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Small angle X-ray diffraction study of blends of nylon 6 and a liquid crystal copolyester

Dedicated to the memory of Prof. Fatou

I. Campoy, M.A. Gómez*, C. Marco

Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain

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Abstract

Small angle X-ray diffraction (SAXS) analysis of blends between nylon 6 and the liquid crystal copolyester Vectra has been performed as a function of composition and thermal treatment in order to make a correlation with the thermal and structural properties of these systems and to get information about their morphological characteristics. Simultaneous small and wide angle X-ray diffraction experiments using synchrotron radiation have been carried out in dynamic experiments to investigate in real time the polymorphic transformations that occur with increasing temperature and the structural changes observed during the melting process. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Small angle X-ray diffraction; Nylon 6; Liquid crystal

1. Introduction

Small angle X-ray diffraction (SAXS) is one of the most useful techniques for structural investigation of solid polymers. In particular, SAXS can provide information about morphological features such as void size, crazing, component segregation in copolymers and lamellar structure of crystalline polymers [1–3].

The use of synchrotron radiation has opened new possibilities to these X-ray studies. The radiation produced in electron or positron storage rings allows to obtain monochromatic beams far more intense than conventional X-ray sources [4,5]. For this reason, it is possible to record SAXS patterns in very short times and to follow, in real time, the structural changes occurring during crystallization, melting and processing of polymers [6–8].

On the other hand, SAXS techniques have also proved to be very useful in the study of polymer blends [9–17]. Particularly, these techniques can give information about the morphology [9,13], phase separation [15] and interlamellar, interfibrillar or interspherulitic placement of the non-crystallizable component [10,16,17].

In this paper, a SAXS study of blends of nylon 6 (N6) and the commercial liquid crystal copolyester Vectra has been performed by using synchrotron radiation. In a previous article, the thermal and structural properties of these blends have been analysed as a function of composition and thermal history [18]. It has been found by wide angle X-ray scattering (WAXS) that the liquid crystal component affects the polymorphic behaviour of nylon 6. In this work, these data are going to be correlated with the changes in the SAXS parameters such as long spacing or invariant.

A previous study of the crystallization kinetics of these N6/Vectra A blends has also been carried out in our group [19], and the calorimetric data were interpreted with the WAXS and SAXS diffraction data obtained from the synchrotron experiments. To the best of our knowledge, no other SAXS study or information about the lamellar morphology of these type of blends has been published.

2. Experimental

The commercial product Vectra A 950 from Hoechst Iberica S.A. is the thermotropic liquid crystal copolyester used in this work. This is a wholly aromatic copolyester consisting of 27 mol% of 2-6 hydroxynaphthoic acid (HNA) and 73 mol% of *p*-hydroxybenzoic acid (HBA). Nylon 6 Akulon K123 was supplied by La Seda S.A.

Eleven compositions of blends N6/Vectra were prepared in the ratios of 100/0, 99/1, 98/2, 95/5, 90/10, 85/15, 70/30, 50/50, 30/70, 15/85 and 0/100 by weight. The blending procedure was reported elsewhere [18].

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[*] Corresponding author.

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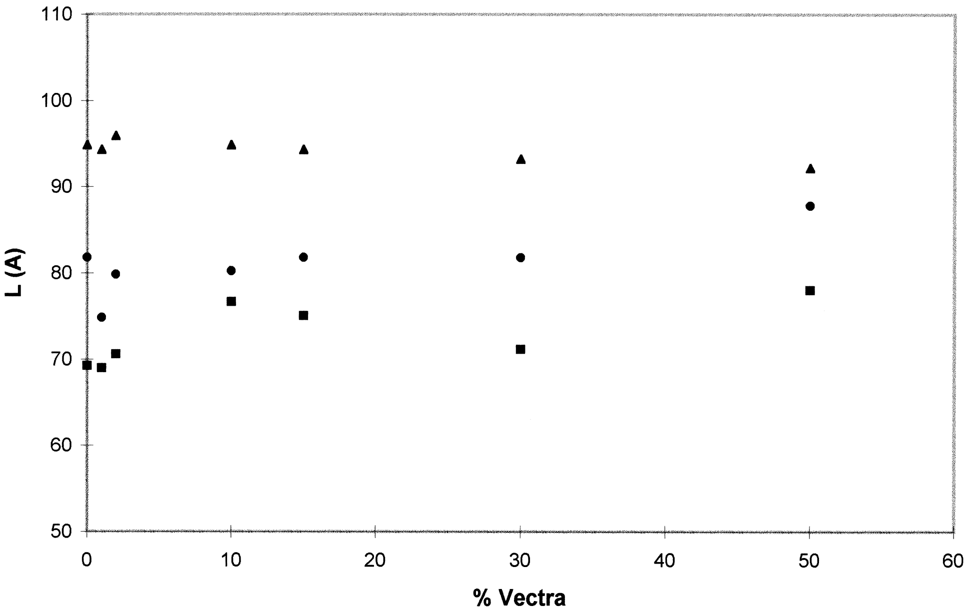

Fig. 1. Plot of the long spacing values as a function of the Vectra A content for (■) quenched (●) original and (▲) annealed samples.

The blends obtained directly from the Haake Rhecord System 60 were prepared as powder samples by grounding and as films by compression moulding at 290°C and 130 bar and quenching down to room temperature with circulating water. These samples were named as original and quenched samples, respectively. In other cases, quenched samples were annealed at 190°C and cooled down to room temperature, as it was described in a previous paper [18]. These samples are referred to as annealed samples.

SAXS and WAXS diffraction patterns were recorded using synchrotron radiation at the polymer beam line at Hasylab (DESY, Hamburg). Further details concerning the instrument and the data analysis are given elsewhere [4,19,20]. The SAXS patterns were obtained at room temperature for the samples with the thermal treatments indicated above. In another set of experiments, original and quenched samples were heated from room temperature to 300°C at a heating rate of 10°C min^{-1} and the SAXS diffractograms were recorded in real time.

3. Results and discussion

A SAXS study of N6/Vectra A blends has been carried out at room temperature as a function of composition for samples with different thermal histories as indicated in the Section 2. A thermogravimetric study of these systems has been previously done in order to discard degradation effects due to the applied thermal treatments [21].

The corresponding long spacing values obtained for original, quenched and annealed samples are shown in Fig. 1 as a function of blend composition. The long spacing values for the original samples are in the same order than those previously reported for nylon 6 [13,22–24], while the values found for the quenched samples are slightly lower than the original ones. These values show a small increase with the liquid crystal content in both cases. However, when the quenched samples are annealed at 190°C and then cooled down to room temperature, the long spacing increases to reach a value close to 95 Å and appears to decrease with blend composition. For each blend composition, there is the expected increase in the long spacing due to an increase in the crystal size with the annealing process. However, the apparent decrease of the long spacing for the annealed samples with increasing Vectra may indicate that the liquid crystal component has been excluded during the thermal treatment.

However, the long spacing values have been correlated not only with the thermal treatment but with the polymorphic structure observed in nylon 6 [23–25]. It has been reported in our group [18] that two different polymorphic forms named as α and γ^* can be observed for the nylon 6 component in the nylon 6/Vectra A blends depending on composition and thermal treatments. Both polymorphs coexist for N6 pure original sample. When the sample is quenched, γ^* is mainly observed, but the annealing of the quenched sample at 190°C enhances the development of the α-form. This behaviour is also found in the Nylon 6/Vectra A blends, but it has been observed that the increasing content of the liquid crystal copolyester favours the formation of the α form in all the cases.

Illers et al. [23] reported the long spacing values obtained for nylon 6 samples with different percentage of α and γ^* forms. They found an increase of the long spacing values with the α form content, from 67 Å for the pure γ^* form to 114 Å when only the α form is observed. These results completely agree with the data shown in Fig. 1. The increase of long spacing with the liquid crystal content observed in

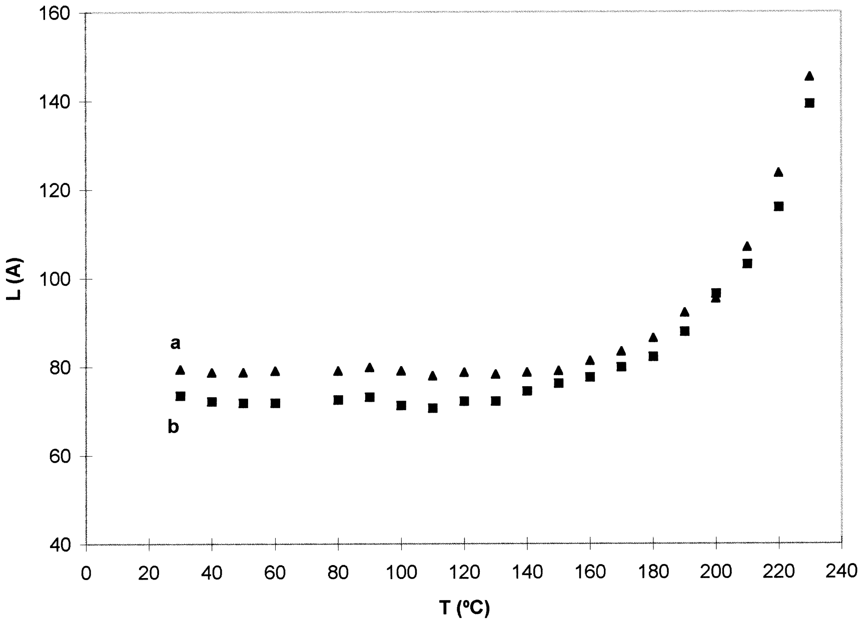

Fig. 2. Plot of long spacing values as function of temperature for the 85/15 blend composition: (a) original and (b) quenched.

the original and quenched samples can be related with the development of the α crystalline form due to the increasing proportion of Vectra in the blends.

In our case, the enhancement of the long period data as the Vectra content increases is moderate and a minimum in the long spacing values is observed for liquid crystal content lower than 15% in the original samples. These results may agree with previous studies about the isothermal crystallization of these Nylon 6/Vectra A blends [19] that showed that a partial miscibility between the blend components occurs in the amorphous phase at early stages of the crystallization process for the lower Vectra content compositions. In the case of the 85/15 blend composition, the liquid crystal component is completely rejected from the interlamellar region at the beginning of the process [19].

In the case of the quenched samples considered in this work, the fast cooling process does not allow the completely segregation of the Vectra component. The long period values are lower than those obtained for the original samples with the same composition as the stronger cooling conditions leads to lower crystalline sizes and higher percent of the γ^* crystalline form as it was indicated previously.

The annealing of the quenched samples at 190°C favours the formation of the α crystalline form because its crystallization rate is higher in this temperature range as it was previously reported [18,19]. For that reason, the corresponding long period values increases and that behaviour is more evident for the samples with lower Vectra content in which the percentage of the γ^* form is higher prior to annealing.

The melting behaviour of the thermal treated samples have also been investigated by SAXS, and the obtained results have been interpreted according to previous DSC and WAXS studies [18]. The corresponding values of long period obtained from the maximum of the SAXS curve are plotted in Fig. 2 versus temperature for the original and quenched 85/15 N6/Vectra samples. It can seen that the long spacing values stay almost constant with the temperature at $T < 150°\text{C}$ in both cases, and the long spacing data obtained for this quenched sample are always lower than that for the original samples at temperatures below 150°C. For higher temperatures, the long period values increase strongly with temperature in both cases and the differences observed between both samples decrease.

In order to explain this behaviour, the SAXS results have been compared with the simultaneously obtained WAXS data. It can be seen that the quenched sample exhibits a higher percent of the γ^* form than the original sample at temperatures $T \leq 150°\text{C}$ and that justify the lower long period values observed for this sample in this temperature range as it was pointed out above. At temperatures $T > 150°\text{C}$, the WAXS patterns are very similar for both samples and the α form is predominant and that agrees with the increase of the long spacing observed getting similar values in both cases. The increase in the long spacing at temperatures close to the melting temperature has been previously reported for other systems [7,8,26].

In order to get more information about the structural changes that occur during the melting process, the area under the crystal reflections, A_c, and the invariant, Q, have been compared. The shape of this curve approximately corresponds to the diffractogram obtained for the completely molten material. The A_c values are related to the degree of crystallinity (x_c) as follows:

$$A_c = \int_0^\infty I_c s^2 \, ds \tag{1}$$

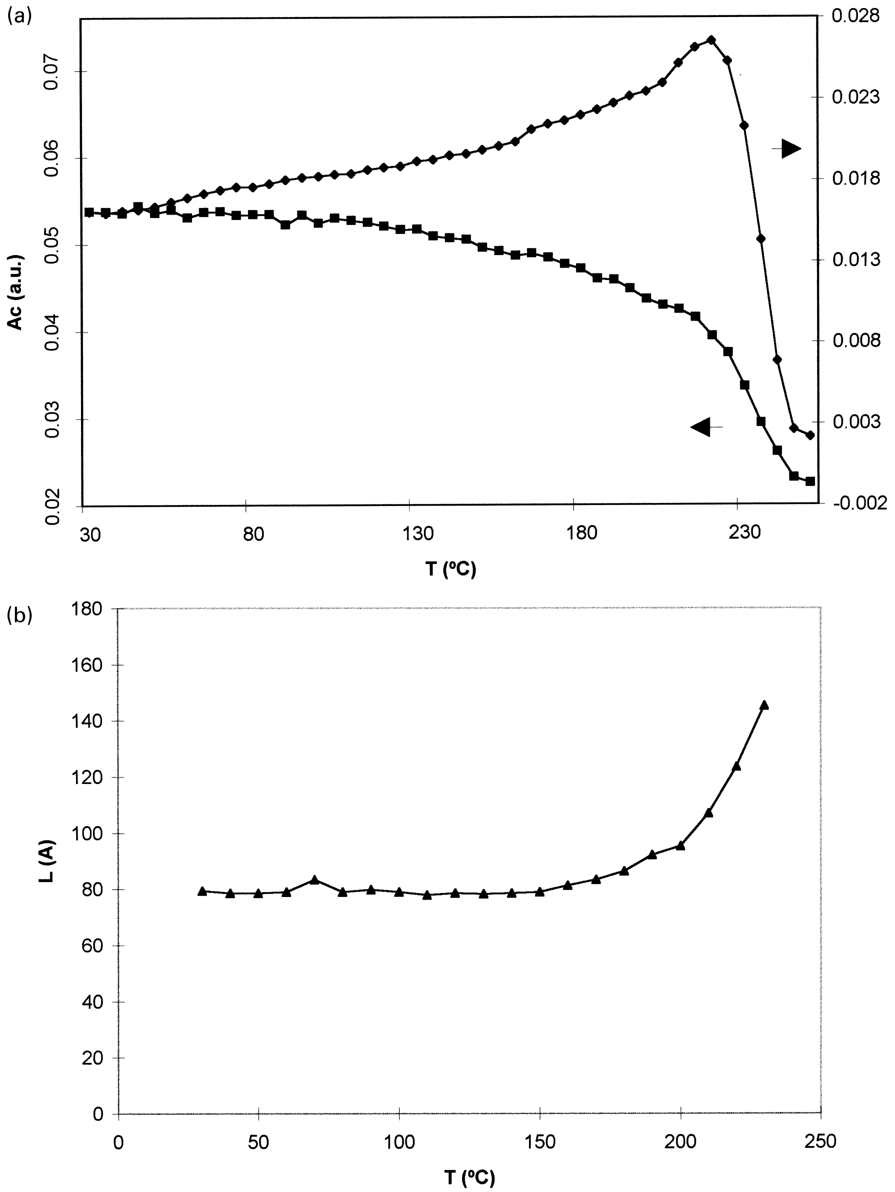

Fig. 3. Plot of (a) A_c, Q and (b) L values versus temperature for the 85/15 blend composition, original sample.

$$x_c = A_c / \int_0^\infty Is^2 \, ds \qquad (2)$$

I is the total scattering intensity, I_c is the scattering intensity of the crystal reflections and s is the scattering vector.

The invariant Q that can be obtained from the SAXS experiments, is defined as

$$Q = 4\pi \int_0^\infty Is^2 \, ds \qquad (3)$$

where I is the scattering intensity normalized to the intensity of primary beam and the volume of the sample. The invariant can also be defined considering the supramolecular structure:

$$Q = x_s x_L x_{cL}(1 - x_{cL})(\Delta\rho)^2 \qquad (4)$$

being x_s the volume fraction filled with spherulites, x_L the volume fraction which has been transformed into lamellar stacks, x_{cL} the crystallinity within the spherulites and $\Delta\rho$ the difference between the densities of the crystalline and that of the amorphous region. When the growth of the spherulites is finished and all the superstructures are completely filled with lamellar stacks, x_s and x_L are equal to 1. The degree of crystallinity x_c can be defined as a function these parameters by the following expresion:

$$x_c = x_s x_L x_{cL} \qquad (5)$$

It is clear from this expression that if some lamellar stacks are melting inside the spherulites, x_L decreases and for that, Q and A_c will be reduced in the same proportion. However, if only individual lamellar crystals are melting, the crystallinity within the spherulites, x_{cL} will be lower. As indicated in the Eqs. (4) and (5), A_c is proportional to x_{cL}, but Q is proportional to $x_{cL}(1 - x_{cL})$ and the change of $x_{cL}(1 - x_{cL})$ will be very small. In this case, A_c is expected to decrease while Q stays almost constant.

The values of A_c, Q and L obtained in the dynamic experiments for the 85/15 blend original samples are compared in Fig. 3(a) and (b). The same patterns have been observed for the quenched samples. It can be seen in Fig. 3(a) that while the A_c values progressively decrease with temperature, the Q data show a slight increase prior to the melting transition. This behaviour has been also observed in some copolyesters [8]. According to the previous discussion, it can be concluded that during melting of these samples, the melting of the individual lamellas is the most important effect rather than the melting of the whole lamellar stacks.

This partial melting of the lamellar stacks can be a consequence of two different process as it was previously reported [7]: the surface melting of the crystals that must be accompanied by a decrease of the crystal thickness and an increase of the amorphous region or the melting of the thinner crystal lamellas. In this last case, an increase of the long period must be expected and it is evident from Fig. 3(b) that this effect must be dominant in our experiments.

4. Conclusion

The long spacing values of N6/Vectra blends samples, obtained from SAXS experiments at room temperature have been related to the polymorphic structure observed depending on the composition and the applied thermal treatment. Lower long period values have been found when the γ^* form is predominant.

On other hand, dynamic experiments have been carried out by simultaneous SAXS and WAXS techniques using synchrotron radiation. The change in the long spacing values observed as a function of the temperature and thermal treatment have been correlated with the polymorphic transformation of these samples.

The comparison between the invariant, Q, obtained by SAXS and the integrated area under the crystal reflections, A_c, determined from the WAXS experiments has provided some information about the mechanism of the melting process. It has been found that partial melting of the lamellar stacks occurs as a consequence of the melting of the thinner crystals.

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References

[1] Balta Calleja FJ, Vonk CG. X-ray scattering of synthetic polymers. Amsterdam: Elsevier, 1989.
[2] Guinier A, Fournet G. Small angle scattering of X-ray. New York (London): Wiley (Chapman and Hall), 1955.
[3] Glatter O, Kratky O. Small angle X-ray scattering. New York: Academic Press, 1982.
[4] Elsner G, Riekel C, Zachmann HG. Adv Polym Sci 1985;67:1.
[5] Spells SJ. Characterization of solid polymers. London: Chapman and Hall, 1994. p. 3, 56.
[6] Zachmann HG. Nucl Instrum Methods Phys Res 1995;97:209.
[7] Krüger KN, Zachmann HG. Macromolecules 1993;26:5202.
[8] Bark M, Zachmann HG. Acta Polymer 1993;44:259.
[9] Lin JS, Sheu EY, Jois YHR. J Appl Polym Sci 1995;55:655.
[10] Lee CH, Okada T, Saito H, Inoue T. Polymer 1997;38:31.
[11] Zin WC, Roe RJ. Macromolecules 1984;17:183.
[12] Cheng YY, Brillhart M, Cebe P, Capel M. J Polym Sci Polym Phys 1996;34:2953.
[13] Rabiej S, Wlochowicz A, Janicki J, Bryjak M. Acta Polymerica 1986;37:286.
[14] Annis BK, Wignall GD, Hopkins AR, Rasmussen PG, Basheer RA. J Polym Sci Polym Phys 1997;35:2765.
[15] Li Y, Jungnickel BJ. Polymer 1993;34:9.
[16] Huo P, Cebe P. Macromolecules 1993;26:3127.
[17] Crevecouer G, Groeninckx G. Macromolecules 1991;24:1190.
[18] Campoy I, Gómez MA, Marco C. Polymer 1998;39:6279.
[19] Campoy I, Gómez MA, Marco C. Polymer 1999;40:4259.
[20] Bark M, Zachmann HG, Alamo R, Mandelkern L. Makromol Chem 1992;193:2363.
[21] Campoy I, Gómez MA, Marco C. J Therm Anal 1998;57:705.
[22] Dreyfuss P, Keller A. J Polym Sci Polym Phys 1973;2:193.
[23] Kaji K, Sakurada I. J Polym Sci Polym Phys 1974;12:1491.
[24] Illers VKH, Haberkorn H. Die Makromol Chem 1971;142:31.
[25] Gogolewski G, Gasiorek M, Czerniawska K, Pennings AJ. Colloid Polym Sci 1982;260:859.
[26] Sakurai K, Mitasaka K, Ishikawa K. J Polym Sci Polym Phys 1974;12:1587.