

Anisotropic properties of aromatic polyamides containing non-rigid rodlike units

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SUMMARY

Three kinds of aromatic polyamides were synthesized by Higashi reaction: aromatic polyamides with even, odd number of methylenes and a meta phenylene as a joint in the main chain. Each polymer consisted of 7 p-phenylene-amide elements as a rigid segment. The polymer with even number of methylenes showed a lyotropic liquid crystalline behavior and a broader biphasic region than the fully para aromatic polyamide such as poly(p-phenylene terephthalamide). Most polymers with odd number of methylenes did not form a liquid crystalline phase and showed a crystallo-solvate. Exceptionally, the polymer with glutaryl unit was observed to have the swollen gel of colored pattern by the polarized microscope. The zigzag polymer, characterized by the highly kinetic rigidity, revealed an anisotropic gel phase in a solution.

INTRODUCTION

The anisotropic nature of a liquid crystalline state has been well proved by plentiful experimental and theoretical results for low molecules or polymers. There are lyotropic or thermotropic liquid crystalline phases by the conditions of mesomorphism: aromatic polyamides, cellulose derivatives and poly(N-alkyl isocyanate) are lyotropic but aromatic polyesters are thermotropic. Generally, most of these polymers have the rigid rodlike molecular structure (called a rodlike segment). But some polymers have the rigidity of secondary structure which is formed by the interaction of polymer chain with solvent [1-2]. In the case of semi-rigid polymer it is also necessary to take into account the nature of non-rigid part in the polymer chain as well as the rodlike part. When adipoyl or suberoyl chloride, for example, is used as an acid monomer with the diamine such as N,N'-bis(4-aminophenyl)terephthalamide, it has been well known that the resulting polymers have some lyotropic liquid crystallinity [3]. On the other hand, the liquid crystallinity is not shown for the polymer made from the same diamine with other acid monomer, azelaoyl or sebacoyle, which has an odd number of methylenes. These examples indicate that the orientation of a rodlike segment consisting of three p-phenylene-amide units is closely affected by its neighboring non-rigid segments. In addition, the zigzag polymer, whose rodlike segments are connected each other by a meta phenylene, does not show the liquid crystallinity [4].

It will be very interesting to examine the possibility of the existence of an anisotropic phase by introducing much longer rigid part into above semi-rigid polymer because the polymers have short rodlike segments. For this purpose, six polyamides with a long rodlike segment and a meta phenylene or a methylene unit are prepared by Higashi

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reaction.

EXPERIMENTALS

a) Monomer preparation

N,N'-bis(4-aminophenyl)terephthalamide was prepared by the reduction of nitro compound in the presence of Raney Ni under the pressured hydrogen. The nitro compound was obtained from the reaction of para-nitroaniline (2mol, Fluka Co.) with terephthaloyl dichloride (1mol, Aldrich Co.). Various acid monomers containing a few performed amide linkages were synthesized by the following procedures. First, 2 moles of amino-acid (compound I), which was obtained from para-nitroaniline and terephthalic acid monomethylesterchloride (Tokyo Chem. Co.), reacted with 1 mol of acid chloride, ClOC-(X)-COCl, in N-methyl-2-pyrrolidinone (NMP). The acid product precipitated during the reaction was washed twice by NMP and water before drying in vacuum oven for 24 hrs at 100°C. Yields were about 40 mol% on the basis of compound I. All monomers were identified by using IR, NMR and Atomic Analyzer.

b) Polymerization

The polymerization via the phosphorylation reaction, which was first reported by Ogata and later modified by Yamazaki and Higashi [5-7], is very suitable for the reaction of the acid monomer which is not easily chlorinated. It is also good for screening some polyamides. In our study Higashi reaction was selected because the monomer has high contents of para-phenylene units [8] and the chlorination of the acid monomer is difficult. Polymerization was performed following the method given by Krigbaum et al [8]. The monomer concentration was 0.078 mol/L NMP and the reaction time lasted over 3 hrs. Other factors such as

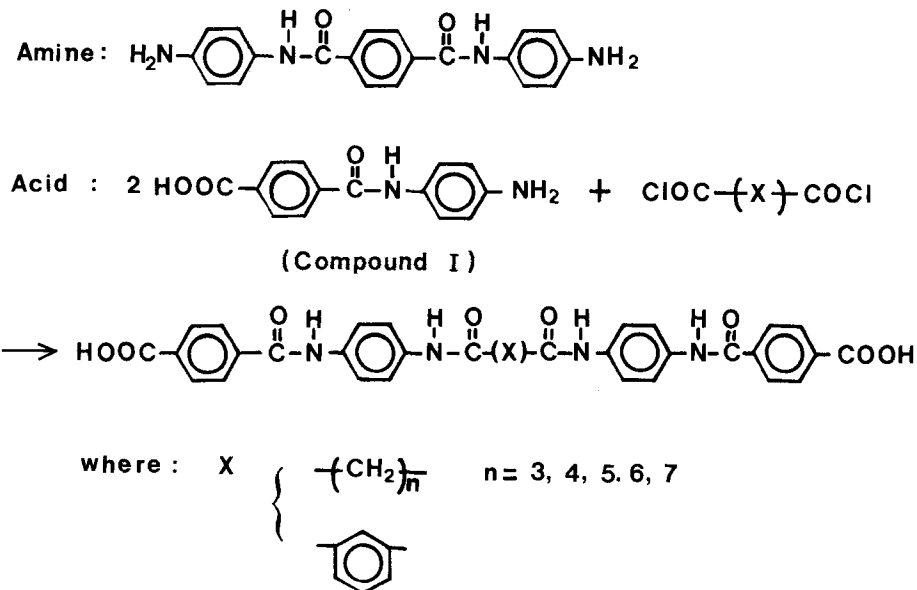
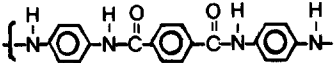

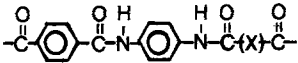
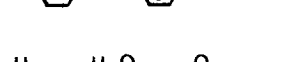
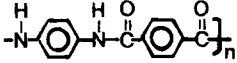




Table.1) Polyamides and their inherent viscosities.

POLYMER STRUCTURE	POLYMER CODE	-X-	I.V. (η^*)
	M3	$(\text{CH}_2)_3$	1.34
	M4	$(\text{CH}_2)_4$	1.29
	M5	$(\text{CH}_2)_5$	1.21
	M6	$(\text{CH}_2)_6$	1.67
	M7	$(\text{CH}_2)_7$	1.22
	DC7		1.53

reaction temperature, amounts of salt and the ratio of pyridine/NMP were used without any modification. Inherent viscosities of all polymers were generally high as listed in Table 1. The reaction mediums of M3 and DC7 maintained the clear transparency until the complete polymerization. The medium of M3 showed the Weissenberg effect with stirring. The polymers except M3 and DC7 precipitated within 1hr from the beginning of the reaction. All polymers were precipitated in methanol, washed by water and then dried.

c) Measurements

Inherent viscosity was measured by Ubbelohde viscometer (No.2) at 30°C in 96% sulfuric acid. Other solutions for the test of anisotropy were prepared from 100% sulfuric acid, which was made by mixing Oleum with 96% sulfuric acid. The solution were slightly heated in order to certify the complete dissolution of the polymer and then maintained in the chamber of constant temperature. Optical polarizing microscope (Photomicroscope III Carl Zeiss Co.) was used to identify the anisotropic property of polymers with a temperature controller (Leitz Co.). All solutions were treated under the nitrogen atmosphere.

RESULTS AND DISCUSSION

It is easily recognized that M6 and M4 polymer solutions show the liquid crystalline state because the polymers have the linear and stable trans conformation due to even number of methylenes. It is also recognized that these phases are nematic when compared other analogous polymers [3,9]. The polyamide, which has three para-phenylenes connected alternatively with the flexible suberoyl by an amide bond, reveals the anisotropy when the concentration is over 30wt% in sulfuric acid [3]. A similar polyamide containing a flexible unit of $-(\text{CH}_2)_8-$ or $-(\text{CH}_2)_{10}-$

shows the anisotropic phase in the range of 25-40wt% [9]. The critical concentration of M6 is at 15.5 wt%. Fig.1(a) shows the typical nematic phase. It seems that the polymer with a longer rodlike structure forms an anisotropic phase at the lower concentration. The phase was biphasic up to 19% and anisotropic over 20%. Biphasic region was broadened by adding flexible units to the backbone chain while it was very narrow for the wholly aromatic polyamides such as poly(*p*-phenylene terephthalamide) and poly(*p*-benzamide). M4 polymer solution showed the phase transition similar to M6 solution but the different value of critical concentration. It showed the biphasic region of 12-15wt%, which was narrower than M6 polymer solution. It is understood that the length of a flexible unit has an important effect on the liquid crystallinity as well as the length of a rigid segment.

The polymers M3, M5 and M7 with odd number of methylenes did not show any liquid crystal behaviors. Substantially, they were prepared to know the length effect of a rodlike segment in the main chain, that is, whether the length is long enough to ignore the even-odd number effect of the flexible units. If an anisotropic phase is obtained by increasing only the length of a rodlike segment, the theory developed for the molecules with the rigid segments connected freely each other will be applicable to this type of polymer [10,11]. M7 polymer was dissolved in sulfuric acid up to the limit of 27% solubility. Up to 17% the solution did not show anisotropic but clearly isotropic phase. On the other hand, the 18% solution showed an anisotropic phase as shown in Fig.1(b), which was formed 1 day after dissolution. It did not show any change of the birefringent pattern or the spherulitic domain when it was sheared. This spherulite disappeared and reappeared slowly by a minor heating and cooling around 63°C. From this low melting point as well as the fact of slow formation and destruction of the spherulite structure by adding water, it can be inferred that the spherulite is a crystallo-solvate which have been frequently observed in the relatively high concentration of either aromatic polyamides such as poly(*p*-benzamide) and poly(*p*-phenylene terephthalamide) or a flexible polymer of poly(*m*-phenylene isophthalamide) [12-15]. The spherulite has a concentric circle pattern which appears frequently in the liquid crystalline spherulite of poly(*γ*-benzyl-L-glutamate) [16]. The interactions between the amide polymer with a long flexible unit and the polar solvent may cause this peculiar spherulite formation.

The polymer M5 also shows the crystallo-solvate but a little fuzzy spherulite as in Fig.1(c) for the concentration above 21%. M7 which contains larger flexible segment than M5 shows the large size of spherulite with some concentric circles. But it fails to obtain any liquid crystalline phase. According to the fact that the polyester based on 4,4'-dihydroxybiphenyl and dibasic acid of odd methylenes is thermotropic [17], the polymer with the odd number of methylenes may have a possibility to form a liquid crystalline structure when its concentration is high. This polymer can also form liquid crystalline states when its rodlike segments become longer. But the M3 polymer, which has the largest rigid segment relatively among the polymers with odd number of methylenes shows only birefringent patterns (Fig.1(d)) of the swollen gel type as reported by Aharoni [4,18]. This polymer solution also formed the spherulite pattern after 8 days elapsed.

Aharoni [4] reported that the polyamides with a meta phenylene connecting the adjacent rodlike segments did not show any liquid crystalline state. The polyamide with maximum 5 *p*-phenylene showed only

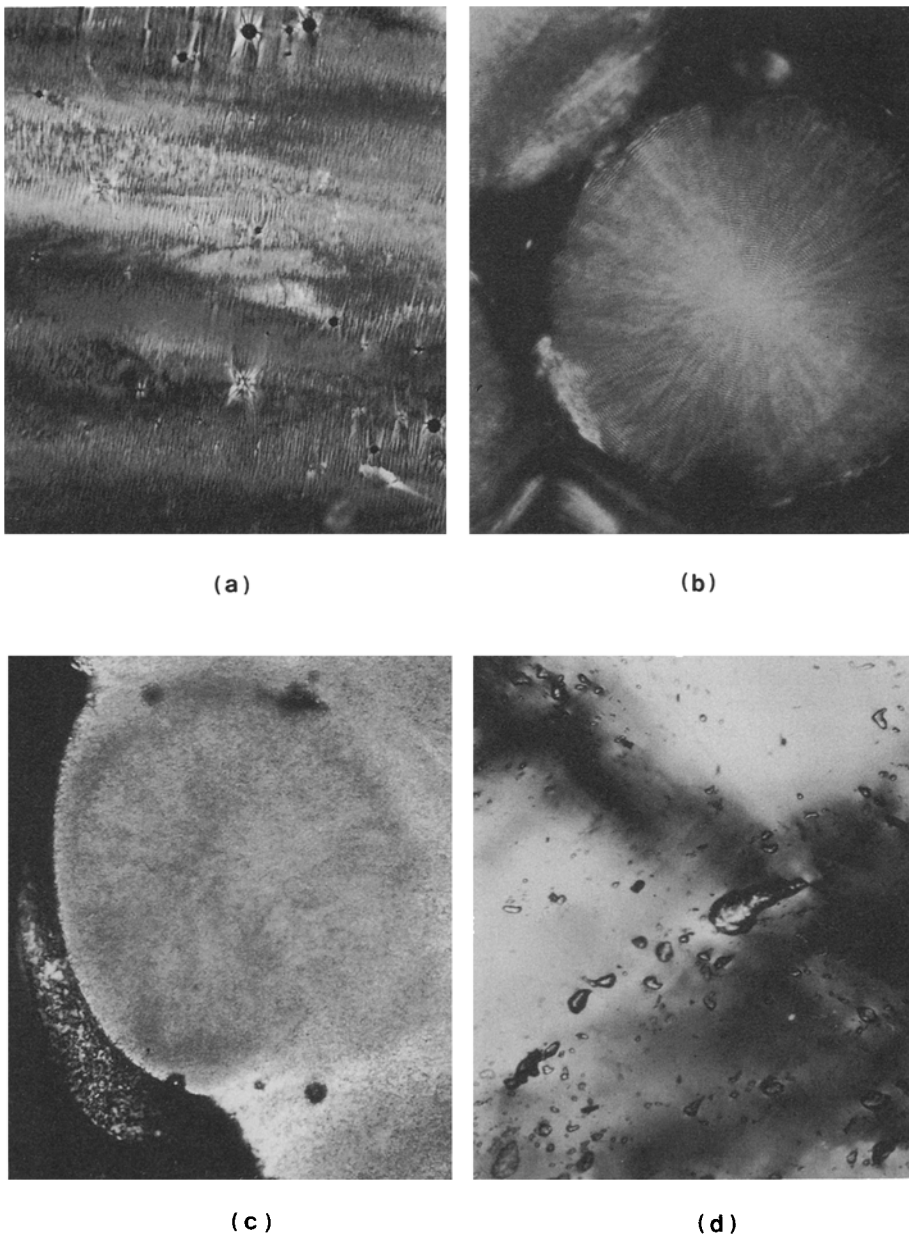


Fig.1) The phase characteristics of the polyamides comprising even-odd methylenes; (a) M6 (16%,80X) (b) M7(18%,128X) (c)M5 (21%, 80X) (d) M3 (20%,80X).

a birefringent pattern when sheared and the gel characteristics like the M3 solution. Our 20 wt% DC7 solution formed a spherulitic gel (Fig.2(a)) spontaneously and slowly after 1 day elapsed from the complete dissolution at the temperature 22°C but not a crystallo-solvate. At the lower temperature of 15°C it showed a colored pattern like a liquid crystal over the whole domain (Fig.2(b)). The structure formed in DC7 solution may be called a gel-like because of its spontaneous and slow formation. An analogous example has been reported by Harris et al.[19]. It can be noticed that the anisotropic properties of liquid crystalline order showed partly some possibility of packing the molecules of zigzag polymer in solution state.

In conclusion, three kinds of the aromatic polyamides showed different anisotropic characters: the polymer with even number of methylenes showed a typical lyotropic liquid crystal, the polymer with odd number of methylenes the crystallo-solvate structures and finally, DC7 zigzag polyamide the anisotropic phase with the gel-like characteristics of liquid crystalline order. Therefore, it may be inferred that the flexible unit of methylene linkage is very important for mesomorphicity. It is said that the solution properties are mainly characterized by the flexible unit because all polymers have the rodlike structure of the same length. As the length of a flexible unit is decreased, the polymer with even number of methylene has higher liquid crystallinity. On the other hand, the polymer of odd methylenes showed the crystallo-solvate, especially M7 solution concentric circle pattern. In addition, M3 solution showed deeper color pattern than M5 and M7 solutions. Finally, the zigzag polymer showed the anisotropic phase with gel-like characteristics, which could not be clearly understood. It is recognized from the experimental results that it is possible to obtain an anisotropic phase by making the rodlike segment longer.

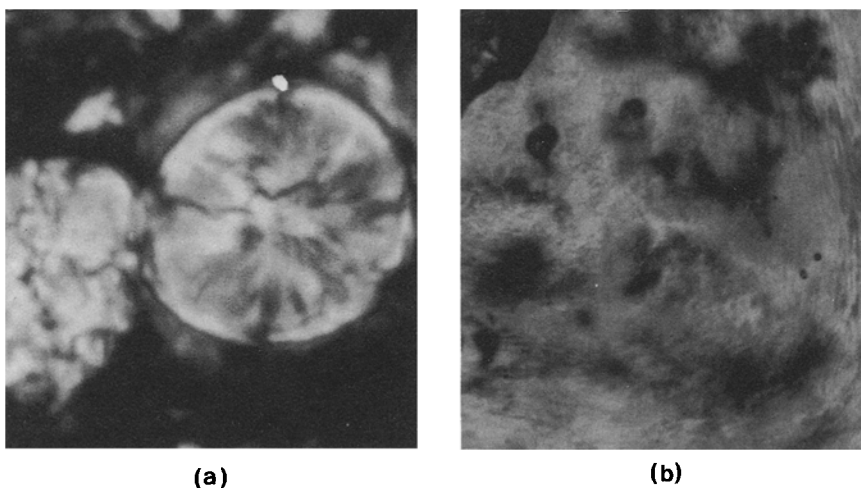


Fig.2) The anisotropic phase of the 20% DC7 solution; (a) 22°C (320X) (b) 15°C (80X).

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