Morphology and Electrical Properties of Carbon Black-Filled Poly(ε-caprolactone)/Poly(vinyl butyral) Blends

JEONG-CHANG LEE, TAKAYUKI IKEHARA, TOSHIO NISHI

Department of Applied Physics, School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

ABSTRACT: Electrical properties of poly(ε-caprolactone) (PCL)/poly(vinyl butyral) (PVB) blends containing carbon black (CB) were studied as a function of a small amount of PVB content and a wide range of molecular weight of PVB. For samples with the same CB content, the intensity of positive temperature coefficient (I_{PTC}, defined as the ratio of peak resistivity to resistivity at room temperature) of the blends was increased, with PVB content greatly and molecular weight of PVB weakly. As the band spacings of PCL spherulites in PCL/PVB blends decrease with PVB content and molecular weight of PVB, the changes of the positive temperature coefficient property are ascribed to the morphological difference (i.e., period of twisted lamellae) in the blends. We confirmed our previous conclusion that the origin of the positive temperature coefficient phenomenon is the changes of the distribution of the CB on the melting of the crystalline phase. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 193–199, 1998

Key words: poly(ε-caprolactone); poly(vinyl butyral); polymer blend; positive temperature coefficient; carbon black

INTRODUCTION

It is well known that the electrical resistivity of the insulating polymers can be decreased by dispersing a conductive filler [e.g., carbon black (CB)] throughout the polymer matrix. A crystalline polymer filled with certain amount of CB shows a sharp increase in resistivity with temperature around the melting point of the polymer [positive temperature coefficient (PTC)].[1] In the past two decades, a considerable amount of research has been conducted to understand the PTC phenomenon.[2–6] However, no satisfactory theory to explain the PTC phenomenon has been reported in the literature, whereas industrial application of PTC materials has been developed in many aspects.

On the other hand, the effect of blend morphology on the electric conductivity of CB-filled polymer blends was reported based on the percolation theory.[7–13] The critical amount of CB necessary to build up a continuous conductive network is referred to as the percolation threshold, and several blends were reported to conduct at a much lower volume fraction of CB than expected theoretically. This low threshold was explained by double percolation. In this idea, either one of the two polymer phases is continuous, and CB particles are localized in the continuous phase, or the two phases are cocontinuous and the CBs are at the interface. However, these studies were focused on the continuous conductive network of conducting component in the matrix, not directly on the PTC phenomenon. On the other hand, it is certain that the conductivity of the polymer blends is sensitively influenced with the morphology of the blends. In line with this idea, we have reported the electric properties of poly(ε-caprolac-

tone) (PCL)/poly(vinyl butyral) (PVB) blends containing CB in our previous work.[14] Because the morphology of the PCL/PVB blends is changed greatly by blending a small amount of PVB,[15–17] both the resistivity and the intensity of PTC increased significantly by blending PVB. We explained that these changes in the PTC property were ascribed to the morphological difference (i.e., cooperatively twisted lamellae in the blends) between PCL/PVB blends and pure PCL, as shown in Figure 1.

In the present study, we focus on a unique approach that relies on the complexity of the displacement of CB induced by the twisted lamellae in the melting process. We investigate the PTC properties as a functions of PVB content and molecular weight of PVB. A morphological difference in PCL/PVB blends containing CB is expected to influence the PTC properties.

EXPERIMENTAL

Materials and Sample Preparation

A list of the materials used in this study is shown in Table I. CB was used as a conductive filler. A PCL master batch containing 40 phr (phr, parts per hundred resin) CB was made using a roll mixer. The PCL/PVB blends containing 5 vol % CB with varying PVB fraction (0–5 wt %) were prepared by adding pure PCL and PVB to the PCL master batch dissolved in a common solvent tetrahydrofuran. Uniform thin films were prepared by casting the solutions. After the solvent was removed at room temperature, the samples were kept under vacuum at 40°C for 1 week.

Electrical Resistivity Measurements

Figure 2 shows the schematic illustration of sample configuration. The film sample (15 mm long, 8 mm wide, and 0.1 mm thick) was placed between glass plates. Silver paste (Fujikura kasei, Dotite 500) was painted on each end of the sample surface to ensure electrical contact with the electrodes. The current and the voltage between the electrodes were measured with a Keithly 480 picoammeter and a Keithly 195A digital multimeter. The power supply was a Metronix DMS 35–1.5. In an earlier article,[14] we have reported that the temperature-resistivity curve of isothermally crystallized sample shifted upward relative to the solvent-cast sample as a result of the heating-cool-
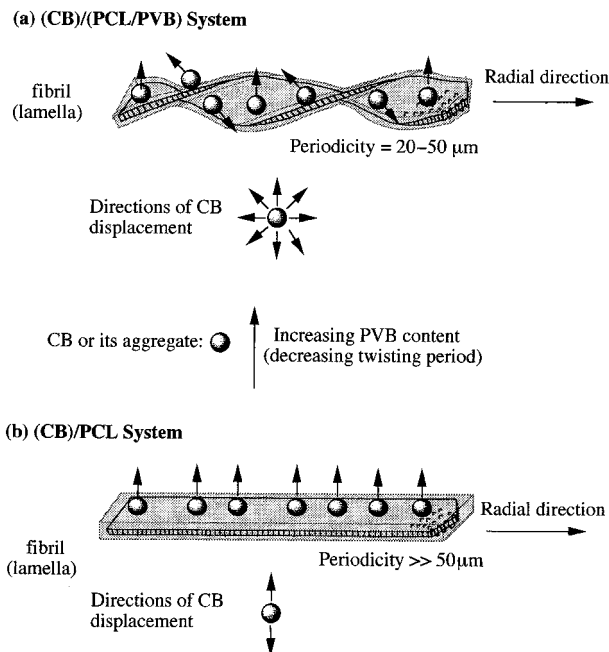
(a) (CB)/(PCL/PVB) System

(b) (CB)/PCL System

Figure 1 Schematic presentation of possible directions of the displacement of CB particles and aggregates around a lamella (or a fibril) in a PCL/PVB blend. In the melting process, the volume expansion and the molecular motion of polymer chain displace CB particles, which are located near the lamella (shaded area). Increasing the PVB, the period of lamella twisting is shortened and it will cause more complex displacement of CB. The more random distribution of the interparticle gaps is achieved with a shorter periodicity. (a) A PCL/PVB blend, periodicity = 20–50 μm. (b) Pure PCL, periodicity $\geqslant$ 50 μm (ref. 14).

ing cycle. However, there were no noticeable differences in PTC intensity I_{PTC} between the isothermally crystallized samples and the solvent-cast samples. In this article, we report the PTC property of the solvent-cast sample. Solvent-cast samples were heated at 2°C min^{-1} to 80°C during resistivity measurement. We measured at least three samples for a given blend, and we report the mean value herein.

Differential Scanning Calorimetry (DSC)

TA Instruments DSC 2910 with a Thermal Analyst 2000 was used to determine the melting temperature and the degree of crystallinity of PCL crystals in the blends. The degree of crystallinity of PCL was calculated from the area of melting endotherms, using the value of the heat of fusion of 100% crystalline PCL ($\Delta H^0_{\mathrm{PCL}} = 136$ J g^{-1}) and

Table I   Characteristics, Sources, and Codes of the Materials

Material	Source	Code	M_w	T_g (°C)[a]
PCL	Polysciences, Inc.	PCL	35,000	−63
PVB	Polysciences, Inc.	PVB(38K)	38,000	61
PVB	Polysciences, Inc.	PVB(100K)	100,000	58
PVB	Polysciences, Inc.	PVB(180K)	180,000	66
PVB	Polysciences, Inc.	PVB(305K)	305,000	63
CB	Cabot Co.	CB (Vulcan XC-72)	—	—

[a] Measured by DSC using a scan rate of 20°C min^{-1}.

normalized with respect to blend composition. The scan rate was 2°C min^{-1}.

Optical Microscopic Observation

To study the effect of PVB blending on the band spacings of PCL spherulite, samples without CB sandwiched between two cover glasses were observed under a polarizing microscope (OLYMPUS BHA-P) equipped with a temperature controller (LINKAM TH-600). The samples were heated to 80°C for 1 h and then rapidly cooled to the crystallization temperature (T_c). Photographs were taken during crystallization.
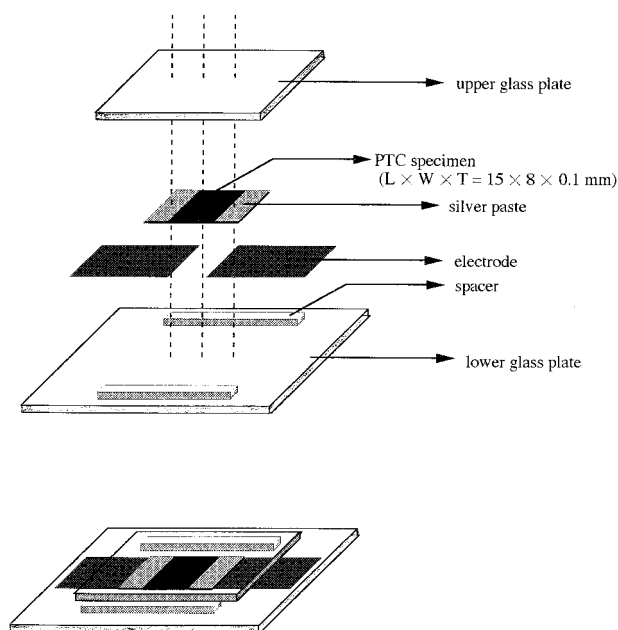

Figure 2   Schematic illustration of the sample configuration.

RESULTS AND DISCUSSION

Band Spacing of PCL Spherulites in PCL/PVB Blends

Figure 3 shows polarized optical micrographs of various PCL/PVB blends without CB crystallized at 41°C. Large spherulites were observed in the blends, because the nucleation density of PCL is depressed with the addition of small amount of PVB. The regularity of the extinction bands increased with PVB content, and the onset of banding is observed to occur in the blends containing PVB as small as 0.5%. Band spacings are decreased with increasing PVB concentration, and this indicates that increasing the PVB content shortens the period of lamellar twisting.[15,16] However, the spacings varied from place to place even in the same spherulite, and quantitative comparison was impossible in Figure 3.

On the other hand, Urai and colleagues[16] analyzed the changes of band spacings in PCL/PVB blends without CB quantitatively using digital image analysis. They used the phase-contrast microscope rather than conventional polarizing microscope to exclude the Maltes cross in analyzing the band spacings and reported that the band spacing decreased when the concentration of the PVB in the blends increased. Finally, they showed the relationship between the band spacing L and the concentration of PVB ϕ_{PVB} as

$$L \sim \phi_{\text{PVB}}^{-x},$$

where x is 0.2–0.3. They also reported that the band spacing was a function of the molecular weight of PVB. Band spacing decreased with the molecular weight of PVB at the same blend composition. However, the influence of PVB concentration on the band spacings of the blend was more profound than that of the molecular weight
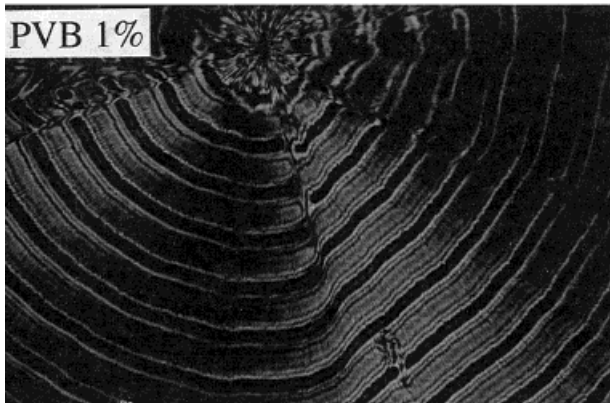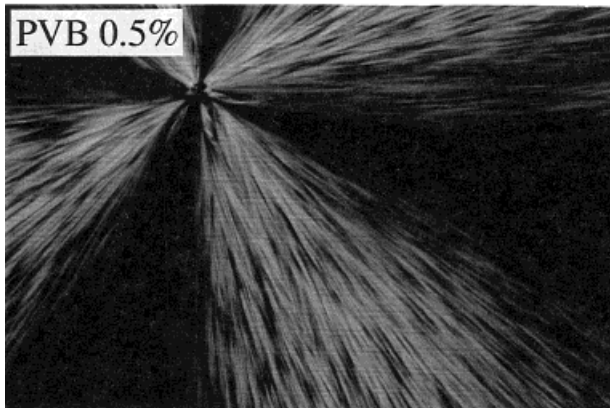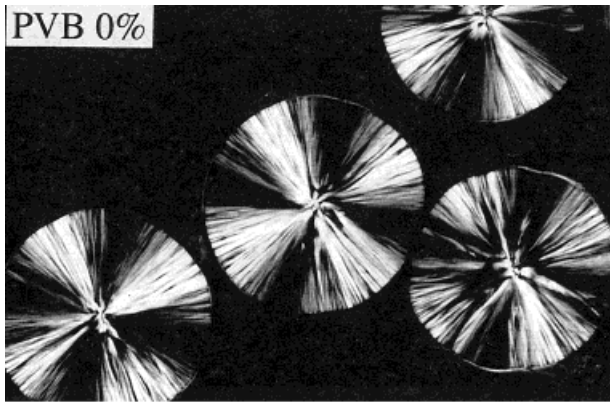
Figure 3 Cross-polarized optical micrographs describing the extinction rings of PCL/PVB spherulites crystallized at 41°C. All samples are without CB.

of PVB. If our previous conclusion[14] was correct (see Fig. 1), PTC property of the PCL/PVB blends should be dependent on the blend composition and

the molecular weight of PVB. We verified these two facts as described in the next sections.

Influence of PVB Concentration

Figure 4 shows the effect of the PVB blend ratio on the PTC properties containing the same amount of CB. The M_w of the PVB was 100,000. The intensity of PTC I_{PTC}, defined as the resistivity ratio ρ_{max}/ρ_{min}, increased with the PVB blend ratio. Herein, ρ_{max} is the maximum value of the PTC curve, and ρ_{min} is the resistivity at room temperature. Figure 5 and Table II show the summary of these results. We measured at least three specimens for a given blend ratio, and the mean values of I_{PTC} were plotted. By blending as small as 0.5% PVB, I_{PTC} increased more than 30 times than that of pure PCL. For the blend samples, the I_{PTC} increased with ϕ_{PVB}. Surprisingly, I_{PTC} of the blend with 5% PVB was larger than that of pure PCL by almost 3 orders of magnitude. Note that
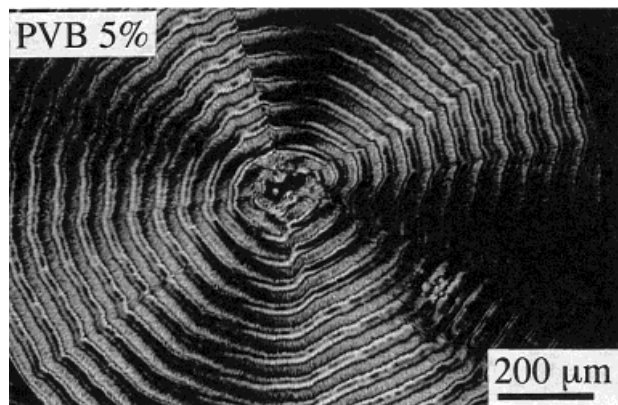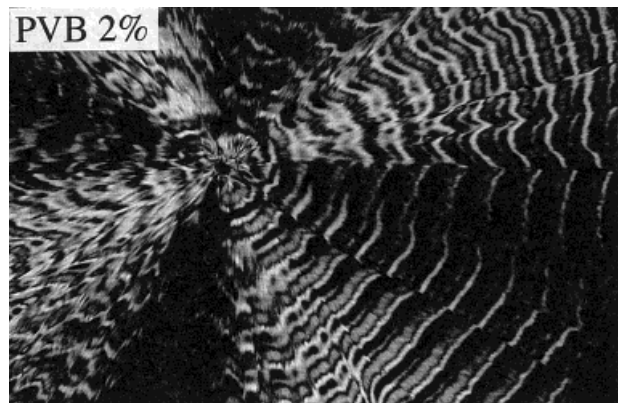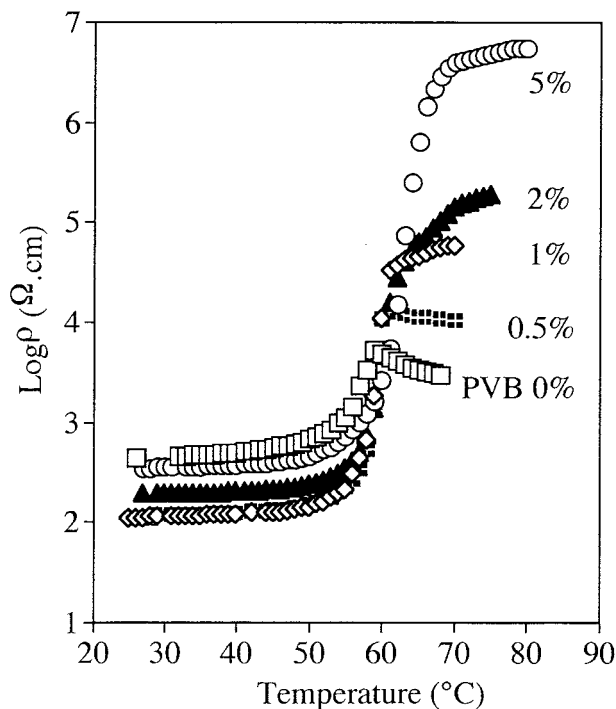

Figure 3 (*Continued*)

Figure 4 Typical temperature-resistivity curves of solvent-cast PCL/PVB blends containing 5 vol % CB, which is dependent on the small amount of PVB content.

Figure 5 Dependence of PTC intensity I_{PTC} of solvent-cast PCL/PVB blends containing 5 vol % CB on the PVB content. The molecular weight of PVB was 100,000. Solid line is drawn as a guide.

these blends had the same amount of CB, and the difference was only in the PVB blend ratio. Additionally, to verify the fact that the drastic changes in PTC properties do not come from the changes in crystalline properties of PCL, we examined melting temperatures and degree of crystallinities of the solvent-cast blends. Figure 6 shows DSC thermograms of the blends containing 5 vol % CB. No noticeable changes in melting temperatures and degree of crystallinities were observed within experimental error (Table III). The same results were reported by other researchers using the PCL/PVC system.[18,19] The cause of the drastic changes in PTC property of the PCL/PVB blend with varying PVB content will be discussed in the next section.

Influence of the Molecular Weight of PVB

Figure 7 and Table IV show the effect of the PVB molecular weight on the PTC properties. Blends were filled with 5% CB, and the blend composition was 99.5 : 0.5. I_{PTC} of the blends also increased with molecular weight of PVB, as in the case of varying PVB blend composition. However, the influence of the molecular weight of PVB on the I_{PTC}
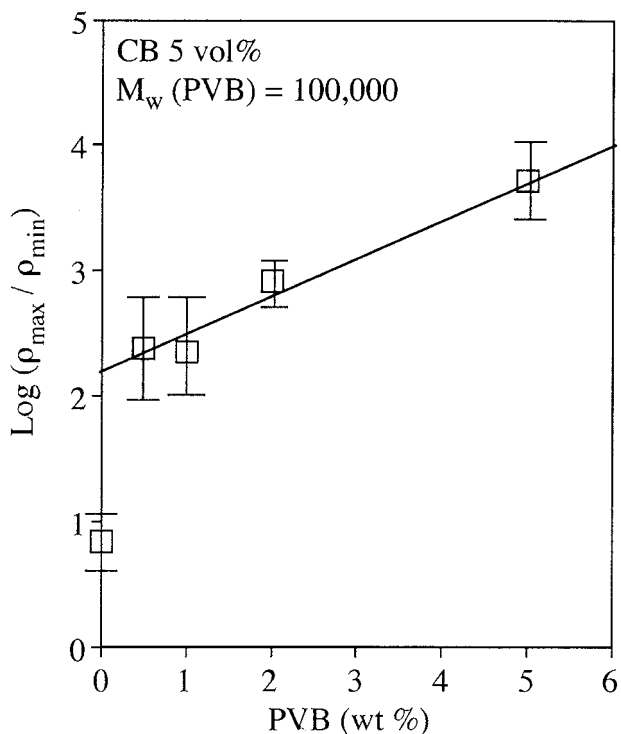
was less profound than that of the PVB concentration. When we compare the results obtained from the microscopic observations of the band spacings of spherulites in the section on Band Spacing of PCL Spherulites in PCL/PVB Blends, and the resistivity changes in the sections on the Influence of PVB Concentration and the Influence of the Molecular Weight of PVB, we can find interesting relationships between the two different measurements. With increasing PVB concentration in PCL/PVB blends, the band spacing decreased, whereas the intensity of PTC increased. Band spacing of the blends also decreased with the molecular weight of PVB at the constant blend com-

Table II   Values of I_{PTC} of Solvent-Cast PCL/PVB Blends Containing 5% CB

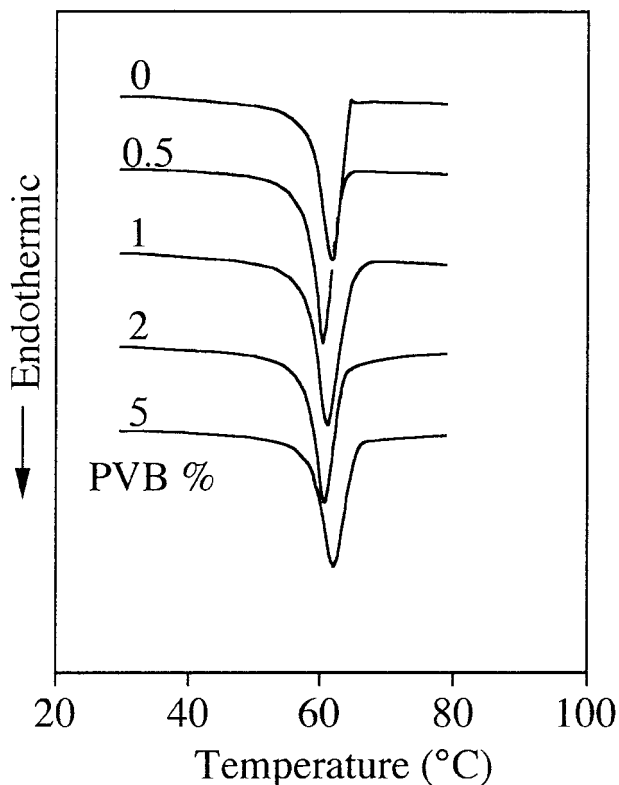|	PCL : PVB				
	100 : 0	99.5 : 0.5	99 : 1	98 : 2	95 : 5
I_{PTC}	7	240	230	830	5300

PVB had a molecular weight of 100,000.

Figure 6 DSC melting endotherms of solvent-cast PCL/PVB blends containing 5% CB, with various amounts of PVB. Scanning rate was 2°C min^{-1}.

Figure 7 Dependence of PTC intensity I_{PTC} of solvent-cast PCL/PVB blends containing 5 vol % CB on the molecular weight of PVB. All blends have the same PVB content. Solid line is drawn as a guide.

position, whereas the PTC intensity I_{PTC} increased. Finally, the influence of PVB concentration was more profound than that of the molecular weight of PVB in both measurements. This relationship indicates that the PTC property is originated from the following process: increasing the PVB content or the molecular weight of PVB shortens the period of lamellar twisting and causes more complex displacement of CB in the melting process; this increases the I_{PTC} according to Ohe's theory.[4,14] The results obtained in this study agree with the results shown in our previous article.[14] Therefore, we confirmed the origin of the PTC phenomenon again using the drastic
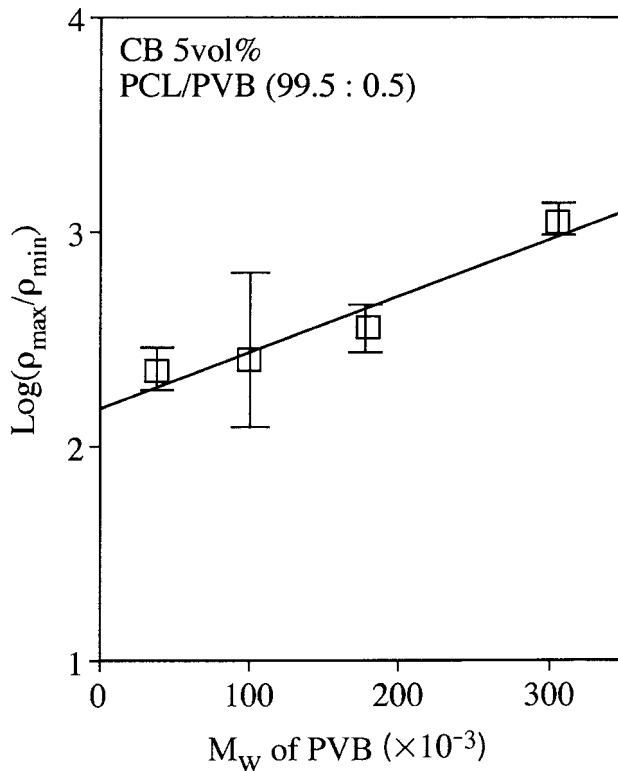
morphology changes induced by blending a small amount of PVB.

CONCLUSIONS

1. In PCL/PVB blends containing CB, the PTC property changes greatly with PVB concentration or molecular weight of PVB.
2. The changes of PTC property are ascribed to the morphological difference (i.e., period of lamellar twisting) between the blends and pure PCL. As the increase of the PVB concen-

Table III   DSC Endotherm Peak Temperature T_m and Degree of Crystallinity of Solvent-Cast PCL/PVB Blends Containing 5 Vol % CB

	PCL : PVB				
	100 : 0	99.5 : 0.5	99 : 1	98 : 2	95 : 5
T_m (· C)	62.1	60.8	61.3	61.0	62.3
Degree of crystallinity (%)	61	64	63	64	58

Table IV   Molecular Weight Dependence of the Values of I_{PTC} of Solvent-Cast PCL/PVB Blends Containing 5% CB

	M_w (PVB)			
	38,000	100,000	180,000	305,000
I_{PTC}	220	240	360	1,100

PVB blend ratio was 99.5 : 0.5.

tration or the molecular weight of PVB shortens the period of lamellar twisting, this increases the displacement of the CB more randomly in the melting process. Therefore, with decreasing band spacings, the PTC intensity I_{PTC} increases.

3. We confirmed that the origin of the PTC phenomenon is based on the changes of the distribution of the CB (or interparticle gap between CB) on the melting of the crystalline phase.

REFERENCES

1. M. Narkis, A. Ram, and F. Flashner, *Polym. Eng. Sci.,* **18,** 649 (1978).
2. J. Mayer, *Polym. Eng. Sci.,* **14,** 706 (1974).
3. J. Mayer, *Polym. Eng. Sci.,* **13,** 462 (1973).
4. K. Ohe and Y. Naito, *Jpn. J. Appl. Phys.,* **10,** 99 (1971).
5. M. Narkis, A. Ram, and F. Flashner, *J. Appl. Polym. Sci.,* **22,** 163 (1978).
6. M. Narkis, A. Ram, and Z. Stein, *J. Appl. Polym. Sci.,* **25,** 1515 (1980).
7. M. Sumita, K. Sakata, S. Asai, K. Miyasaka, and H. Nakagawa, *Polym. Bull.,* **25,** 265 (1991).
8. M. Sumita, K. Sakata, Y. Hayakawa, S. Asai, K. Miyasaka, and M. Tanemura, *Colloid Polym. Sci.,* **270,** 134 (1993).
9. M. Reghu, C. Yoon, C. Yang, D. Moses, A. Heeger, and Y. Cao, *Macromolecules,* **26,** 7245 (1993).
10. K. Levon, A. Margolina, and A. Z. Patashinsky, *Macromolecules,* **26,** 4061 (1993).
11. F. Gubbles, R. Jerome, P. Teyssie, E. Vanlathem, R. Deltour, A. Calderone, V. Parente, and J. Bredas, *Macromolecules,* **27,** 1972 (1994).
12. F. Gubbles, S. Blacher, E. Vanlathem, R. Jerome, R. Deltour, F. Brouers, and P. Teyssie, *Macromolecules,* **28,** 1559 (1995).
13. M. A. Knackstedt and A. P. Roberts, *Macromolecules,* **29,** 1369 (1996).
14. J. C. Lee, K. Nakajima, T. Ikehara, and T. Nishi, *J. Appl. Polym. Sci.,* **65,** 409 (1997).
15. H. D. Keith, F. J. Padden, Jr., and T. P. Russell, *Macromolecules,* **22,** 666 (1989).
16. Y. Urai, T. Ikehara, T. Nishi, *Trans. Mater. Res. Soc., Jpn.,* **15A,** 221 (1994).
17. J. C. Lee, K. Nakajima, T. Ikehara, and T. Nishi, *J. Appl. Polym. Sci.,* **64,** 797 (1997).
18. S. Nojima and H. Tsutsui, *Polymer J.,* **18,** 451 (1986).
19. S. Nojima and K. Watanabe, *Polymer J.,* **20,** 823 (1988).