diameter. In this study, the crystallization process of poly(ε-caprolactone) (PCL) and a compatible blend of PCL with poly(vinyl chloride) (PVC) was observed both by the SAXS method with a synchrotron radiation[19] and an optical microscope. This blend system is known to be compatible at all compositions and the morphology organized by the crystallization of PCL has extensively been studied.[20,21]

EXPERIMENTAL

Materials and Sample Preparation

The PCL supplied from Science Polymer Products, Inc. was fractionated with a benzene/*n*-heptane system. The weight-average molecular weight M_w and its ratio, M_w/M_n, to the number-average molecular weight M_n determined by gel-permeation chromatography were 23,300 and 1.58, respectively. The PVC obtained from Aldrich Chemical Company, Inc. was fractionated with a tetrahydrofuran (THF)/water system. The values of M_w and M_w/M_n were 144,000 and 1.56, respectively. The PCL/PVC blend with the weight fraction of PCL $\phi_{\mathrm{PCL}}=0.90$ was prepared by solving both polymers in a common solvent THF and evaporating THF for 40 h at 80°C.

Small Angle X-Ray Scattering (SAXS)[19]

The SAXS measurements were carried out using small angle X-ray equipment for solution (SAXES) with the synchrotron radiation set up at National Laboratory for High Energy Physics, Japan.[22] The storage ring was operated at an energy level of 2.5 GeV with the beam current of 50—150 mA. The wave length of the X-ray used for the experiment was 1.4881 Å, which corresponds to the absorption edge of nickel. The scattering intensity was detected by a position sensitive proportional counter (PSPC) with 512 channels, the distance between the sample and PSPC being 1,924 mm. The intensity during crystallization was recorded every 10—20 s from the beginning of crystallization and the measurement was continued until the integrated intensity ceased to change. The scattering intensities were corrected for the Lorentz factor and background intensity.[23] The temperature of the sample holder was controlled by circulating water at constant temperature. The temperature fluctuation of the sample during crystallization was within $\pm 0.2°\mathrm{C}$ throughout the experiments. The temperature drop from the molten state ($\sim 65°\mathrm{C}$) to the crystallization temperature T_c (28—43°C) was achieved within 60—100 s. Since this cooling rate was rather slow, the experiment could be conducted only at rather high temperature close to T_m, where crystallization did not start until the temperature of the sample reached T_c.

Microscopic Observation

The behavior of spherulite growth during crystallization was observed by an optical microscope and was recorded on a photograph. The sample was about 0.1 mm in thickness. Measurement was continued until the spherulites impinged on each other and growth terminated. The method of temperature control was similar to that for the SAXS experiments.

RESULTS

Figure 1 shows a typical example of Lorentz-corrected scattering intensity obtained for pure PCL at $T_c=40.9°\mathrm{C}$. Immediately after the beginning of crystallization, the peak of the scattering intensity appeared at about $s=0.06\,\mathrm{nm}^{-1}$, which corresponds to the period

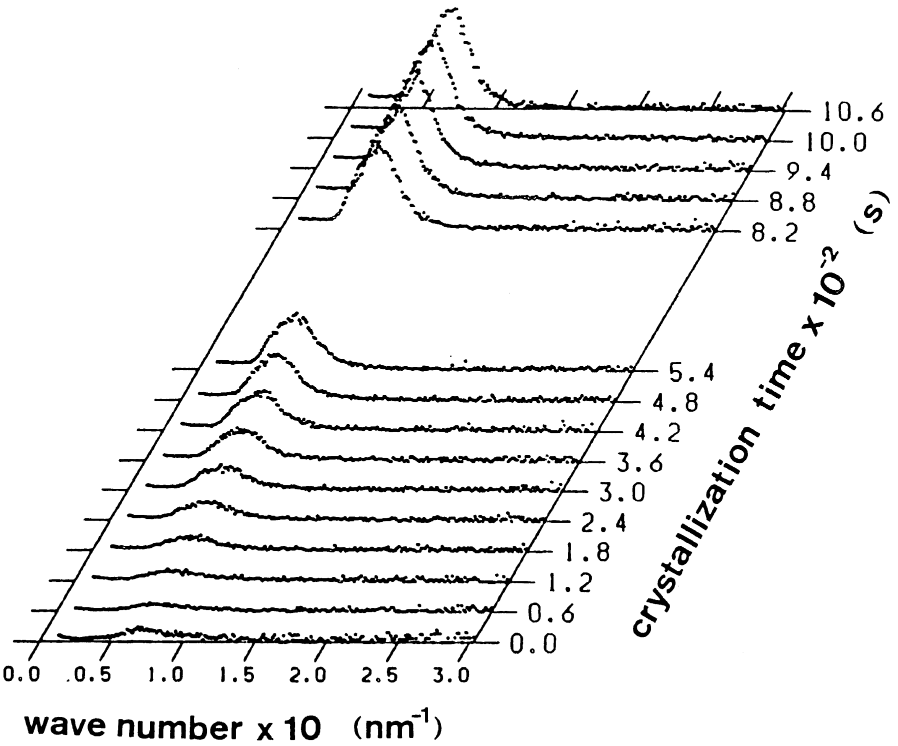

Figure 1. Time resolved scattering intensity corrected for Lorentz factor for pure PCL at $T_c=40.9°C$. Numerals in the Figure represent the crystallization time t_c.

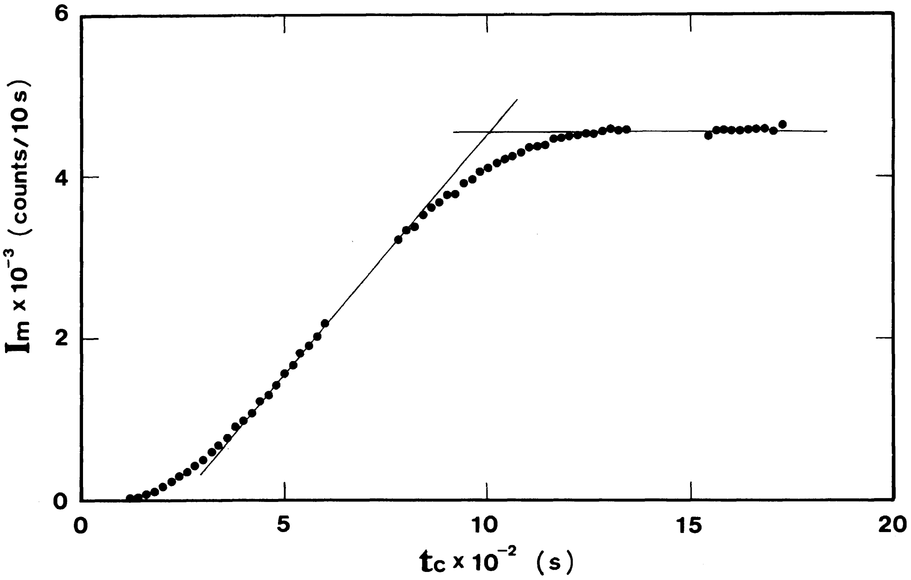

Figure 2. The maximum intensity of the peak against t_c for pure PCL at $T_c=40.8°C$.

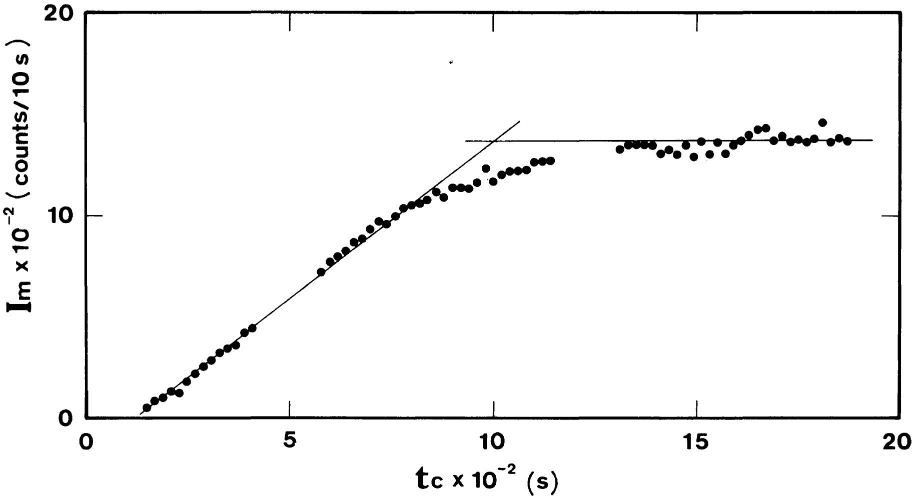

Figure 3. The maximum intensity of the peak against t_c for the blend with $\varphi_{PCL}=0.90$ at $T_c=39.6°C$.

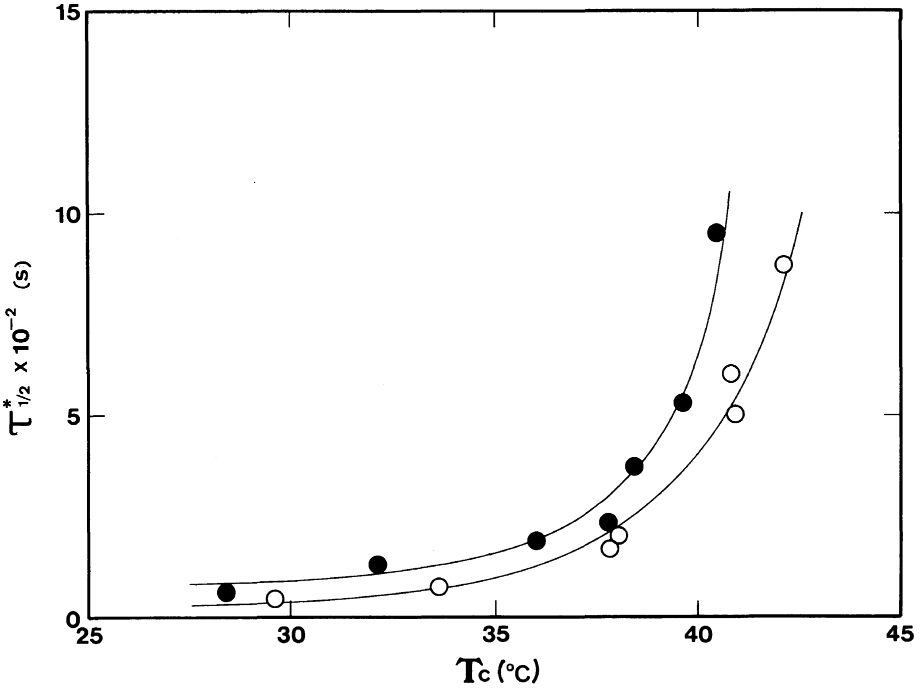

Figure 4. $\tau^*_{1/2}$ obtained in Figures 2 and 3 against T_c: ○, pure PCL; ●, blend with $\varphi_{PCL}=0.90$.

of 16.6 nm. This peak is considered to arise from alternate stacks of lamellae and a thin amorphous layer organized within the sample. The peak intensity I_m became larger with the crystallization time t_c and reached a constant value $I_m(\infty)$. Figure 2 shows the t_c dependence of I_m for pure PCL at $T_c=40.8°C$ and Figure 3 that for the blend at $T_c=39.6°C$. The time $\tau^*_{1/2}$, at which I_m becomes $I_m(\infty)/2$, may be regarded as a measure of the time necessary for crystal-

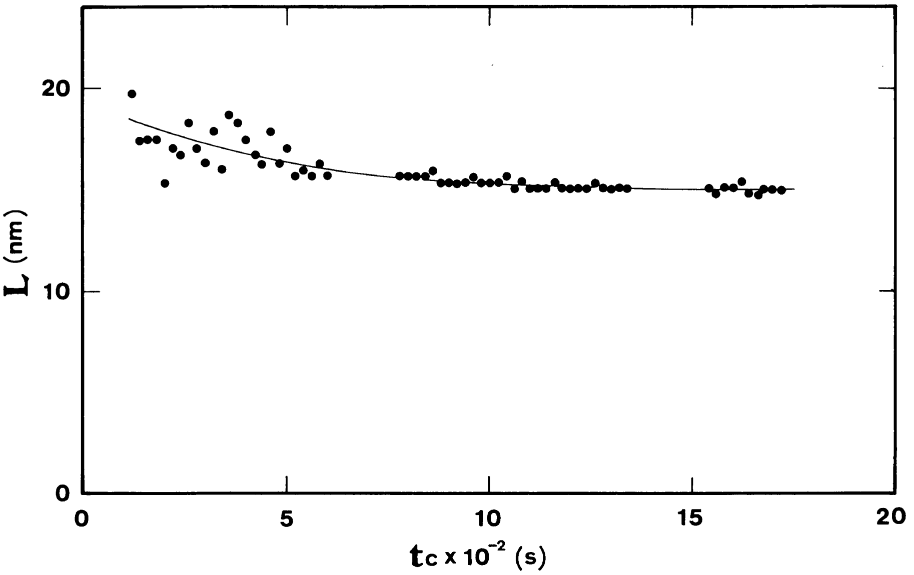

Figure 5. The long period against t_c for pure PCL at $T_c = 40.8$°C.

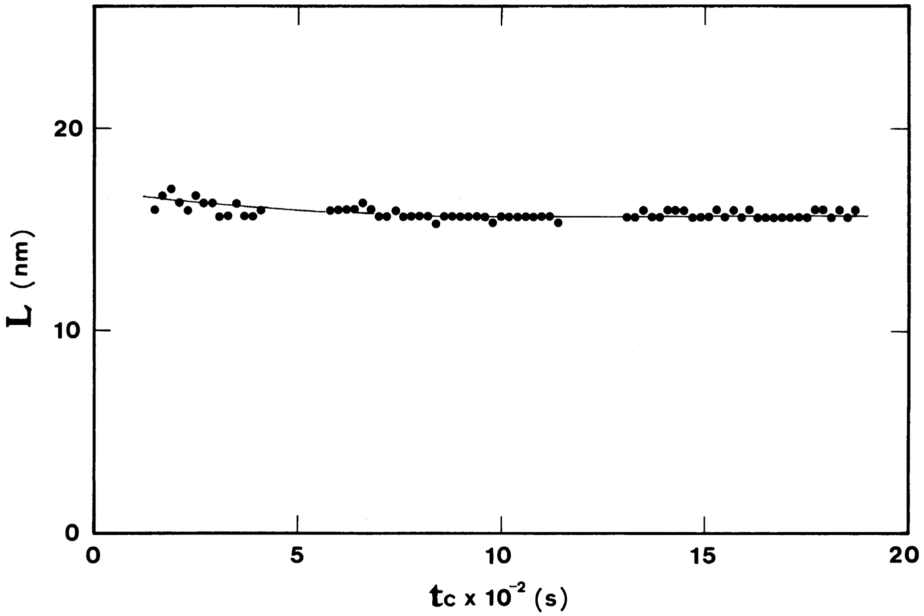

Figure 6. The long period against t_c for the blend at $T_c = 39.6$°C.

lization. Figure 4 shows the T_c dependence of $\tau^*_{1/2}$. For both samples, $\tau^*_{1/2}$ increased abruptly with elevation of T_c. At the same T_c, $\tau^*_{1/2}$ for pure PCL was smaller than that for the blend, indicating that the crystallization for the blend took longer time than that for pure PCL. The behavior shown in Figure 4 is similar to the T_c dependence of $\tau_{1/2}$, a half time of crystallization, obtained by other methods, for instance DSC measurement for a polypropylene/poly-

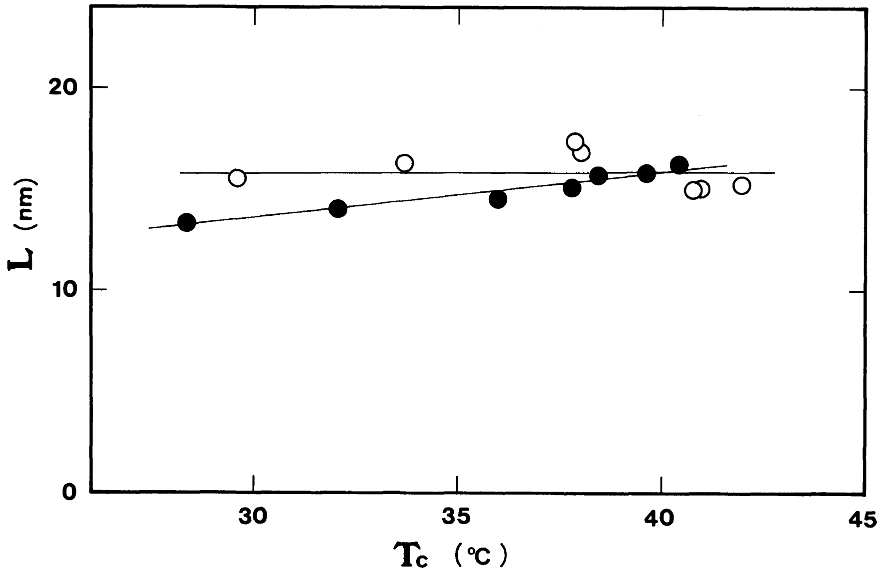

Figure 7. The long period obtained in Figures 5 and 6 against T_c: ○, pure PCL; ●, the blend.

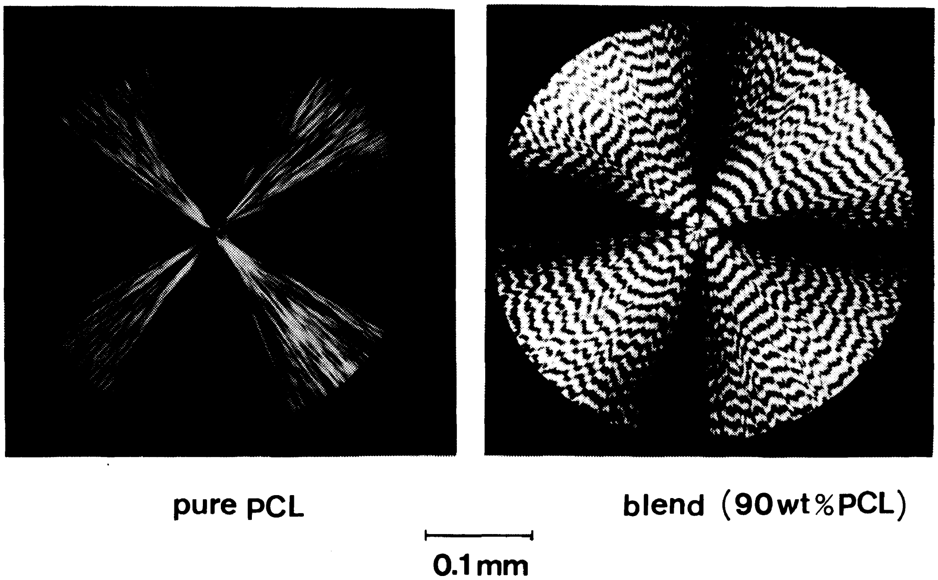

Figure 8. Typical photographs of the spherulite for pure PCL and the blend.

ethylene blend.[24] Figures 5 and 6 show the t_c dependence of the long period L, which is defined as the inverse of the wave number of the scattering peak. In both Figures, L is nearly constant or slightly decreased with t_c, though some decrease of L was observed at the initial stage of crystallization. Figure 7 shows T_c dependence of L. The period, L, slightly increased with T_c for the blend, and was nearly constant for pure PCL.

Figure 8 shows typical photographs observed for pure PCL and the blend. The spherulite

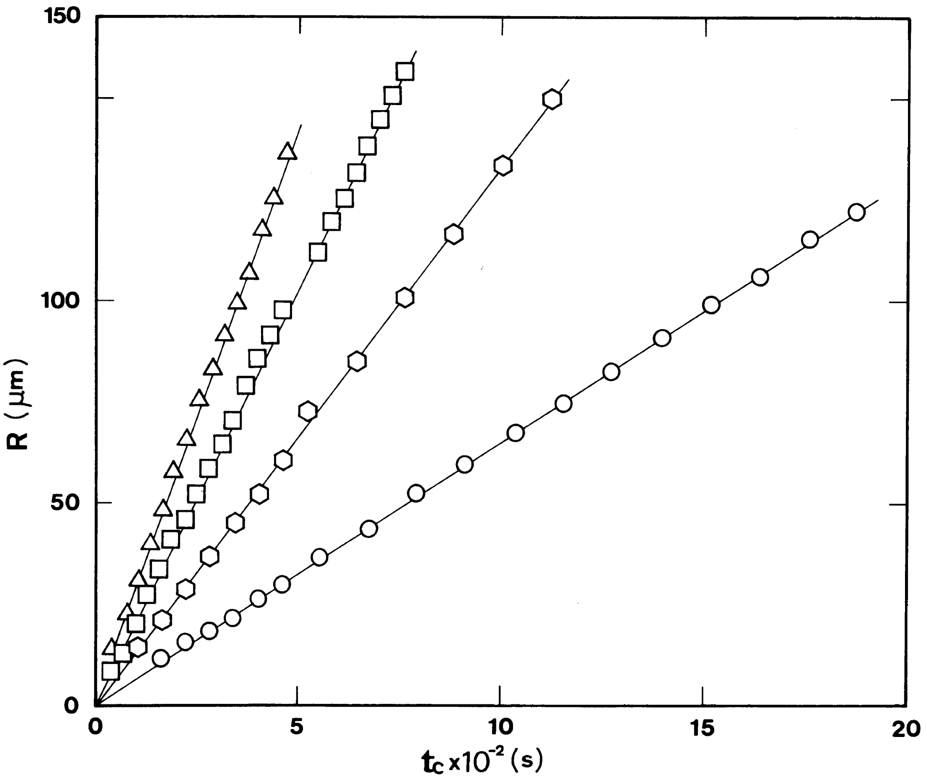

Figure 9. The spherulite radius against t_c for the blend: ○, $T_c=39.2°C$; ⬡, $T_c=37.8°C$; □, $T_c=35.1°C$; △, $T_c=33.2°C$.

for the blend had extinction rings at every T_c, but no ring was observed for pure PCL in the temperature range in this experiment. Our preliminary experimental results showed that the distance between the extinction rings became shorter and the ring itself became wider with the decrease of PCL content in the blend. Such behavior of the extinction ring must be related to the crystallization mechanism in the polymer blend. It is, however, still an open question why the extinction ring appears only in the blend and why the morphology of the spherulite changes with the PCL content in the blend. The t_c dependence of the spherulite radius R for the blend is shown in Figure 9. Although there was a large difference in the spherulite structure between pure PCL and the blend, R increased linearly with t_c for both samples. Such a linear growth has been reported for many crystalline polymers and polymer blends.[8] The slope of R gave the linear growth rate G of the spherulite which is shown in Figure 10. The rate G increased with the decrease of T_c. At the same T_c, G for pure PCL is larger than that for the blend, indicating that the crystallization of PCL in the blend is retarded by the addition of the amorphous polymer, PVC. The microscopic observation showed that the addition of PVC plays a complicated role in the course of crystallization.

DISCUSSION

Analysis by the Avrami Equation

The analysis of the crystallization of polymers is usually made by the use of the Avrami equation on the basis of a volume change

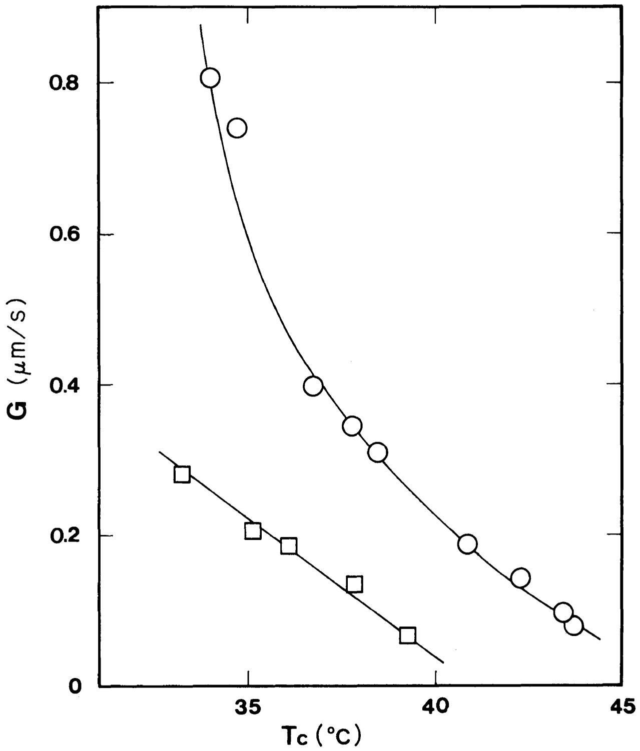

Figure 10. The linear growth rate G of the spherulite against T_c: ○, pure PCL; □, blend.

measured by dilatometry, an exothermic change by DSC, and an integrated intensity change of a specific reflection in wide angle X-ray scattering. The Avrami equation is written as:

$$\alpha = 1 - \exp\{-k(t_c - t_0)^n\} \qquad (1)$$

where α is the weight fraction of the sample transformed at crystallization time t_c, t_0 is the time at which crystallization begins, n is an integer characteristic of the nucleation type and the crystal growth geometry, and k is a constant related to the crystallization rate through the relation,[7]

$$\tau_{1/2}^n = \ln 2/k \qquad (2)$$

where $\tau_{1/2}$ is the half time of crystallization. The t_c dependence of I_m obtained in this study may be regarded as a measure of the crystallization of the sample. The process may be studied by applying the Avrami equation in the form:

$$I_m(t_c) = I_m(\infty) - \{I_m(\infty) - I_m(t_0)\} \times \exp\{-k(t_c - t_0)^n\} \qquad (3)$$

which is obtained from eq 1 assuming

$$\alpha = \{I_m(t_c) - I_m(t_0)\}/\{I_m(\infty) - I_m(t_0)\}$$

The parameters k and n in eq 1 are usually determined by plotting log{log(1 − α)} against log(t_c). In this study, eq 3 was directly fitted to the experimental data by adjusting the parameters, $I_m(\infty)$, k, n, t_0, and $I_m(t_0)$. The algorithm used in this fitting procedure is the Gauss–Newton method.

Whether the Avrami equation (eq 1) can be applied to the present data or not is beforehand deduced from a plot of $I_m(t_c)/I_m(\infty)$ ($\equiv \tilde{I}_m$) against $t_c/\tau_{1/2}^*$ ($\equiv \tilde{t}$), because if eq 1

Table I. Kinetic rate constant k, Avrami exponent n, and half time of crystallization $\tau_{1/2}$ (calculated by eq 3) and $\tau^*_{1/2}$ (obtained from Figures 2 and 3) for a pure PCL and a blend at various T_c

	T_c (°C)	n	$k^{1/n}$ ($s^{-1} \times 10^3$)	$\tau_{1/2}$ (s)	$\tau^*_{1/2}$ (s)
PCL	29.6	3.5	19.95	45	47
	33.6	2.9	11.47	77	74
	37.8	2.3	4.69	182	168
	38.0	2.2	3.88	217	200
	40.8	2.3	1.45	588	600
	40.9	2.2	1.60	529	500
	42.1	2.4	1.01	848	870
PCL/PVC	28.4	2.1	13.80	61	60
	32.1	1.9	5.80	142	130
	36.0	1.9	3.89	213	190
	37.8	—	—	—	230
	38.4	1.7	2.16	374	370
	39.6	1.7	1.58	511	530
	40.4	1.9	0.87	949	950

holds, the plot gives a sigmoidal curve dependent only on n as[25]:

$$\tilde{I}_m = 1 - \exp(-C\tilde{t}^n) \tag{4}$$

where C is a constant. In the present study, a plot of $\tilde{I}_m$ against $\tilde{t}$ for pure PCL formed a single curve at every T_c except for the two lower T_c, 29.6 and 33.6°C, indicating that t_c dependence of I_m was satisfied with the Avrami equation with the same n except for the above two cases.

Table I shows the parameters calculated, together with $\tau^*_{1/2}$ obtained from Figures 2 and 3. The values of $\tau_{1/2}$ obtained from the Avrami analysis using eq 2 agreed with $\tau^*_{1/2}$, indicating that $\tau^*_{1/2}$ could be regarded as a measure of crystallization rate. The Avrami exponent n shown in Table I was about 2 except for pure PCL at $T_c = 29.6$ and 33.6°C. Goldfarb *et al.*[26] obtained $n = 3$ for PCL with wide molecular weight distribution by a dilatometric method. Their experimental value of n could successfully be explained by the model of a three dimensional growth with the heterogeneous nucleation. In our study, however, the values of n were about 2 except those obtained at two lower T_c for pure PCL. There are many experimental results which show low n values ranging from 1 to 3.[27] It is also understood that the magnitude of n is dependent on many factors such as molecular weight of polymers, crystallization temperature and pressure, and the dimensionality of the crystallization. These factors effect sensitively the microscopic crystallization mechanism. The interpretation of the present magnitude of the Avrami exponent n requires additional information on the nucleation mechanism and growth geometry.

The significant increase of n with the decrease of T_c for pure PCL means that the nucleation mode and growth geometry vary with the decrease of T_c. Such a phenomenon has also been observed for pure crystalline polymers.[27] The Avrami exponent n for the blend, on the other hand, remained constant within the present experimental T_c. The present result, therefore, indicates that the addition of the amorphous component not only makes crystallization slower but also changes the nucleation mode and/or growth geometry.

During crystallization, the long period L of the alternate stacks of a lamella and an amorphous thin layer hardly changed if at all, though at the initial stage a slight decrease of L

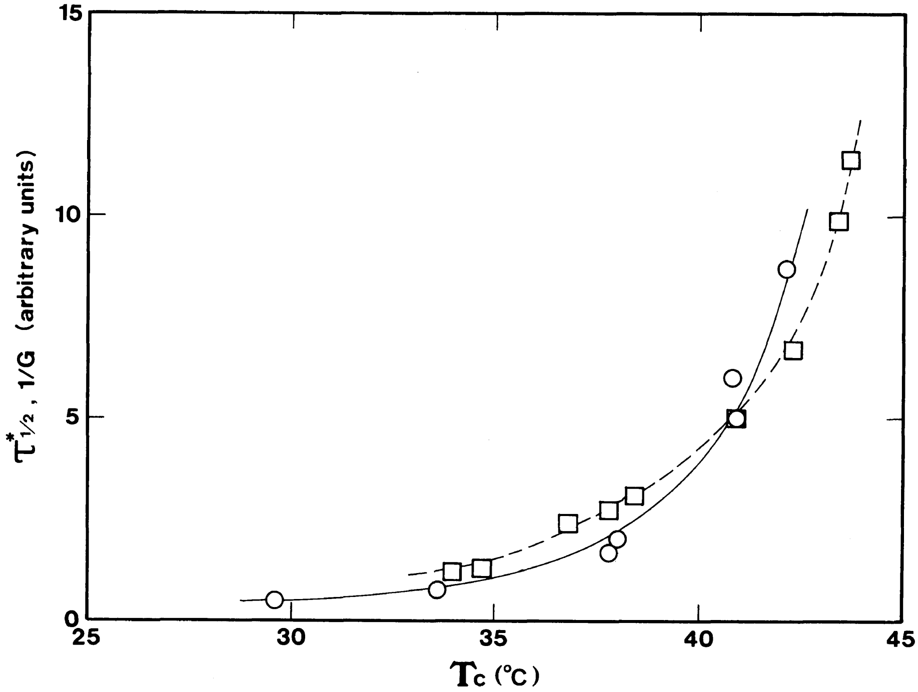

Figure 11. $\tau^*_{1/2}$ and $1/G$ against T_c for pure PCL: ○, $\tau^*_{1/2}$ from SAXS measurement; □, $1/G$ from microscopic observation.

was observed at every T_c for pure PCL and the blend, as shown in Figures 5 and 6. The decrease of L with t_c at the initial stage of crystallization was observed for oriented polybutadiene[28] and poly(ethylene terephthalate),[11] by analysis of the integrated intensity during crystallization. The decrease of the long period was attributed to the generation of new lamellae in the amorphous layers between lamellae[28] or the rearrangement of lamellae.[11] For polyethylene at higher T_c, however, it was reported that the long period was nearly constant throughout the crystallization.[29] For poly(ethylene terephthalate) it was also found[11] that variation of the long period for a sample with lower molecular weight was smaller than that for one with higher molecular weight. Thus, the behavior of the long period in the crystallization process depends intimately on polymers and factors such as T_c and molecular weight. The crystallization temperatures in the present study are rather high and close to T_m and the molecular weight of PCL is relatively low.

Comparison of SAXS Data with Spherulite Observation

The inverse of the linear growth rate of the spherulite, $1/G$, is the time necessary for the growth of a lamella of the unit length. Thus it may be considered as a measure of the time necessary for crystallization, as the case of $\tau^*_{1/2}$. The T_c dependences of $\tau^*_{1/2}$ and $1/G$ for pure PCL are shown in Figure 11, where two curves were scaled so as to lie on nearly the same level. Their T_c dependences are very similar to each other; at the higher T_c both increase abruptly, and at the lower T_c both decrease asymptotically to zero. A similar result was obtained for the blend. Figure 11 indicates that regardless of the difference in the dimensions observed by the SAXS method and an optical microscope, the two methods give similar results for the time necessary for crystallization. It is also concluded by the two experiments that though the addition of an amorphous component PVC effected the spherulite structure of PCL significantly, it contributed only to the retardation of crystallization from the standpoint of the macroscopic crystallization process.

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