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Structural study on rodlike aromatic polyimides derived by solid-state thermal and chemical imidization of poly(amic *n*-dodecyl ester)

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Abstract

Para-linked aromatic poly(amic *n*-dodecyl ester) (PA-12), in which long *n*-alkyl side chains are attached on rodlike aromatic polyamide, was prepared by polycondensation of 2,5-bis(1-dodecyloxycarbonyl)terephthaloyl chloride and 1,4-diaminobenzene. In as-cast PA-12 film, formation of layered structure with alternating main-chain-segregated and side-chain-segregated layers is suggested by X-ray diffraction measurement. PA-12 is a precursor of rodlike aromatic polyimide, poly(1,4-phenylene pyromellitimide) (PPPI). Solid-state thermal imidization and base-catalyzed chemical imidization of PA-12 film has been investigated. Although the layered structure of PA-12 was destroyed during the imidization reaction, the obtained PPPI exhibited lower density than densely packed PPPI. This result may indicate that the side chain-segregated domain was transformed to a cavity surrounded by PPPI after the imidization reaction. Chemical imidization in pyridine/toluene mixture and subsequent heating at 200 °C was the optimum condition to obtain low density PPPI.

Keywords: Polyamide; Polyimide; Chemical imidization; Layered structure; Density

1. Introduction

Rodlike aromatic polyesters, polyamides, and polyimides are expected as high performance materials because of their excellent mechanical and thermal properties. Some rodlike polymers, on which flexible side chains are introduced, have been investigated for the purpose of good processability and solubility. Because of the difference in chemical structure of the aromatic main chain and aliphatic side chain, it has been reported that the main chains and side chains forms respective segregated domains [1–7]. As the result of this micro-segregation, these rodlike polymers form ordered morphology, i.e., layered structure with alternating main chain- and side chain-segregated layers.

Recently, Watanabe et al. [8,9] reported a unique mesophase in rodlike polyesters, poly(*p*-biphenylene terephthalate) with flexible alkoxy side chains on the terephthalate moiety (PBpT-O*n*). For long alkyl side chains (carbon number $n > 16$), ordinary layered mesophase was observed below the mesophase-isotropic transition temperature. On the other hand, polyesters with shorter alkyl side chains than $n = 12$ exhibited hexagonal columnar phase, in which the alkyl side chains form segregated cylindrical domain, and the strongly associated main chain are surrounding the cylindrical domain like honeycomb structure. These layered and honeycomb structures have analogy with the microphase separated structure of diblock copolymer, i.e., lamellar and cylinder structure [10,11]. In diblock copolymers, the segregation power of the consisting block chains induces the formation of segregated domains, and its morphology depends on the volume fraction of each block. When the volume fraction of the diblock copolymer is asymmetric, the minor block forms cylindrical domain and the major block surrounds the cylinder as the matrix domain. The formation of honeycomb or layered structure in rodlike polyesters with depending on the alkyl chain length can also be described by the volume fraction of main chain and side chain.

Because the size of the side-chain-segregated domain depends on the alkyl chain length, the diameter

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distribution of the cylinder should be sharp with nanometer order. The segregated alkyl-chain domain and matrix aromatic main chain domain have different physical properties, i.e., the former contains flexible non-polar chains and liquid-like above ~50 °C, and the latter contains rigid aromatic and polar ester group. In this sense, the surrounded cylindrical domain can be regarded as a liquid-like path in the rigid matrix, and the diameter of the path is close to low-molecular-weight substances. If the alkyl chains can be removed without any influence on the matrix domain, a unique mesoporous material [12–14] with nanometer-sized voids or cavities will be possibly prepared.

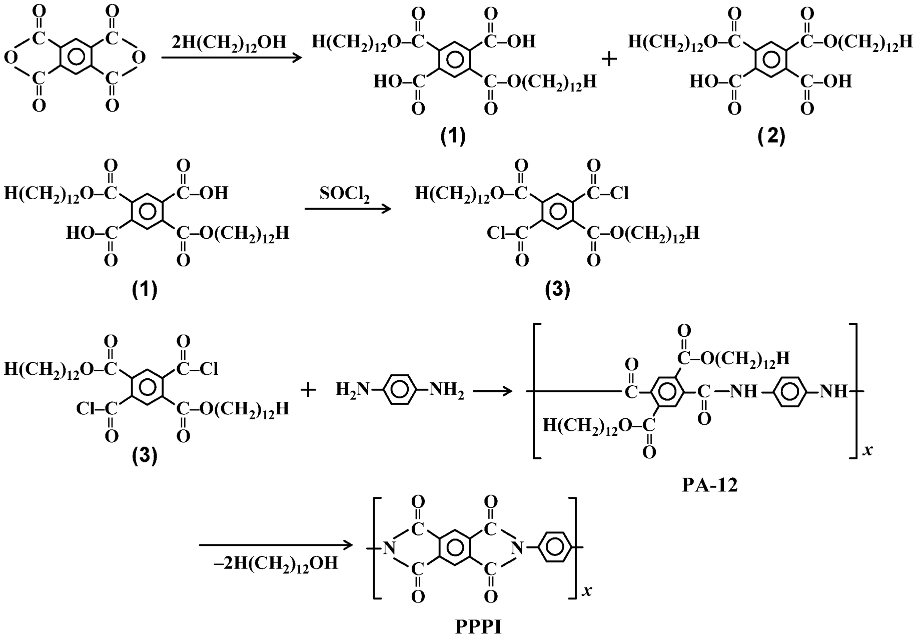
Following the above considerations, we have prepared rigid rodlike polyamide with flexible alkyl side chains. Para-linked aromatic poly(amic *n*-dodecyl ester) (PA-12), polymerized by polycondensation of 2,5-bis(1-dodecyloxy-carbonyl)terephthaloyl chloride and 1,4-diaminobenzene, have similar molecular structure with the rodlike polyesters by Watanabe et al. [8,9], and is expected to form the main-chain- and side-chain-segregated domains. As is well known, poly(amic alkyl ester)s have been used as precursor of polyimides because its chemical stability is better than that for poly(amic acid)s [15–22]. Thermal imidization of poly(amic alkyl ester)s with short alkyl chain length have been investigated in detail [15–21]. In this case, the cyclization reaction from the amic alkyl ester to imide ring occurs with removing alkyl alcohol. Kakimoto et al. [20] reported the structure and mechanical properties of poly(amic alkyl ester)s with long alkyl chains and poly(*p*-phenylene pyromellitimide) derived by thermal imidization, and succeeded to prepare oriented PI fiber with high tensile modulus by drawing the precursor fiber before imidization. On the other hand, there have been only limited reports about the chemical imidization of poly(amic alkyl ester)s [22].

The objective of this report is to perform the imidization reaction for PA-12 in solid-state. If the imidization reaction and removal of the alkyl chain proceed with maintaining the morphology of PA-12, the alkyl-chain-segregated domains in PA-12 will be transformed to cavities in fully aromatic polyimide, poly(1,4-phenylene pyromellite imide) (PPPI). For application use, these 'molecular cavity' may be suitable for separating membranes in order to separate substances by their molecular size. In this report, we have investigated the change of morphology formed by PA-12 after the chemical and thermal imidization reactions to PPPI by means of infrared spectrum, X-ray scattering, and density measurements.

2. Experimental

2.1. Materials

Outline of polymer synthesis is shown in Scheme 1 [4,18]. Twenty grams of pyromellitic dianhydride and equimolar 1-decanol was heated at 150 °C for 1 h. Because the reaction mixture contains *para* (**1**) and *meta* (**2**) isomers, 400 ml of acetone was added and stirred for 24 h in order to remove the *meta* isomer. This extraction process was repeated for three times. Finally, the precipitate was thoroughly washed with dichloromethane, and pure *para*



Scheme 1.