THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 37, No. 2, 1967

PHYSICO-CHEMICAL STUDIES OF POLYAMIDES I

Polyamides Having Long Methylene Chain Units

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The polyamides having long methylene chain units have been prepared by the condensation of diamines with dicarboxylic acids, both having long chains of even number methylene units. The effects of the length of the methylene chain units on the melting points, the glass transition points, the densities and X-ray diffractions of these polyamides were investigated. By plotting the melting points and densities against the amide concentration, both the density and the melting point extrapolated to the zero amide concentration are found to be below the value for polymethylene. The calculated density extrapolated to the zero amide concentration from the X-ray data is also found to be below the value for polymethylene. The glass transition temperatures lie in the range of 45 to 52°C.

Introduction

Various kinds of polyamides have been prepared from diamines with dicarboxylic acids after Carothers' original work, and the relationship between the chemical structure of the polymers and their physical properties has been reported by many authors. Coffman *et al.*1) studied various aliphatic polyamides from the diamines consisting of carbon atoms up to C_{12} with dicarboxylic acids. Kinoshita2) and Slichter3) discussed the molecular structure of the polyamides consisting of methylene chain up to C_{11}. However, no systematic study of the polyamides consisting of methylene chains longer than C_{10} has been carried out. In the preceding paper4), the synthesis of diamines and dicarboxylic acids with long methylene chains up to C_{22} was reported. In the present investigation, the polyamides having long methylene chain units have been prepared by the condensation of diamines with dicarboxylic acids, both having long chains of even number methylene units, and examined from various points, such as the measurements of the melting point, density, glass transition temperature and X-ray diffraction. This study was designed to secure informations about them and to discuss the molecular motion of polyamides.

Experimentals

Materials

The preparation and the characteristic of long chain diamines and dicarboxylic acids were des-

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(*Received May, 2 1967*)

1) D. D. Coffman, C. J. Berehet, W. R. Peterson and E. W. Spanagel, *J. Polymer Sci.*, **2**, 306 (1947)
2) Y. Kinoshita, *Makromol. Chem.*, **33**, 1 (1959)
3) W. P. Slichter, *J. Polymer Sci.*, **36**, 259 (1959)
4) K. Saotome, H. Komoto and T. Yamazaki, *Bull, Chem. Soc. Japan*, **39**, 485 (1966)

cribed in the preceding paper4).

Procedure

Polymer melting points: The melting point was determined by observing solid particles of the polymer between crossed nicols polarizers on an electrically heated hot-stage microscope. The melting point was taken as the temperature at which the last trace of crystalline birefringent completely disappeared. This is the crystalline melting point of the polymer.

Glass transition temperatures: The glass transition temperature was determined on small film strips in an apparatus designed to measure the dynamic modulus of elasticity (at the resonant vibration frequency 110 cps) as a function of temperature. The temperature at which the maximum loss modulus (E''_{max}) was observed was taken as T_g5).

Densities of polymers: The density was measured at 25°C in a density gradient tube prepared by using toluene and carbon tetrachloride. The polymer particles used for the measurement were prepared by annealing at the temperature of 10°C below the melting point after gradual cooling from the melt.

X-ray diffractions: Each polymer was spun from the melt, cold drawn and then annealed at the temperature of 10°C below the melting point under tension. Fiber diffraction photographs were taken with the X-ray beam perpendicular to the fiber axis. The copper radiation filtered through nickel foil was used throughout this investigation.

Preparation of nylon salts: The equimolar diamine and dicarboxylic acid dissolved in alcohol at the concentration of 10% were mixed, and the mixture thus obtained was refluxed for 0.5 hr. After being cooled, the precipitated salt was filtered off and recrystallized from water. The yield of the nylon salts was quantitative.

Polycondensation of nylon salts: A few grams of nylon salt was sealed in a glass tube under reduced pressure. The glass tube was heated in an oil bath at 230°C for 1 hr. The glass tube was opened, and the content was heated at 260°C for 1 hr and then for 0.5 hr under a reduced pressure of 1 mmHg to complete the reaction. All polymers obtained are white, horn-like crystalline solids and their intrinsic viscosities are higher than 0.8 (*m*-cresol, 25°C).

Results and considerations

Melting point and density: The melting points and densities of polyamides containing long methylene chains are plotted against the amide group numbers per 100 chain atoms in Figs. 1 and 2. It can be readily seen that the melting point decreases with the decrease of the amide group concentration, which is apparently related to the hydrogen bonds or the cohesive force between the molecules.

The properties of polyamides are summerized in Table 16).

The extrapolation of the melting point at zero amide number affords the value of 90°C. This

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5) K. H. Illers and H. Breuer, *J. Kolloid. Sci.*, **18**, 1 (1963)

6) K. Saotome and H. Komoto, *J. Polymer Sci.*, **44**, 1463 (1966)

7) C. W. Bunn, *J. Polymer Sci.*, **16**, 323 (1955)

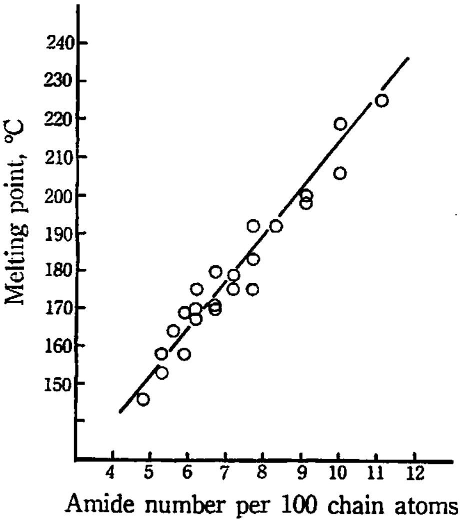

Fig. 1 Melting points of polyamides *vs.* amide number per 100 chain atoms

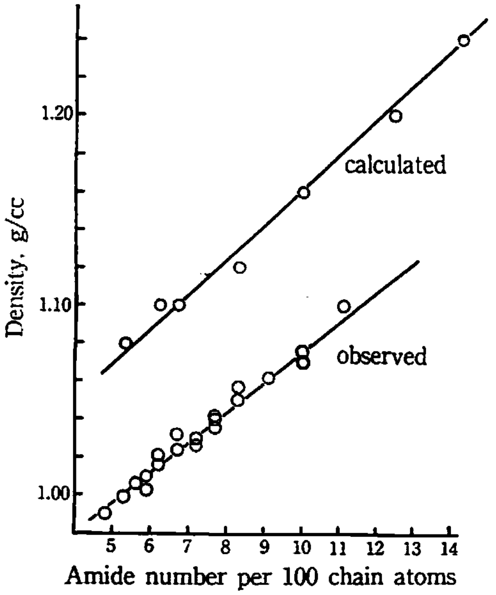

Fig. 2 Densities of polyamides *vs.* amide number per 100 chain atoms

agrees well with Bunn's result[7], which was obtained in the plots of the melting points against the cohesion energy of polyamides by the extrapolation of the melting point to the cohesion energy for polymethylene.

On the other hand, Izard[8] described an equation representing the melting point of long straight chain aliphatic polyamides with n methylene groups per repeating chain unit as; $T=\Delta H/\Delta S=2300+220n/0.654\,(n+4)$, for $n\to\infty$, $T\to 66°C$. He estimated that there existed the minimum melting point at about the polyamide 20–20, which is calculated from the above equation as 120°C. The melting point of 18–22 which corresponds to 20–20 is obtained as 140°C, while the melting point of polymethylene prepared from diazomethane is reported as 136.5°C[9]. Considering the linear relationship between the melting points and amide concentrations, the fact that the melting point of 18–22 is only 4°C higher than that of polymethylene suggests that the melting points of polyamides of lower amide concentrations are lower than that of polymethylene. Obviously, the minimum melting point should appear at a lower point which corresponds to a lower amide concentration than that of 18–22 (20–20). A similar linear relationship is also found between the observed densities and the amide concentration. This phenomenon has a significant feature in itself from the fact that the relation between the density and the CH_2 number is related to the characteristic of molecular packing.

X-ray diffraction: The X-ray fiber diagrams of these polyamides shown in Fig. 3 show that the crystal structures are very similar to each other. The structure (Fig. 4) appears to be closely analogous

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[8] E. F. Izard, *J. Polymer Sci.*, **8**, 503 (1952)

[9] L. Mandelkern, M. Hellman, D. W. Brown, D. E. Roberts and F. A. Quinn, *J. Am. Chem. Soc.*, **75**, 4093 (1953)

Table 1 Physical properties of polyamides of α, ω-alkylenediamines with α, ω-alkanedioic acids

$-NH(CH_2)_m-NHCO(CH_2)_n-CO-$		Polymer code	Nylon-salt mp	Polymer mp °C	Polymer density	Tg
m	n		°C	T_m	g/cc	°C
6	8	6–10	171	226	1.101	51
6	10	6–12	166	219	1.070	50
6	16	6–18	151	192	1.040	
6	20	6–22	152	180	1.032	
8	8	8–10	168	206	1.075	
8	10	8–12	167	200	1.062	50
8	16	8–18	150	179	1.030	
8	20	8–22	151	175	1.021	48
10	8	10–10	183	198	1.063	
10	10	10–12	169	192	1.057	49
10	16	10–18	150	170	1.024	
10	20	10–22	150	169	1.010	
12	8	12–10	158	192	1.050	
12	10	12–12	178	183	1.036	
12	16	12–18	150	167	1.010	50
12	20	12–22	150	164	1.006	
14	8	14–10	149	175	1.042	
14	10	14–12	150	175	1.027	
14	16	14–18	152	158	1.013	48
14	20	14–22	149	153	0.999	
18	8	18–10	148	171	1.024	
18	10	18–12	147	170	1.015	
18	16	18–18	148	158	0.998	50
18	20	18–22	152	146	0.990	

to those of 6–6 and 6–10 which have been determined by Bunn and Garner[10]. The specimens of these polyamides usually contain two different crystalline forms, α, β, which have the same chain repeated distance and differ only in the side-by-side arrangement of the molecules, ordinary specimens chiefly consisting of the α-form. Usually the diffraction patterns can mainly be explained in terms of the predominant α-form and the streaks near the meridian seem to be associated with the existence of β-form. The striking feature of these polyamides is the intensity of the reflections of the layer line corresponding to a spacing of about 2.5Å. The reflections on this layer line are extremely stronger than those on other layers (apart from the equator). This shows that the spacing of the chain atoms is at an approximately uniform interval along the fiber axis, indicating the existence of a subperiod. The repeated distance for these polyamides along the fiber axis given by the layer line spacings suggests that the chains are fully extended, or nearly so.

Unit cell: The c axis (the height of the cell) is the same as the molecular distance. The dimen-

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[10] C. W. Bunn and E. V. Garner, *Proc. Roy. Soc.*, A **189**, 39 (1947)

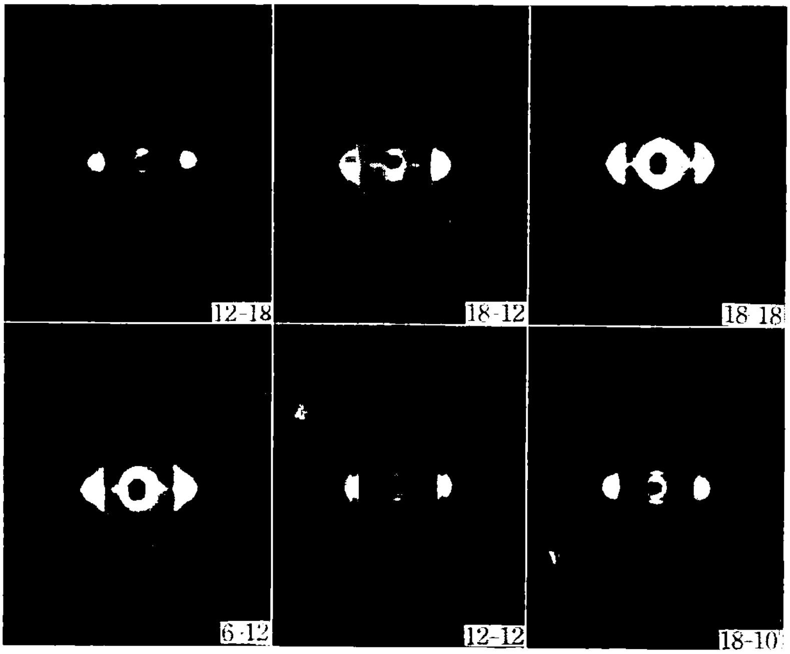

Fig. 3 X-ray fiber diagrams of long methylene polyamides

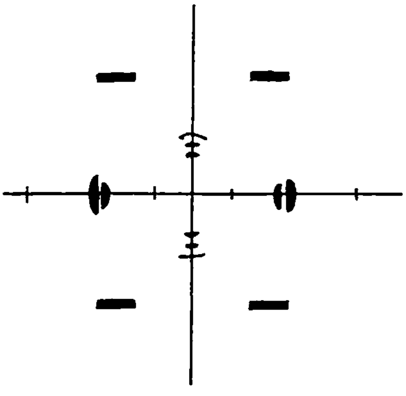

Fig. 4 X-ray diffraction patterns of long methylene polyamides

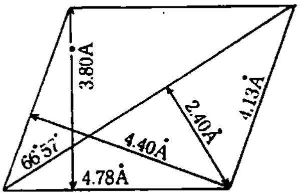

Fig. 5 Unit cell base projection on a plane perpendicular to *c* (fiber axis)

sions of the base of the cell, projected on to a plane normal to the *c* axis, are obtained from the positions of the spots on the equators of the photographs. It is important to note that both the positions and intensities of these equatorial reflections are much the same for these polymers. This fact suggests that the molecules are packed side-by-side in much the same way in these polymers. The simplest projected cell-base which fits the positions of the equatorial reflections has edges of 4.13 Å and 4.77 Å with an angle of 66°57′ between them (Fig. 5): there can be only one chain molecule passing through the cell, for the distance between the unbranched chain molecules packed side-by-side is always of the order of 4.2 Å. The volume of the cell is equal to the product of the height and the area of the projected cell base. The projected unit cell bases and the calculated density are shown in Table 2.

Table 2 Projected unit cell bases and calculated densities

Polymer code	a', Å	b', Å	c', Å	α'	Volume Å^3	Density calc.
6–6a	4.03	4.77	17.2	66°.15′	301	1.24
7b	4.13	4.77	9.85	66 57	174	1.20
6–12	4.13	4.78	25	66 57	454	1.16
10–12	4.13	4.78	29.5	66 57	536	1.12
12–10	4.13	4.78	29.5	66 57	536	1.12
18–10	4.13	4.77	37.0	66 57	672	1.10
18–12	4.13	4.78	39.5	66 57	717	1.10
18–18	4.13	4.78	47.0	66 57	854	1.08

a: nylon 6–6[10], b: nylon 7[8]

A linear relationship is also found between the calculated densities and the amide concentrations (Fig. 2). The density extrapolated to zero amide concentration is given as 0.98 g/cc, while the density of polymethylene was calculated to be 1.006 g/cc from X-ray analysis[11]. On the other hand, the observed density extrapolated to zero amide concentration is given as 0.91 g/cc which is lower than that of polymethylene (0.988 g/cc[12]). These facts show that the chain packing of polymethylene is better than that of polyamide having long methylene chain units.

Two different explanations have been given for the depression of the melting points of polyamides with very low amide concentrations below that of polymethylene. Izard[8] discussed this depression from Flory's theory[13] which described the lowering of melting point in terms of copolymerization. Bunn[7] contradicted the application of Flory's treatment to these crystalline homopolymers by pointing out the differences between a copolymer with random train of chain units and a homoplymer in which different chain units are arranged into crystals and suggested that the depression of the melting point is due to the introduction of easily rotating bonds; the CO–NH bonds appear to have double bond character, and so any additional ease of rotation should be in the adjacent CO–NH$_2$ and NH–CH$_2$ bonds. However, there is no possibility of chain packing in either of these arguments. In the polyamides in which long methylene chains are sparsely interspersed with amide groups, the contribution of the methylene chains toward the cohesion energy which binds the chain molecules together is estimated to become so predominant that the cohesion energy contributes mainly to the total heat content of fusion. Since the melting point is expressed by $T=\Delta H/\Delta S$, the introduction of easily rotating groups obviously enlarges the entropy of fusion to depress the melting point. The intermolecular spacing between the polymethylene chains which occupy the dominant portion must be affected by the insertion of the amide groups, since the calculated density extrapolated to zero amide concentration is lower

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[11] C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939)

[12] R. R. Richards, *J. Appl. Chem.*, **1**, 370 (1951)

[13] P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949)

than that of polymethylene and the chain packing of polymethylene is better than that of polyamides.

The amide group itself has obviously a greater cohesion energy and a larger density than the methylene group. For the polyamides with compositions close to polymethylene, the increase of the intermolecular spacings might give dominant effects on the melting point and on the density. Although contribution of the increase of the entropy of fusion by the introduction of the easily rotating bonds can be neglected, the increase in the intermolecular spacings which causes an enormous decrease of the heat content of fusion is considered to be the main factor for the depression both of the melting points and the densities to the minimum point below those of polymethylene.

Glass transition temperature: The values of the glass transition temperatures of poly-caproamide and poly-hexamethyleneadipamide often quoted in the literature lie in the range of 45 to 50°C14). The values of the glass transition temperatures of long methylene polyamides also lie in this range. Rybnikar15) evaluated the T_g of nylon 6 and 6–6 by the penetrometer method. Both polymers exhibited a remarkably low glass transition temperature -65°C. The change of the crystalline structure of 6–6 begins at 160°C16). The higher constant value of T_g which does not depend on the amide concentration is probably related to the temperature at which the frozen amorphous phase is molten as a consequence of the breaking up of the hydrogen bonds between chains17).

Acknowledgement

The author wishes to express his sincere thanks to Prof. Jiro Osugi for valuable guidance. The author wishes to express his gratitude to Dr. Kazuo Saotome for valuable guidances and discussions throughout this work. His hearty thanks are also due to Dr. Akira Suzuki, the director and to Dr. Hidehiko Kobayashi, the chief researcher, Technical Research Laboratory of Asahi Chemical Industry Co., Ltd. for supports and encouragements.

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15) F. Rybnikar, *J. Polymer Sci.*, **28**, 633 (1958)
16) G. F. Schmidt and H. A. Stuart, *Z. Naturforsch.*, **13a**, 222 (1958)
17) A. E. Woodward, J. M. Cussman and J. A. Sauer, *J. Polymer Sci.*, **44**, 23 (1960)