Relations between molecular aggregation state and mechanical properties in poly(diisopropyl fumarate)

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The backbone chain of poly(diisopropyl fumarate) (PDiPF) has a high rigidity. PDiPF molecules are aggregated as a nematic liquid crystal-like structure in film cast from solution. The lateral extent of the liquid crystal-like order is evaluated to be ~9 nm. The β absorption of loss modulus E'' appeared at 370 K in the film and is associated with the motion of bulky ester groups. The storage modulus E' was ~1 GPa below the β absorption temperature, whereas a relatively high value of ~0.1 GPa was retained in the temperature range from 390–500 K, since the high rigidity of the backbone chain is kept.

(Keywords: poly(diisopropyl fumarate); rod-like polymer; differential radial distribution curve; dynamic viscoelasticity; tensile property)

INTRODUCTION

Dialkyl fumarates with bulky ester substituents were found to homopolymerize easily in the presence of 2,2′-azobisisobutyronitrile as a radical initiator by Otsu *et al.*[1–3]. Poly(diisopropyl fumarate) consists of a less-flexible rod-like chain from the molecular model[1,2], in which the polymer is surrounded by bulky ester groups and its diameter is calculated to be ~1.4 nm. From the relation between the number average molecular weight and the intrinsic viscosity, the value of exponent '*a*' in the Mark–Houwink–Sakurada equation was found to be 1.0 in the number average molecular weights, $\bar{M}_n$ of 70 000 to 180 000, supporting the rod-like polymer[3]. The chain rigidity of poly(diisopropyl fumarate) is largely different from those of poly(alkyl acrylate) and poly(alkyl methacrylate), since for example, the value of exponent '*a*' of poly(methyl acrylate) is 0.795 in $\bar{M}_n$ of 150 000 to 1 400 000 (ref. 4) and that of poly(methyl methacrylate) is 0.76 in $\bar{M}_n$ of 40 000 to 1 000 000 (refs. 5 and 6). The repulsive force between neighbouring ester groups in a poly(diisopropyl fumarate) chain would be very high in comparison with poly(alkyl acrylate) and poly(alkyl methacrylate). Such a repulsive force results in high chain rigidity.

In this work relations between the molecular aggregation state and the mechanical properties of poly(diisopropyl fumarate) will be investigated and the effect of the ester groups on the temperature dependence of dynamic viscoelastic properties will be clarified.

EXPERIMENTAL

Poly(diisopropyl fumarate) (PDiPF) was presented by Prof. Otsu, Osaka City University. The sample was prepared by polymerization of diisopropyl fumarate with 2,2′-azobisisobutyronitrile as a radical initiator[1]. The number average molecular weight of PDiPF used in this work was 20 800. A 0.025 g ml^{-1} benzene solution of PDiPF was prepared in and cast at room temperature as a film, which was dried *in vacuo* at 340 K for 8 h after casting. The dried films were annealed in an atmosphere of nitrogen at <530 K for 1 h.

Wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) photographs of the cast film and drawn film were obtained with a Rotaflex RU-200 X-ray generator (Rigaku Denki Co. Ltd.). The X-ray diffraction intensity curve was measured with a Rigaku automatic full circle goniometer (Rigaku Denki Co. Ltd.) to obtain a differential radial distribution curve of the cast film; a monochromatic incident X-ray beam was used. The Bragg spacing of the strong Debye ring observed in WAXD was measured with a standard X-ray diffractometer. Optical anisotropy in the film was observed with a POH polarizing microscope (Nippon Kogaku Co. Ltd.) under crossed Nicols. Density was measured at 298 K by a float method in glycerol–water mixture.

The temperature dependence of dynamic viscoelastic properties was measured in an atmosphere of nitrogen with a Rheovibron DDV-IIC dynamic viscoelastometer (Toyo Baldwin Co. Ltd.). The stress–strain curve was obtained at an initial strain rate of 33% min^{-1} with a Tensilon UTM-III tensile tester (Toyo Baldwin Co. Ltd.). Thermal degradation was evaluated at a heating rate of 10 K min^{-1} in an atmosphere of nitrogen with a Shimazu DT-30 thermal analyser (Shimazu Seisakusho Co. Ltd.).

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RESULTS AND DISCUSSION

Molecular aggregation state

Figure 1(a) shows a WAXD photograph of cast film annealed at 443 K, in which the strong ring corresponding to Bragg spacing, d_b, of 1.04 nm can be observed. Outside this ring another weak and diffuse ring corresponding to $d_b = 0.44$ nm can be discerned. *Figure 1(b)* shows a WAXD photograph of the oriented sample, which was obtained by uniaxially drawing the cast film at 383 K to the draw ratio 1.4. The drawing direction is parallel to the meridan of the WAXD photograph. The inner ring on the equator was more intense than that on the meridian. Under the polarizing microscope the cast film appeared almost optically isotropic, but optical anisotropy appeared after uniaxial drawing. The direction of the maximum principal refractive index was found to be perpendicular to the drawing direction, which means that in the drawn film the ester groups are oriented mainly perpendicular to the drawing direction, which accords with the molecular axis direction.

Figure 2 shows a differential radial distribution curve of the cast film at room temperature. A damping factor of $\exp(-3.32\sin^2\theta)$ as a function of Bragg angle θ was used in obtaining the differential radial distribution curve. Peaks 1, 2 and 3 in the figure correspond to intramolecular maxima, whereas peaks 4, 5, 6 and 7 correspond to intermolecular maxima. The formation of four intermolecular maxima can be explained only by the parallel packing of chain molecules. It can be confirmed that PDiPF molecules are aggregated as nematic liquid crystal-like structure. The average distance between the cores of the molecules is evaluated from peak 4 to be ~1.4 nm, which is in agreement with the diameter of the molecule calculated from the molecular model[1,2]. It can be confirmed from the results of *Figures 1* and *2* that the core of PDiPF molecule is surrounded by hydrophobic isopropyl groups and the molecule forms a rod-like structure owing to the repulsive force between ester groups. The extent of the nematic liquid crystal-like order is conceived to be small enough to give an appearance of an almost optically isotropic state to the film, in relation to the wavelength of visible light. The lateral extent of nematic liquid crystal-like order is ~9 nm from *Figure 2.* On the other hand, it is estimated from the average length of the molecule that the longitudinal extent of the liquid crystal-like order may be several 10 nm. Therefore the liquid crystal-like order with this extent is homogeneously distributed in the cast film to show an optically isotropic state. Such a homogeneous distribution is supported by SAXS from which specific electron density fluctuation was absent in the film.

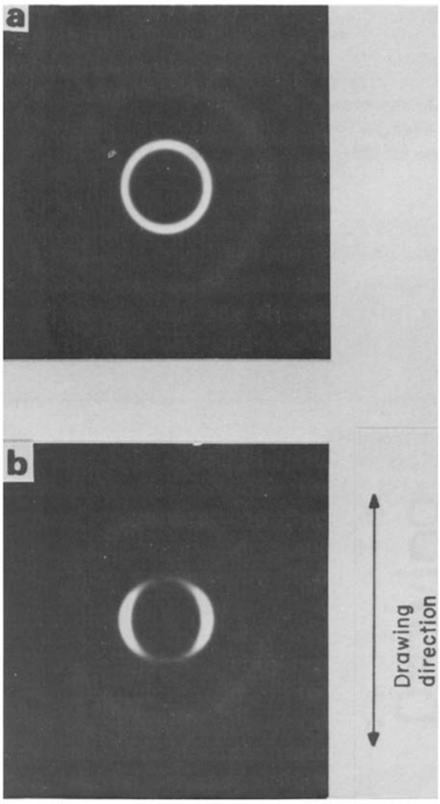

Figure 1 Wide-angle X-ray diffraction photographs of (a) cast film annealed at 443 K and (b) drawn film

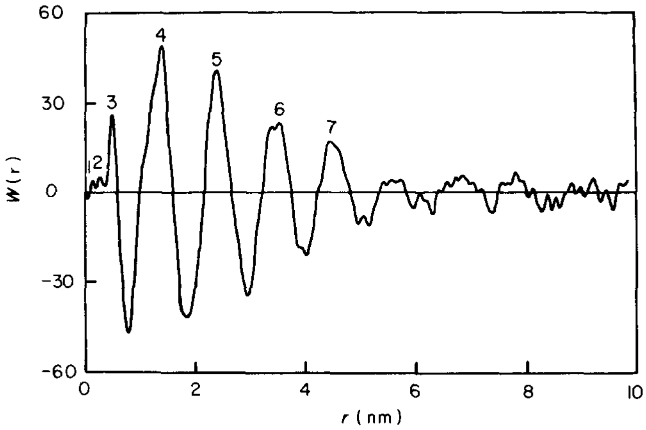

Figure 2 Differential radial distribution curve of cast film annealed at 443 K

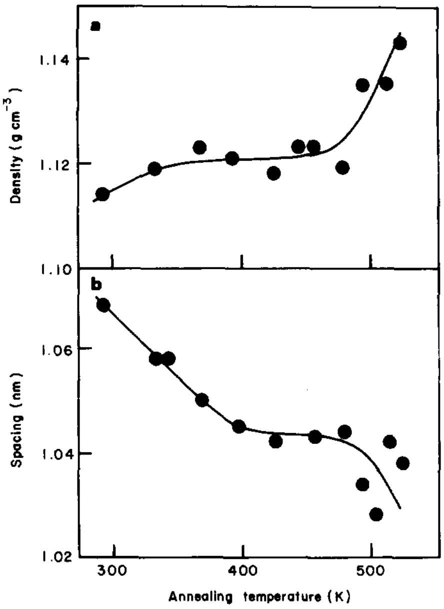

Figure 3 (a) Density and (b) Bragg spacing of the inner ring as a function of annealing temperature for as-cast film

Figure 3(a) and *(b)* show the effect of annealing temperature on density and Bragg spacing of the inner ring for unannealed film. The density and the spacing were measred at 298 K. The density increased gradually in a range from room temperature to 370 K and maintained an almost constant value below 470 K. Above 470 K the density increased markedly. The dependence of spacing on annealing temperature well corresponded to that of the density, which means that the increase of the density is caused by an increase in packing density of the molecular cores. It was also noticed that the film became increasingly optically anisotropic when annealed above ~470 K, which shows that the lateral extent of the liquid crystal-like order increases above ~470 K.

Mechanical properties

Figure 4 shows the temperature dependence of storage modulus E' and loss modulus E'' at 11 Hz for film annealed at 443 K. Broad, small absorptions appeared at ~160 K (δ) and 230 K (γ) and a large absorption at 370 K (β). Another small absorption was detected at ~530 K (α). E' decreased from ~1 GPa to ~0.1 GPa over the temperature range 340–400 K. E' is maintained at ~0.1 GPa in the β–α temperature range but falls markedly above the α temperature. *Figure 5* shows stress–strain curves at various drawing temperatures for film annealed at 443 K. Brittle fracture took place at 290–333 K, while large plastic deformation occurred at 383–473 K. The largest value of strain at break was obtained at ~383 K.

Figure 6 shows the temperature dependence of the Bragg spacing of the inner ring for film annealed at 443 K. The intermolecular spacing increased with increasing temperature and its rate of increase became marked near the β absorption temperature, but fell after completion of the β absorption. The interchain interaction decreases sharply about the β absorption temperature, above which the increase of the spacing reverts to normal van der Waals expansion. Above 450 K, another increase of slope is seen. The large increase in the spacing that accompanies the β process results in a decrease of E' from 1 GPa to 0.1 GPa and the drastic change of stress–strain behaviour shown in *Figure 5*. It is assumed that the β absorption is mainly associated with the side chain motion which does not result in a large lowering of the rigidity of the backbone chain. Mikhailov and Borisova[7] reported an activation energy of 67 kJ mol^{-1} for the β process in poly(isopropyl methacrylate) (PiPMA). This β process arises from the hindered rotation of the ester group around the C–C bond that links it to the main chain. The activation energy of the β process for the PDiPF film was 215 kJ mol^{-1}. In the film, the hindered rotation of ester groups would be higher than that in PiPMA and gives rise to the increased value of activation energy. It is

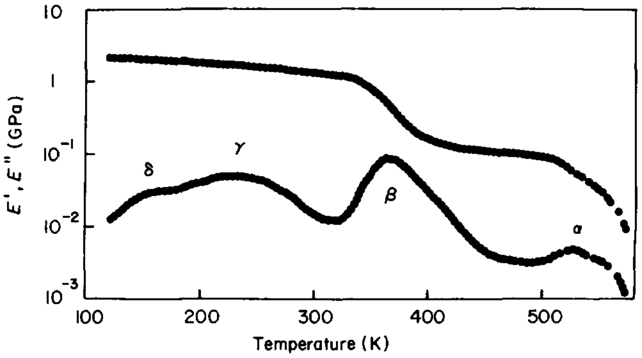

Figure 4 Temperature dependence of E' (upper curve) and E'' (lower curve) for cast film annealed at 443 K

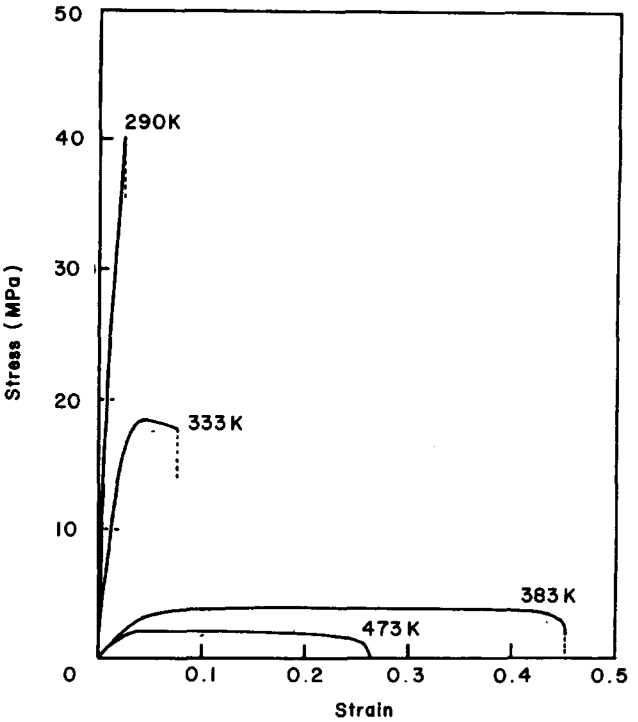

Figure 5 Stress–strain curves at various temperatures and initial strain rate of 33% min^{-1} for cast film annealed at 443 K

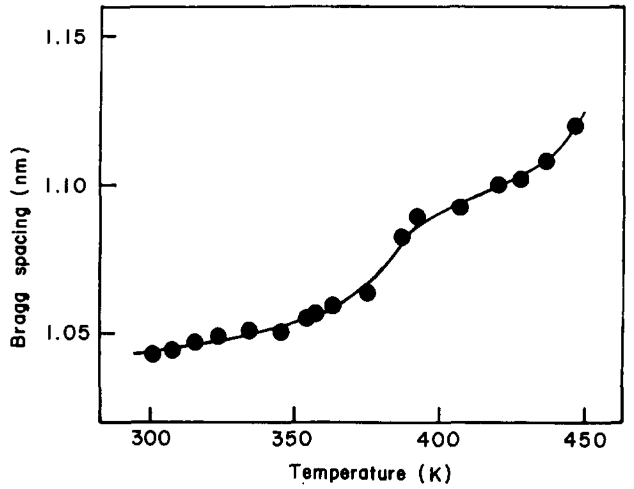

Figure 6 Temperature dependence of Bragg spacing of the inner ring for cast film annealed at 443 K

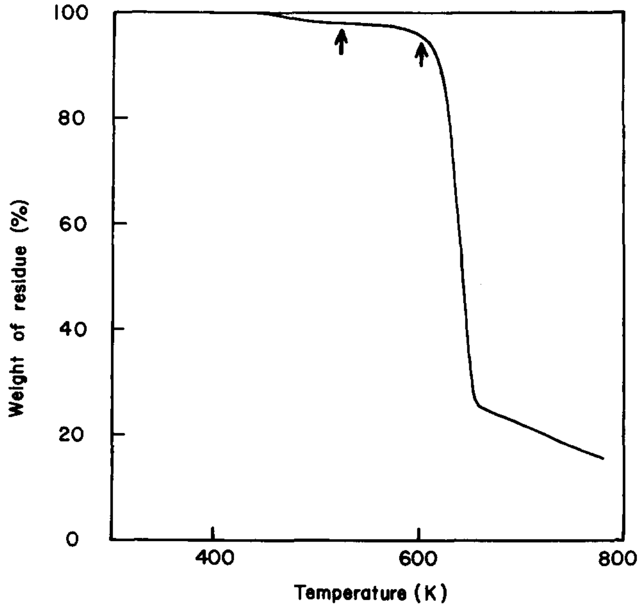

Figure 7 Decrease in weight of cast film in an atmosphere of nitrogen as a function of temperature at heating rate of 10 K min^{-1}. The arrows in the figure indicate the weights of residues at 522 K (98%) and 600 K (95%)

conceivable that the neighbouring backbone chains are pushed apart by the thermal motion of the side chains near the β absorption temperature, which markedly decreases the interchain interaction, as shown in *Figure 6*.

Figure 7 shows the result of thermogravimetry of the film at the heating rate of 10 K min^{-1}. The temperatures at 98% and 95% residue weight were 522 K and 600 K respectively. The α absorption near 530 K is considered to be associated with partial decomposition of the molecules and the main chain motion as a whole. The latter is restricted by the bulky ester groups as micro-Brownian motion of the backbone chains does not take place, since optically anisotropic order grown above the annealing temperature of $\sim$470 K, as described previously, also could be observed above the α absorption temperature. However the main chain motion brings about lowering of the rigidity of the main chain and therefore results in the growth of nematic liquid crystalline order. When the sample in the liquid crystalline state is quenched to room temperature, the high density and the small spacing, as shown in *Figure 3*, and a strong birefringent image could be observed, since the liquid crystalline order grown is fixed by quenching.

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