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Phase transition, structure/properties of poly(p-phenylene terephthalamide) films post-polymerized by pyridine in NMP/$CaCl_2$ solvent

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SUMMARY

During polymerization of PPD(para-phenylene diamine) and TPC(terephthaloyl chloride) in NMP/$CaCl_2$ solvent,the pahse transition from isotropic to anisotropic phase was investigated. A reaction-induced transition point can be confirmed by a flat plateau indicative of the development of anisotropic phase in the torque-time curve and also can be identified by the striated band structure under shear. Water and pyridine were used as the coagulating agent. Due to the post polymerization effect,the structures (crystallinity, orientation, fibrillation) and properties of films were affected by the shear given during the coagulation in pyridine.

INTRODUCTION

Since the successful commercialization of aramid fiber known as Kevlar Dupont, there have been active studies on the structure/properties of aramid.(1)

The phase transition of poly(p-benzamide) in dimethyl acetamide/LiCl solution was studied by Kwolek.(2) As the polymer and LiCl concentrations change, there appear several phases such as solid polymers in isotropic phase, purely isotropic phase, mixture of isotropic and anisotropic phase, purely anisotropic phase and solid polymers in anisotropic phase. Similar results were also reported in the 4-20 wt% PPTA(poly(p-phenylene terephthalamide)) sulfuric acid solutions.(3) It is well known that there exists a critical concentration where the viscosity becomes minimum.(4,5)

In both the thermotropic and the lyotropic liquid crystalline polymers, periodic bands produced perpendicular to the shear direction are characteristic features of liquid crystallinity. Many researchers(6-8) have studied this phenomena and concluded that a band is attributed to the elastic property of the liquid crystalline polymer. The weakness in the compressive strength when compared to the tensile strength is due to this band structure.

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In recent years, a new method of obtaining short pulp-like aramid fibers from shearing the polymerizing mixture in thepresence of pyridine was reported.(9) But the reaction time was so short that it was very difficult to control the process and to study the reaction variables and properties of the product. Rhim et al studied the structure of the pulp-like PPTA fiber produced by directly polymerizing and then separately shearing in the presence of pyridine, and concluded that since the solvents employed were free from ion clustering effects, no band structure could be observed.(10)

In this study, the reaction temperature was lowered to investigate the phase behavior during polymerization without the reaction accelerating agent, pyridine. The properties and the morphology of thin film obtained from the drum coater with the aid of the coagulant such as water and pyridine were also studied.

EXPERIMENTAL

Materials

Terephthaloyl chloride and p-phenylene diamine were purified by vacuum distillation. The solvent,N-methyl pyrrolidone(NMP) and pyridine, were used after dehydrating with the molecular sieve(Type 5A). Other chemicals used were of reagent grade.

Polymerization

Polymerization was conducted as follows; After a 1 L 4-neck flask was sufficiently purged of air by dry nitrogen gas, 185 ml of dry N-methyl pyrrolidone containing 19 g of $CaCl_2$ and 1.85 ml of pyridine was introduced into the flask. The temperature of the solvent was increased to 60℃, and in this solvent 9.09 g(0.084 mole) of p-phenylene diamine was dissolved. The solution was cooled to 6℃, and then 17.05 g(0.084 mole) of terephthaloylchloride was added while stirring. In this reaction the solid content was 8.8 wt% and the reaction was carried out in an ambient temperature of 25℃.

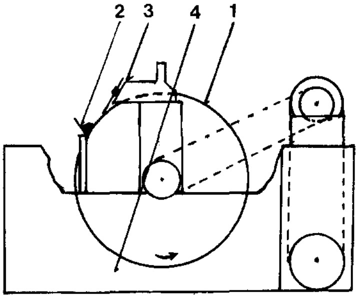
Drum coating apparatus

In order to investigate the effect of coagulant on the orientation and crystallization, thin film was prepared by drum coating method. The arrangement of the drum coating apparatus is shown in Fig.1. It consists of a constant speed drum revolved in coagulating bath containing pyridine or water. The reacted polymer was poured onto the surface of the drum and a knife was placed to adjust the film thickness.Thin film was made while coagulating in the bath. The role of the wiper is to remove the coagulating agent remained on the revolving drum surface.

Film preparation

In order to evaluate the effect of the post-polymerization occurring in the presence of pyridine and the effect of the shear rate during the structure development when the coagulation was initiated at different levels of conversion of the PPD and TPC reaction,films were made when the reacting mixture was in the isotropic state, in the onset of the anisotropic phase, completely in the anisotropic phase and the final state of reaction.The total reaction time for the 8.8 wt% solids reaction system was 6.5 minutes and the film was cast at 1.5, 2.5, 4 and 5.5 minutes after the reaction has started, which corresponds to each state described previously.

The clearance between the knife and the drum was set at 0.1mm. After the removal of solvent, the thickness of the film is around 20-30μm. The shear rate in the drum coater was controlled by adjusting the rotating speed of a drum as 5, 10, 15 and 20 rpm which were corresponding to the shear rates of 785, 1570, 2355 and 3140 1/sec. respectively.



1. drum
2. knife
3. wiper
4. coagulating bath

Figure 1. Schematic diagram of the drum coating appratus.

Measurement

The crystallographic data were measured with X-ray diffractometer(Rigaku, D-MAX IIIB). Nickel filtered CuKα radiation was used as the source. Orientation angle and crystallinity were measured to evaluate the effects of the shear rate.

The samples were also examined with a polarized microscope (Zeiss, Photomicroscope III) between crossed polars to identify the phase transition from isotropic to anisotropic state at the room temperature. Samples were prepared by quenching the polymer solution between the glass slides by liquid nitrogen, and exerting shear force by a glass rod.

The fibril formation and the molecular orientation were studied by transmission electron microscope (Jeol, JEM 2000 FX). Films were ground in the homomixer at 3,000 rpm in water, and NaCl crystal was added to act as an abrasion agent.

The mechanical properties of the film were measured with a tensile tester (INSTRON Model 1123) with a crosshead speed of 2 cm/min. under the grip length of 2 cm.

RESULTS AND DISCUSSION

Phase transition

Fig.2 shows the typical torque-reaction time curve for the polymerizing mixture containing 8.8 % solid by weight and the reaction started at 6℃. As the polymerization reaction is proceeded, there is an initial rise in torque as the monomers begin to polymerize in the isotropic phase. When the reacting mixture shows opalescence, there appears to be a plateau observed indicative of the lowering of viscosity as the anisotropic phase sets in. In this reaction there appears a flat plateau region from 2 and 4 minutes after reaction started. During this time, of course,the molecular weight continuously increases(inherent viscosity; 1.4 at 2.0 minutes, 2.5 at 5.0 minutes). Therefore,there must be some changes of phase. A "banded structure" appears to be one of the structural and morphological features characteristic of the sheared or elongated liquid crystalline polymers, and this has become of great interest in recent years.the structure can be observed as an image with periodic alternation of a dark striation and a bright layer along the direction of extension when viewed at the extinction position using polarizing microscope. This kind of structure has been found in a wide range of liquid crystalline polymers including aromatic polyamides(11),aromatic polyesters(12), and synthetic polypeptides(13).

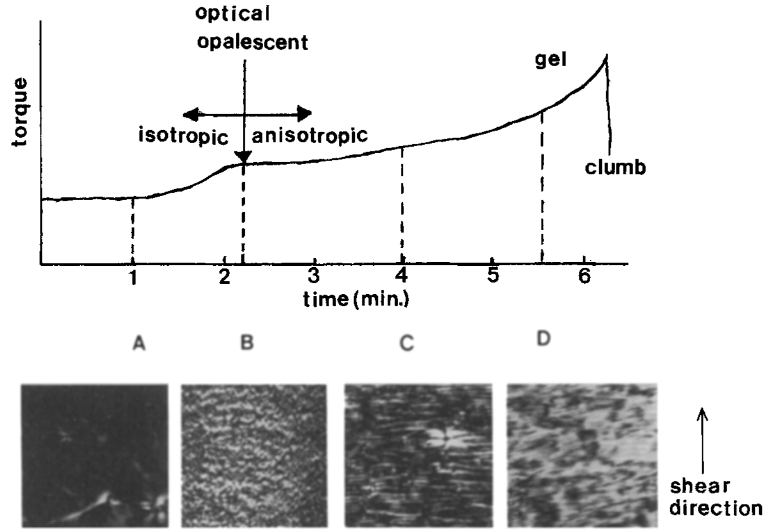


Figure 2. A typical torque-time curve and band structures developed during reaction in 8.8 wt% solids content.

In order to identify the band structure, samples sheared with a glass rod and instantly quenched in liquid nitrogen were prepared at the interval of 1 minute during the whole reactionperiod. As can be seen in Fig.2, the sample at 1 minute shows dark phase when viewed between crossed polars under a polarizing microscope which represents the isotropic phase. The sample at 2minutes which is close to the beginning of the flat plateau region shows band structure, which means the onset of anisotropic phase. As the reaction time is proceeded, the striation patterns becomes clear and distinct. This phenomena reveal the development of an anisotropic phase.

The polymerization reaction was proceeded under agitation of 300 rpm. Shear force was exerted to the polymerizing mixture and the shear-induced optical opalescent structure was observed at the time similar to that of the beginning of the flat plateau region with naked eyes. The beginning of the flat plateau was named as the opalescent point. In order to compare the time to reach the opalescent point, polymerization with 6.6 wt% solids content was also run. As the initial reaction temperature was varied from -5, 0, 6℃, the time to reach the opalescent point was varied from 6.2, 4.6, 3.2 minutes. The inherent viscosity at these points was nearly constant in the range of 1.97 to 2.21. It seems that the molecular weight corresponding to this inherent viscosity is critical about transition from isotropic to anisotropic phase. The inherent viscosity was measured at 25℃ in 97% sulfuric acid solution of 0.5 g/100mL concentration.

X-ray analysis and mechanical properties.

Films were prepared after coagulating in water and pyridine and the effect of the coagulating agent, the shear rate and the molecular weight of the polymerizing mixture at the point of coagulation were investigated. Water only acted as the precipitation, but in the presence of pyridine, post-polymerization was proceeded and the crystallinity and orientation was developed during the film forming process.

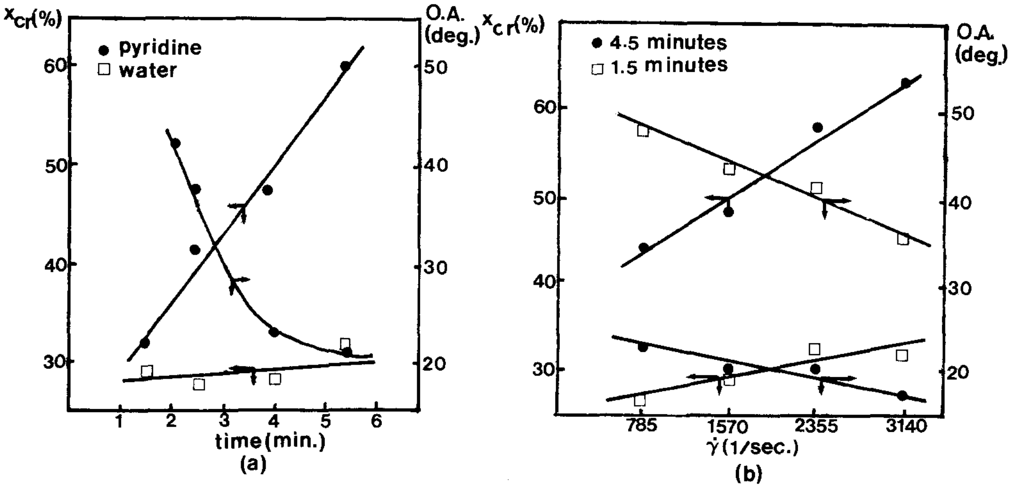


Figure 3. Changes in crystallinity and orientation angle of coagulated films
(a) effect of coagulating agent
(shear rate 2355/sec.)
(b) effect of reaction time in pyridine.

Figure 3(a) shows the changes in crysallinity and orientation angle of films made with the shear rate of 2355/sec. in water and pyridine coagulating agent. In water system, there were no increase in crystallinity and orientation angle was not detected in X-ray diffraction. As soon as polymer mixture containing NMP/CaCl$_2$ solvent was contacted with water coagulant, precipitation occurred and molecular weight was frozen. These facts suggested that there should be critical molecular weight for crystallization and orientation. But in pyridine system, where the pyridine played a role as the acid acceptor produced in the reaction and the I.V. of the polymer instantaneously increased to around 4.0, as reaction time proceeded, crystallinity increased linearly up to 60 % and orientation angle was developed up to 20 degrees.

Figure 3(b) shows the changes in crystallinity and orientation angle of films made with shear rate of 785, 1570, 2350, 3140/sec. respectively. In the case of the reaction time of 4 minutes (when the mixture had developed anisotropic phase), crystallinity and orientation angle increased linearly as the increasing shear rate, but for reaction time of 1.5 minutes (when the reaction mixture was in the isotropic state), the structures were not well developed. These facts imply the important role of the anisotropic phase in processing the liquid crystalline polymers since the final films have nearly same I.V.(Two polymers have final I.V. of 3.7-3.9). From Table 1, it can be seen that tensile strength of the former is 7-10 times higher than that of the latter.

Table 1. Properties of films prepared under varying shear rates in pyridine coagulating agent.(8.8 wt%)
(a) 4 minutes reaction time (anisotropic)
(b) 1.5 minutes reaction time (isotropic)

(a)

shear rate(sec^{-1})	initial I.V.	final I.V.	tenacity (kg/mm^2)	modulus (kg/mm^2)
785	2.10	4.01	95	1229
1570	2.07	3.98	119	1695
2355	1.91	3.90	113	2079
3140	1.98	3.54	131	2175

(b)

shear rate(sec^{-1})	initial I.V.	final I.V.	tenacity (kg/mm^2)	modulus (kg/mm^2)
785	1.27	3.75	16	326
1570	1.20	3.43	13	250
2355	1.25	3.78	15	366
3140	1.26	3.67	19	324

I.V. ; inherent viscosity

Electron diffraction pattern

Figure 4 shows an electron micrograph of fibrils which were torn from films by grinding in water. At several places microfibrils with submicron width can be seen. An electron diffraction pattern from the white spot of the fibril together with a schematic diagram is shown in Figure 4. The (110), (200) reflections in the perpendicular and (006) reflection in the parallel to the fibril axis were observed. It is seen that the molecular axis of PPTA lies along the fibril.

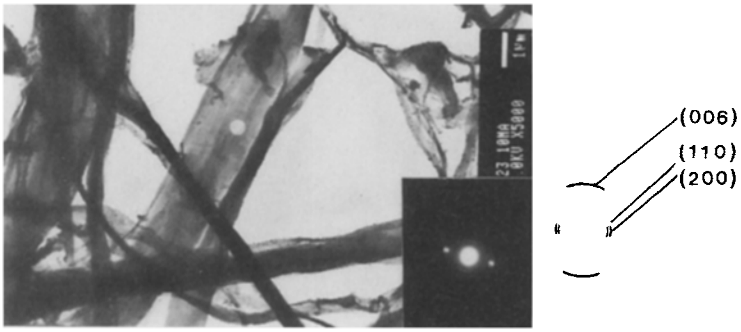


Figure 4. Micrograph of fibrils and electron diffraction with a schematic diagram.

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