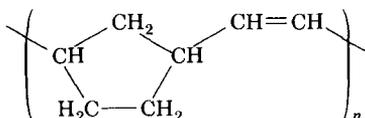


Strain-Induced Crystallization in Polynorbornene

INTRODUCTION

Polynorbornene has a following chemical structure, which was developed by CdF Chimie Inc. in France about 10 years ago:



This polymer, including the blends with a low molecular weight compound, has been investigated on the practical properties such as thermal, dynamic viscoelastic, and impact absorbing properties, and it has been further noticed as one of polymers having a shape memory.^{1,2} No structural study has yet been undertaken. Recently, we found that this polymer, which had been considered as noncrystalline, could crystallize under certain conditions. In this work we report on the occurrence of crystallization by drawing. For this purpose, differential scanning calorimetry and wide-angle X-ray measurements were carried out.

EXPERIMENTAL

Polynorbornene was kindly supplied by Nippon Zeon Co. having a quoted average molecular weight of 3×10^6 , a density of 0.96 g/cm^3 at 25°C , and a glass transition temperature of 35°C . A film was made by molding the fine powder sample at 150°C under the pressure of 90 kg/cm^2 for 15 min. An oriented sample was prepared by drawing the film four times in a water bath at 70°C and then quenching in an ice-water mixture at 0°C .

Differential scanning calorimetry (DSC) was performed on a Seiko Denshi Kogyo DSC 200 differential scanning calorimeter at a constant heating rate of 10 K/min .

Wide-angle X-ray diffractograms were obtained with a Rigaku Denki Model D-IA X-ray diffractometer equipped with a scintillation counter, utilizing nickel-filtered CuK_α radiation.

Wide-angle X-ray diffraction (WAXD) patterns were also recorded in a flat-plate camera.

RESULTS AND DISCUSSION

Figure 1 shows DSC curves of the undrawn and the drawn films in the first and second heating runs. The first heating run gives a single endothermic peak for the undrawn film (a1) and an additional peak at the higher temperature for the drawn film (b1). In the second heating run the endothermic peaks appeared no longer but only the change of inclination of the base line, which corresponded to the glass transition temperature (T_g), for both films.

Polynorbornene indicated a rubberlike elasticity at temperatures higher than the T_g , i.e., the drawn film immediately shrunk so as to recover the original length at higher temperatures with the ends free. It was considered that the state of both films was identical before the second heating run, resulting in the same DSC curves in the second heating run, from which the T_g could be estimated. Taking the T_g seen in Figures 1 (a2) or 1 (b2) into account, the first peak seen in Figure 1 (b1) can be considered to be due to the change of heat capacity which occurs in the glass transition region. An endothermic peak due to the T_g has been also recognized in other polymers.³

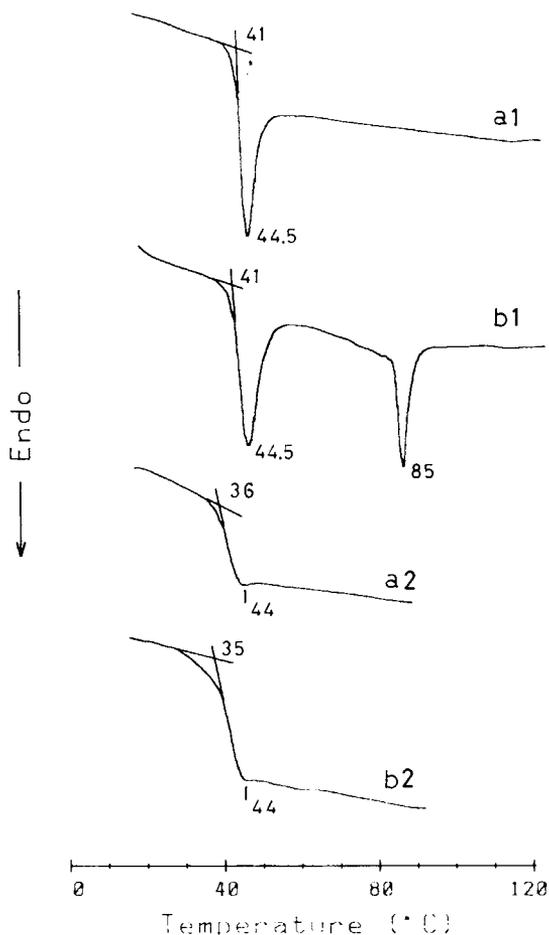
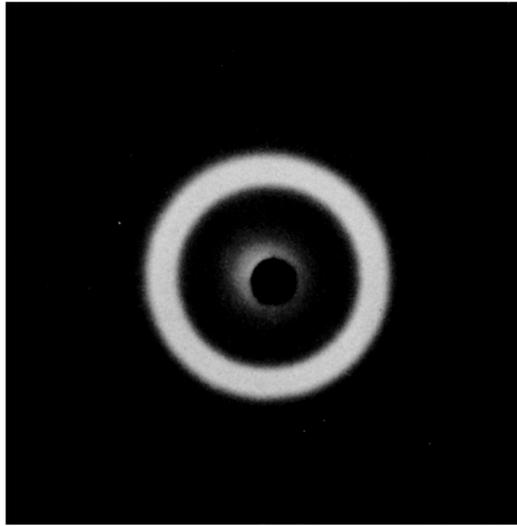


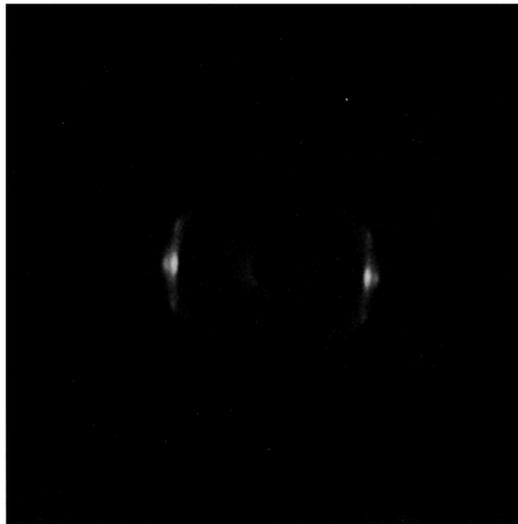
Fig. 1. DSC curves of polynorbornene films: (a1) 1st and (a2) 2nd heating runs for the undrawn films, respectively; (b1) 1st and (b2) 2nd ones for the films drawn four times at 70°C and quenched at 0°C.

Judging from the DSC curves in the first and second heating runs, the initial molded film had the T_g slightly higher than the film subjected to the relaxation of residual strain.

It was noted that the drawn film gave another endothermic peak at 85°C higher than the T_g seen in Figure 1(b1). This may be due to the melting of crystal which results from drawing at the high temperature and quenching at 0°C. The strain-induced crystallization from its amorphous state, i.e., the glassy state or the rubbery state, has been found in many polymers,⁴⁻⁸ for example, in natural rubber from the rubbery state.⁷ We were also able to show the strain-induced crystallization in polynorbornene from the rubbery state. WAXD photographs of the undrawn and drawn films are shown in Figure 2. The two Debye rings with spacings of 0.492 and 0.433 nm were observed in the undrawn film, though the melting behavior of this sample was not obtained by the DSC measurement. On the other hand, Figure 2(b) clearly shows the highly oriented fiber pattern of crystals resulting from the strain-induced crystallization. Thus, it can be concluded that the endotherm at 85°C seen in Figure 1(b1) is due to the melting of crystal, as mentioned above. The meridional reflection is at spacing of 0.575 nm, which corresponds to the repeat unit of polynorbornene along the molecular axis calculated by using the usual bond lengths and angles. Two equatorial reflections were observed at spacings of 0.490 and 0.445 nm, respectively. A detail analysis of the crystal will be given elsewhere.



(a)



(b)

Fig. 2. WAXD photographs of polynorbornene films: (a) undrawn; (b) drawn four times at 70°C and quenched at 0°C.

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