

Structure and Gas Sorption Properties of an Aromatic Polyamide with Long Alkyl Side Chains

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Received 2 March 2004; accepted 8 October 2004

DOI 10.1002/app.21586

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: An aromatic polyamide with long alkyl side chain, A-C12, was synthesized from the condensation of 1,4-didodecylester of pyromellitic acid and *p*-phenylenediamine to clarify the relationship between its higher order structure and gas sorption properties. A-C12 formed a layered structure composed of alternating rigid aromatic main chain layers and flexible dodecyl side chain layers. This polyamide could be imidized by the usual imidization method. Imidized A-C12 could not keep the layered structure of A-C12. CO₂ sorption of A-C12 occurred only in the side chain layer region, which is almost a liquid-like envi-

ronment, and the sorption isotherms obeyed Henry's law. This result also indicates that the main chain layer is very dense and cannot sorb CO₂. On the other hand, imidized A-C12 showed a large sorption amount of CO₂ and dual mode sorption, despite high density, meaning imidized A-C12 does not contain a layered order structure but an amorphous glassy state. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1771–1775, 2005

Key words: long alkyl side chain; Henry mode sorption; membranes; nanolayers; polyamids

INTRODUCTION

Recently, many papers investigating the rodlike polyesters with flexible long alkyl side chains have been reported.^{1–6} For example, these polyesters consist of dialkyl esters of 1,2,4,5-pyromellitic acid and 4,4'-biphenol, B-*C_n* (*n* is the carbon number of alkyl side chain) or hydroquinone, H-*C_n*. The most interesting point of these polyesters is their ability to form layered structures in the crystalline and liquid crystalline states by microsegregation into a rigid main chain region and a flexible alkyl side chain region. That is, the planar aromatic main chains are packed into a layered structure, and the flexible alkyl side chains occupy the space between the layers (see Fig. 1). In other words, the layered structure of B-*C_n* is composed of a layer part of high packing density, containing stacking of aromatic main chains and a low-density alkyl side chain layer. Therefore, B-*C_n* polymers form, in general, low-density liquid crystalline polyesters. One can synthesize B-*C_n* by controlling the carbon number of the side chain, varying the inter-layer spacing between the layered structure.

Based on these structural features, the gas sorption and diffusion properties of B-*C_n* should be very unique relative to those of other dense and glassy

polyesters such as bisphenol-A polycarbonate (PC). If an aromatic polyamide with long alkyl side chains formed a regular layered structure similar to an aromatic polyester acid and was able to keep its structure during imidization, one could develop a highly permselective and temperature-stable membrane. In this study, to clarify the relationship between the layered structure and the gas sorption properties of A-C12 (see Scheme 1), we synthesized noble polyamide from the 1,4-didodecyl ester of pyromellitic acid and *p*-phenylenediamine and prepared film-like samples of A-C12. Structural characterization and gas sorption measurements were performed. Gas sorption behavior in the side chain region is discussed in terms of the Henry mode sorption mechanism.

EXPERIMENTAL PROCEDURE

Materials

Tetrahydrofuran (THF) and toluene, which are used as solvents of monomer, were distilled from LiAlH₄ mixture prior to use. Triethylamine was distilled in NaH. Benzene was distilled from CaH. Hexamethylphosphoramide (HMPA) was distilled in the mixture of CaH and Na. Pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylic dianhydride; Kanto Kagaku) and 1-dodecanol (Nakarai Tesque) were used without further purification. *p*-Phenylenediamine (Nakarai Tesque) of monomer had a purity of 97.0%. Dichloride of the 1,4-didodecylester of pyromellitic acid was synthesized according to the literature.^{1–3}

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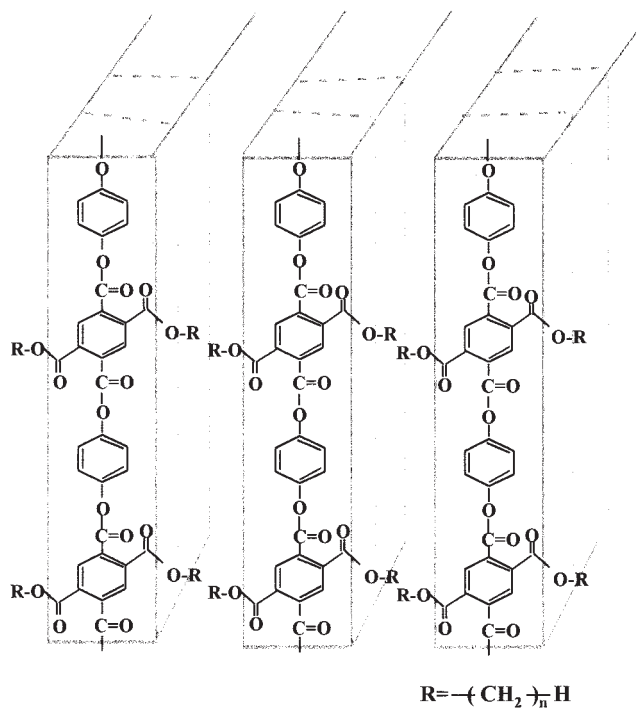


Figure 1 Schematic representation of layered structure of H-C_n.

Synthesis of polyamide

In a 100-mL round-bottomed flask equipped with a magnetic stir bar, 1.523 g (0.0141 mol) of *p*-phenylenediamine was dissolved in 30 mL of HMPA and slightly more than equivalent 2 mol triethylamine. In another 50-mL flask, equiv 1 mol of the diacid chloride was dissolved in 10 mL of benzene. This solution was then added over a period of 1 min to the rapidly stirred *p*-phenylenediamine solution. To ensure complete transfer of the acid chloride, the 50-mL flask was rinsed with about 3 mL of benzene and this was added to the reaction flask. As the reaction proceeded the solution became cloudy due to the formation of triethylamine hydrochloride and there was a marked increase in solution viscosity by condensation reaction as well as an increase in the temperature of the reaction vessel. After 12 h, the polymer solution was poured into 500 mL of methanol. The polymer was purified three times by reprecipitating a DMAc solution into a 10-fold excess of methanol. The synthesis was confirmed by elemental analysis. An as-cast film was obtained by casting from 5 wt % DMAc solution and drying for 12 h at 80°C *in vacuo*. An imidized sample was prepared by thermal curing the as-cast film at 250°C *in vacuo* for 12 h and then cooling to room temperature. Imidization was confirmed by the presence of an imide band in FT-IR spectra. These samples were very brittle at room temperature. Sorbent CO₂ gas used in this study was at least 99.9% pure and was used without further purification.

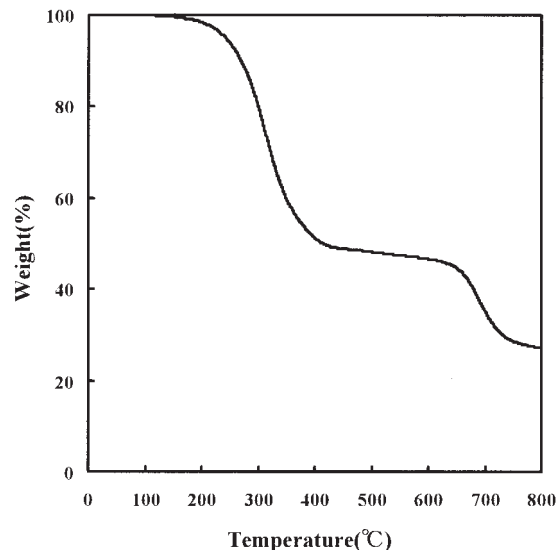


Figure 2 TG curve of as-cast sample obtained under nitrogen atmosphere at the heating rate 10°C/min.

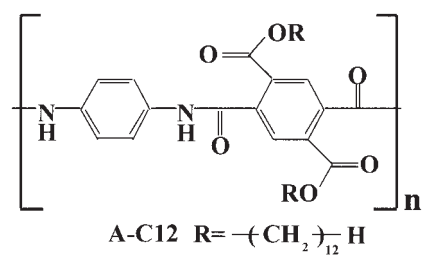
Methods

Densities of A-C12 samples at 25°C were determined by the floatation method using aqueous solutions of NaBr. Differential scanning calorimetry (DSC) measurements were carried out with a Diamond DSC calorimeter (Perkin-Elmer Co.). The wide-angle X-ray diffraction profiles at room temperature were obtained with a RAD-RC (Rigaku Denki Co., Inc.) apparatus using nickel-filtered copper K α irradiation and power settings of 40 kV \times 80 mA. Sorption isotherms of CO₂ gas at 25°C were determined using a gravimetric sorption apparatus with an electromicrobalance 2000 (Cahn Instruments Inc.).

RESULTS AND DISCUSSION

Characterization

Figure 2 shows the TG curve of the as-cast sample of A-C12 at the heating rate of 10°C/min under N₂ atmosphere. Abrupt weight loss starts at about 180°C. This corresponds to the amount of detailing side chains due to thermal imidization of A-C12. Weight



Scheme 1

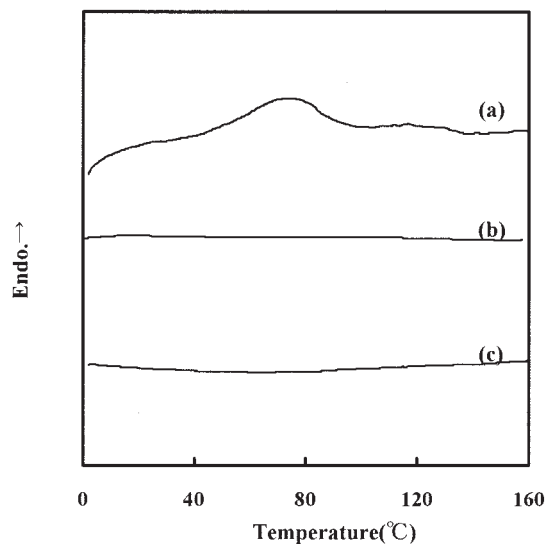


Figure 3 DSC thermograms of A-C12 as-cast membrane obtained under nitrogen atmosphere at the heating rate 10°C/min: (a) 1st heating; (b) cooling; and (c) 2nd heating.

loss during imidization was about 56%, corresponding to all of the side chains detached. Imidization has been completed by about 400°C. One could observe very little weight loss for polyimide between 400 and 600°C. Decomposition of imidized A-C12 backbone (polyimide; PMDA-PDA) started at about 600°C. Imidized A-C12 demonstrated almost the same decomposition temperature as polyimide PMDA-PDA.

DSC thermograms of the as-cast sample of A-C12 are shown in Figure 3. On first heating [Fig. 3(a)], there is one broad endothermic peak at about 80°C. This thermal event may be assigned to the melting of partly crystallized long side chains, although the melting temperature is extremely high for the side chain of carbon number 12. The enthalpy of melting of the side chain crystals is very small (less than 5 J/g) relative to that of ideal crystalline polyethylene (290 J/g),⁷ indicating that the amount of side chain crystallinity in this sample was quite negligible. However, the peak was not observed for second heating [Fig. 3(c)] and cooling process [Fig. 3(b)]. From these facts, A-C12 is not a thermotropic liquid crystal. Moreover, in the imidized sample, no peak is observed over whole temperature range studied.

X-ray diffraction profiles at 25°C of A-C12 samples are shown in Figure 4. The as-cast sample has a similar profile to the B-C_n or H-C_n polymer.¹⁻³ These polymers are common in relatively rigid backbone chains and are considered to form a layered structure mainly due to benzene ring stacking of the backbone chain. Therefore it is adequate that as-cast sample form layered structure. The diffraction peak at about $2\theta = 5^\circ$ corresponds to the layer spacing and $2\theta = 7^\circ$ corresponds to the repeat length (001) of the main chain of

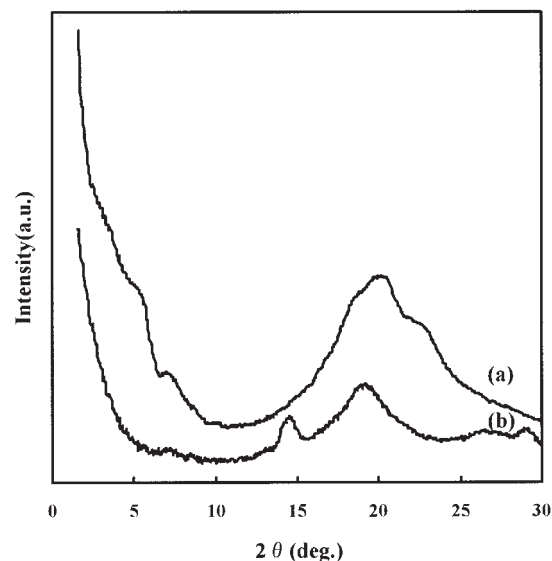


Figure 4 X-ray diffraction profiles of A-C12 samples at 25°C: (a) as-cast and (b) imidized.

A-C12. However, the imidized sample shows a completely different profile. We could not observe the layered structure at all as described above. This means the layer structure collapsed after imidization. The peak at about $2\theta = 15^\circ$ corresponds to (002) of polyimide backbone chain. The index values of samples of A-C12 determined by X-ray diffraction are shown in Table I. The densities observed for as-cast and imidized A-C12 are 1.12 and 1.45 g/cm³, respectively. The low density of 1.12 g/cm³ is characteristic of this aromatic polyamide because of the presence of the long alkyl side chain, which is packed much more loosely. The latter density is slightly lower than that of the polyimide of PMDA-PDA (1.51 g/cm³). Imidized samples showed a very high density compared with the as-cast samples. It is also supported from the density evidence that a layered structure is not held in the polyimide. To hold this ordered structure, it is much milder or lower temperature thermal conditions are required. A further effort must be made to prepare the polyimide with the layered structure to develop high selective and permeable membrane.

TABLE I
X-ray Wide Angle Diffraction Data Observed for As-cast and Imidized A-C12 Samples at 25°C

As-cast		Imidized	
<i>hkl</i>	<i>d</i> _{obs.} (Å)	<i>hkl</i>	<i>d</i> _{obs.} (Å)
001	24.8	001	12.2
100	15.2	002	6.1
002	12.4	110	4.5
200	7.7	004	3.1
010	4.3		
013	3.9		

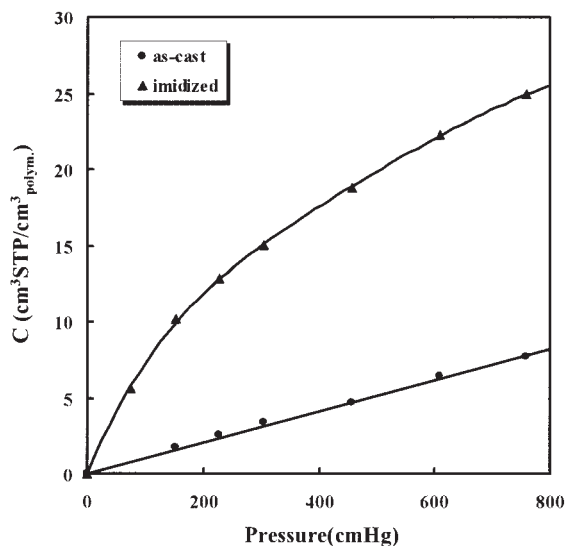


Figure 5 CO₂ sorption isotherms of A-C12 samples at 25°C: (●) as-cast and (▲) imidized.

Gas sorption properties

Figure 5 shows CO₂ sorption isotherms of A-C12 samples at 25°C. If the gas sorption properties of the as-cast sample had similar behavior to those of glassy polymers (such as PC), the gas sorption isotherm should be concave to the pressure axis and interpreted in terms of the dual mode sorption mode.^{8,9} In fact, the CO₂ sorption isotherms of PC can be explained by the dual mode sorption model.^{10,11} However, the CO₂ sorption isotherm of the as-cast sample obeys Henry's law as observed in Figure 5. Therefore, it is found that, in the case of A-C12 as-cast sample, gas sorption presumably occurs only in the looser alkyl side chain layer, which has an almost liquid-like character, because the gas sorption mechanism of rubbery polymers and liquids is, in general, described by Henry's law.^{12–15} The sorption isotherm of imidized A-C12 demonstrates the dual mode sorption type, which is represented by eq. (1):

$$C = C_D + C_H = k_D p + \frac{C'_H b p}{1 + b p} \quad (1)$$

where C is the total concentration of gas in polymer, C_D is the concentration due to Henry's law contribution, C_H is the concentration due to Langmuir mode contribution, k_D is the Henry's law solubility coefficient, C'_H is the hole saturation constant in Langmuir mode, b is the affinity constant of gas to Langmuir site, and p is the pressure.

The sorption parameters of CO₂ for A-C12 samples are shown in Table II, together with those for PC at 760 cmHg. From these values, the amounts of CO₂ sorption in PC at 760 cmHg were about three times larger

than those of the as-cast sample, although the densities of the as-cast sample are considerably lower than that of PC (ρ_{PC} is ca. 1.2 g/cm³). This result suggests that the aromatic main chain layer is very dense and cannot sorb any CO₂, similar to the behavior of crystals of PC or B-C14,^{8,16} which is consistent with the structural features of A-C12.

On the other hand, imidized samples demonstrate the dual mode sorption. Therefore, the amount of sorption is very high compared with the as-cast sample, despite the high density. This means imidized samples were not in ordered but in glassy states. This is also supported by the result of the X-ray diffraction studies.

CONCLUSION

In this study, we have prepared A-C12, poly(*p*-phenylene terephthalamide) with dodecyl side chains attached to the terephthalate moiety. By DSC measurement, no samples showed a thermotropic liquid crystal until they reached the imidization start temperature. The structure of the samples was analyzed by X-ray diffraction and the as-cast sample formed a layered structure composed of rigid aromatic polyamide main chain layers and flexible alkyl side chain layers. However, imidized samples showed different profiles. This fact indicates that the layered structure is not maintained after imidization. The CO₂ sorption is dramatically increased by imidization. This behavior is consistent with the structural change of A-C12. Gas sorption in the as-cast sample occurred only in the looser flexible alkyl side chain layers, indicating that the aromatic main chain layers are very dense and cannot sorb CO₂ to a significant extent. This is similar to the CO₂ gas solubility of B-C14; the aromatic polyester with tetradodecylester side chains is reasonably lower than that of other glassy polyesters, such as PC, even though the density of B-C14 is relatively low. Moreover, the imidized sample at 25°C shows a dual mode sorption pattern and a very high amount of CO₂ gas sorption compared with the as-cast sample, indicative of its glassy state.

The authors gratefully acknowledge partial financial support through a Grant-in-Aid for Scientific Research in Priority Area (B), "Novel Smart Membrane with Controlled Molecular Cavity", No. 13133202 (2001–2004) from the Ministry

TABLE II
CO₂ Sorption Parameters of A-C12 Samples and PC

Sample	C'_H	$k_D \times 10^2$	$b \times 10^3$
As-cast	—	1.03	—
Imidized	21.9	1.10	3.9
PC	—	3.39×10^{-2}	—

of Education, Culture, Sports, Science, and Technology of Japan and the Aichi Science and Technology Foundation of Japan.

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