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PHYSICO-CHEMICAL STUDIES OF POLYAMIDES II

Aromatic Polyamides Having Long Methylene Chain Units

BY HIROSHI KOMOTO

Two series of polyamides having long methylene chain units have been prepared from *p*-xylylenediamine and 2, 2'-*p*-phenylenebisethylamine with α , ω -thiaalkanedioic acids of long methylene chain units; aliphatic diamines of long methylene chain units with terephthalic, benzene-1,4-diacetic, and benzene-1,4-dipropionic acids. The effects of the length of methylene chain units on the melting points, the glass transition temperatures and the densities of these polyamides were investigated. The aromatic polyamides, in which even methylene chains are present between a phenylene and an amide group generally have higher melting points and densities than the corresponding ones with odd methylene chains. The melting points of polyamides having thioether linkages are lower than those of corresponding long methylene polyamides.

Introduction

Frunze *et al.*¹⁾ prepared the polyamides of *p*-xylylenediamine with α , ω -octadecanedioic and α , ω -docosanedioic acids. Saotome *et al.*²⁾ prepared the polyamides of *p*-xylylenediamine with α , ω -oxaalkanedioic acids. In the preceding paper³⁾, the synthesis of diamines and dicarboxylic acids with long methylene chains up to C₂₂ was reported. The present paper deals with the preparation and some properties of the polyamides from these diamines and dicarboxylic acids. The polyamides are classified into the following two series; (1) polyamides from aromatic diamines, such as *p*-xylylenediamine and 2, 2'-*p*-phenylenebisethylamine with α , ω -alkanedioic and α , ω -thiaalkanedioic acids, (2) polyamides from aliphatic diamines having long methylene chains with aromatic dicarboxylic acids, such as terephthalic, benzene-1,4-diacetic, and benzene-1,4-dipropionic acids. The effects of methylene chain length on the melting points, the glass transition temperatures, and the densities of the polyamides of each series have been investigated.

Experimentals

Materials

The preparation of long methylene diamines and dicarboxylic acid was described in the preceding paper³⁾. Terephthalic acid was obtained commercially. *p*-Xylylenediamine was prepared from tere-

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- 1) T. M. Frunze, V. V. Korshak and E. A. Kransnyanska, *Vysokomol. Soedin.*, **1**, 495 (1959)
- 2) K. Saotome and K. Sato, *J. Polymer Sci. A* **1**, 4, 1303 (1966)
- 3) K. Saotome, H. Komoto and T. Yamazaki, *Bull. Chem. Soc. Japan*, **39**, 485 (1966)

phthalonitrile by catalytic hydrogenation⁴⁾. 2, 2'-*p*-Phenylenebisethylamine was prepared from 1, 1'-dichloro-*p*-xylene through the biscyano derivative⁵⁾. Benzene-1,4-diacetic acid, mp 251-252°C, was prepared from 1, 1'-dichloro-*p*-xylene according to the method of Kipping⁶⁾. Benzene-1,4-dipropionic acid, mp 231°C, was prepared from 1, 1'-dichloro-*p*-xylene through the malonic ester synthesis.

Methods

The methods of experiments were the same as those in part I.⁷⁾

Results and Considerations

In the first series of experiments the polyamides of *p*-xylylenediamine and 2, 2'-*p*-phenylenebisethylamine with α, ω -alkanedioic and α, ω -thiaalkanedioic acids having 9-22 carbon atoms were prepared.

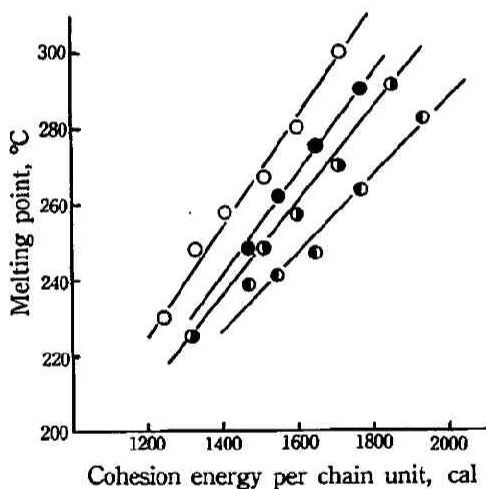


Fig. 1 Melting points vs. cohesion energies per chain unit

○ PBE-even, ● PBE-odd,
◐ PBD-even, ● PBD-odd

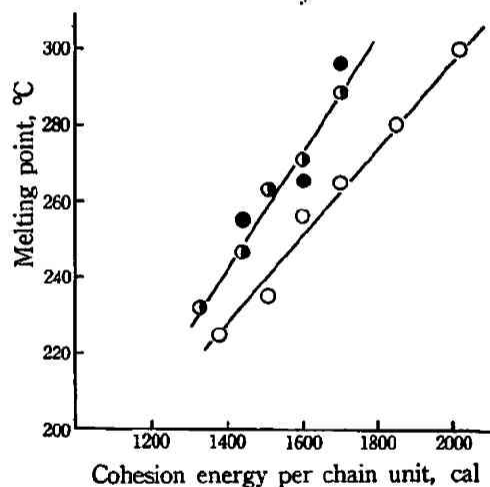


Fig. 2 Melting points vs. cohesion energies per chain unit

● even-T, ◐ even-BDP,
○ even-BDA

The results are summarized in Tables 1 and 2. The polyamides of α, ω -alkylenediamines with such dicarboxylic acids as terephthalic, benzene-1,4-diacetic, and benzene-1,4-dipropionic acids were prepared in the second series. The data are tabulated in Table 3.

The melting points of these polyamides containing benzene rings in the chain are plotted against the cohesion energy per chain unit in Figs. 1, 2 and 3.

4) L. Kh. Freidlin, T. A. Sladokova, G. I. Kudryavtsev, T. N. Shein, E. N. Zil'berman and R. G. Fedoraba, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1961, 1713

5) P. Ruggli, B. B. Bussmaker, W. Muller and A. Staub, *Helv. Chim. Acta*, 18, 1388 (1935)

6) J. S. Kipping, *Chem. Ber.*, 21, 42 (1888)

7) H. Komoto, *This Journal*, 37, 105 (1967)

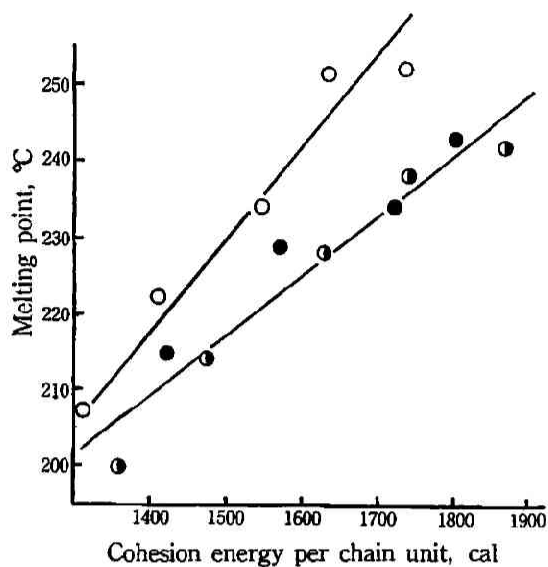


Fig. 3 Melting points vs. cohesion energies per chain unit

○ PBE-nSn,
◐ PXD-nOn,
● PXD-nSn

Table 1 Physical properties of polyamides of *p*-xylylenediamine (PXD) with α, ω -alkanedioic acids, $\text{HOOC}(\text{CH}_2)_n\text{COOH}$ and α, ω -thiaalkanedioic acids, $\text{HOOC}(\text{CH}_2)_{n-1}\text{S}(\text{CH}_2)_{n-1}\text{COOH}$ (nSn)

n	Polymer code	Nylon-salt mp °C	Polymer mp °C T_m^a	η_{sp}/C	Density g/cc	T_g °C ^{a)}
7	PXD-9	197	282	1.15	1.152	
8	PXD-10	215	291	1.25	1.152	115
9	PXD-11	192	264(260)	1.40	1.130	110(107)
10	PXD-12	203	270(270)	1.50	1.129	105(105)
11	PXD-13	189	247	1.30	1.108	100
12	PXD-14	192	257	1.12	1.110	
13	PXD-15	183	241	1.01	1.090	90
14	PXD-16	190	248	1.07	1.092	
15	PXD-17	184	239	1.05	1.080	
16	PXD-18	189	242	1.21	1.075	75
20	PXD-22	187	225	1.31	1.056	
5	PXD-5S5	184	242	0.80	1.201	70
6	PXD-6S6	178	238	0.93	1.175	
7	PXD-7S7	176	228	1.04	1.157	65
9	PXD-9S9	174	214	0.98	1.127	
11	PXD-11S11	167	200	0.75	1.094	

a) T_m and T_g values in parenthesis denote those determined by the dilatometric method (Figs. 4 and 5).

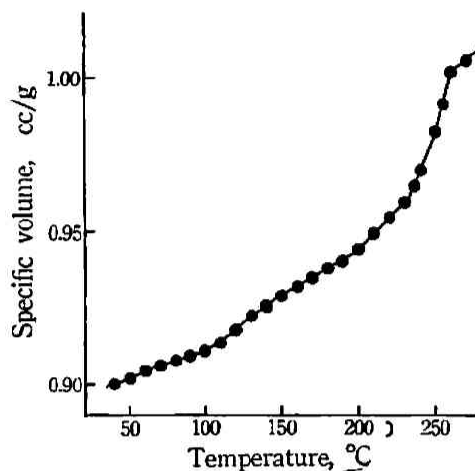


Fig. 4 Temperature-specific volume curve for PXD-11

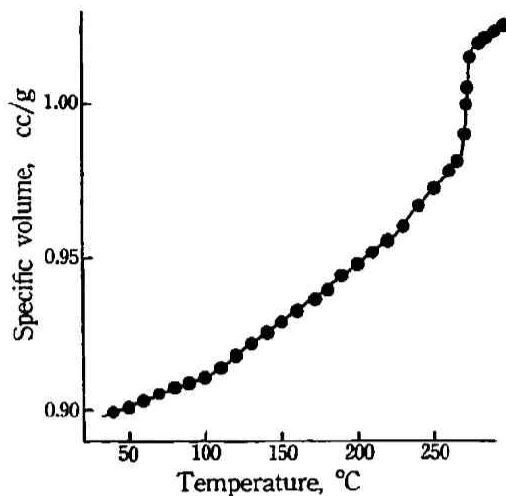


Fig. 5 Temperature-specific volume curve for PXD-12

Table 2 Physical properties of polyamides of 2, 2'-phenylenebisethylamine (PBE) with α , ω -alkanedioic acids, $\text{HOOC}(\text{CH}_2)_n\text{COOH}$ and α , ω -thiaalkanedioic acids, $\text{HOOC}(\text{CH}_2)_{n-1}\text{S}(\text{CH}_2)_{n-1}\text{COOH}$

n	Polymer code	Nylon-salt mp °C	Polymer mp °C T_m	η_{sp}/C	Density g/cc	T_g °C
7	PBE-9	197	290	1.06	1.140	
8	PBF-10	210	300	1.23	1.139	105
9	PBE-11	202	275	1.25	1.108	96
10	PBE-12	201	280	1.28	1.108	
11	PBE-13	191	262	1.30	1.095	
12	PBE-14	177	267	1.15	1.091	93
13	PBE-15	171	248	1.08	1.075	
14	PBE-16	175	258	1.06	1.077	
15	PBE-17	170	249	1.12	1.067	
16	PBE-18	175	248	1.15	1.055	75
20	PBE-22	173	230	1.30	1.050	
5	PBE-5S5	188	252	1.03	1.174	
6	PBE-6S6	182	251	0.90	1.148	
7	PBE-7S7	160	234	0.89	1.132	
9	PBE-9S9	162	222	0.79	1.106	
11	PBE-11S11	155	207	0.10	1.067	58

Table 3 Physical properties of polyamides of α, ω -alkylenediamines, $H_2N(CH_2)_n NH_2$, with terephthalic (T), benzene-1,4-diacetic (BDA) and benzene-1,4-dipropionic acids (BDP)

Acid	Amine n	Polymer code	Nylon-salt mp °C	Polymer mp °C T_m	η_{sp}/C	Density g/cc	T_g °C
T	12	12-T	253	296	0.85	1.152	
	14	14-T	242	265	0.92	1.115	
	18	18-T	228	255	1.03	1.067	
BDA	6	6-BDA	259	300	1.21	1.182	
	8	8-BDA	225	280	1.15	1.152	110
	10	10-BDA	198	265	1.16	1.130	
	12	12-BDA	191	256	1.21	1.095	
	14	14-BDA	184	235	0.75	1.075	
	18	18-BDA	177	225	1.31	1.036	78
BDP	8	8-BDP	197	289	1.23	1.151	
	10	10-BDP	198	271	1.15	1.120	
	12	12-BDP	174	263	1.30	1.080	85
	14	14-BDP	171	246	0.85	1.067	
	18	18-BDP	169	232	1.05	1.034	65

Table 4 Cohesion energies for common groups

Groups	Cohesion energy cal per mole
$-CH_2-$	680
$-C_6H_4-$	3900
$-O-$	1000
$-S-$	2200
$-CONH-$	8500

Table 5 Cohesion energies of polymers

Chemical unit	E , cal per unit	No. of chain units
$-(HN(CH_2)_n C_6H_4(CH_2)_m NHCO(CH_2)_m CO)-$	$20900 + 680(m + 2n)$	$5 + m + 2n$
$-(OC(CH_2)_n C_6H_4(CH_2)_m CONH(CH_2)_m NH)-$	"	"
$-(NH(CH_2)_n C_6H_4(CH_2)_m NHCO(CH_2)_m O(CH_2)_m CO)-$	$21900 + 680(2n + 2m)$	$6 + 2(n + m)$
$-(HN(CH_2)_n C_6H_4(CH_2)_m NHCO(CH_2)_m SCH_2)_m CO)-$	$23100 + 680(2n + 2m)$	$6 + 2(n + m)$

The calculation of the cohesion energy was carried out according to Bunn's method⁸⁾. Table 4 gives cohesion energy for some of the common groups. The figures for a number of polymers are given in Table 5. In the case of terephthalamide, however, the $-OC-C_6H_4-CO-$ group was separated into two

8) R. Hill and E. E. Wacker, *J. Polymer Sci.*, 3, 609 (1948)

chain units, 2CO and phenyl, in accordance with the phenylene groups in benzene-1,4-diacetamide and benzene-1,4-dipropionamide, neglecting the rigidity due to the resonance effects. The plots of the melting point *versus* cohesion energies are separated into two lines according to odd or even numbers of the carbon atoms in the aliphatic component. The melting points of a series of aliphatic polyamides were found to be correlated with varying numbers of CH_2 groups, as already pointed out⁸⁾. There were considerable divergences between the melting points of isomeric polyamides. It can be generally said that the series with even numbers of CH_2 groups have higher melting points than those with odd numbers.

It had been suggested by some authors⁸⁾ that the lower melting points of the polyamides with odd numbers of CH_2 groups compared with those with even numbers due to deficient hydrogen bond formation.

Kinoshita⁹⁾ showed that the odd numbers of CH_2 groups in polyamides did not lead to the deficient hydrogen bond formation, but in general gives rise to somewhat similar configuration to the pleated sheets structure of polypeptide. The melting points of the polyamides of 2, 2'-phenylenebisethylamine are generally higher than those of *p*-xylylenediamine in both of the cases of odd and even numbers in the corresponding aliphatic dicarboxylic acids. Similar relations are observed between the polyamides of terephthalic, and benzene-1,4-diacetic acid and those of benzene-1,4-dipropionic and benzene-1,4-diacetic acid. These tendencies are summarized as follows: in the aromatic polyamides of these five types, the melting point of the polymer which has a methylene chain with even numbers of carbon atoms between the phenylene and the amide groups is generally higher than that of the corresponding one which has a methylene chain with an odd numbers of carbon atoms. The densities of these five polyamides, which are isomers each other when the methylene numbers are equal in the repeating

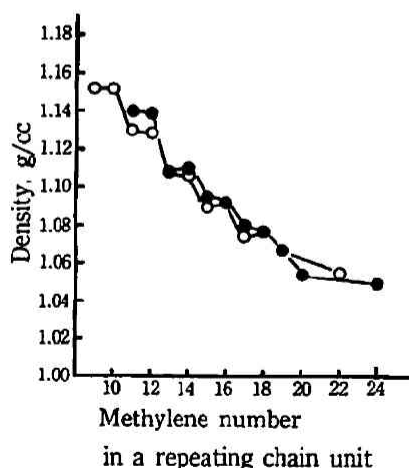


Fig. 6 Densities *vs.* methylene number in a repeating chain unit
○ PXD-n, ● PBE-n

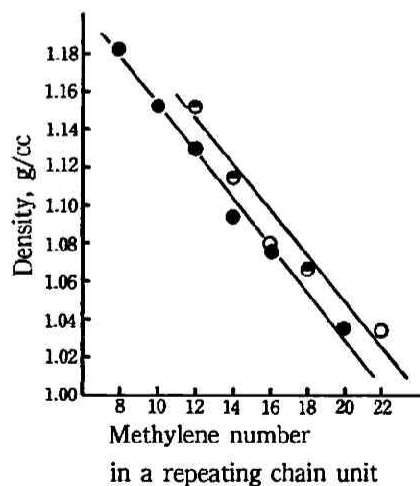


Fig. 7 Densities *vs.* methylene number in a repeating chain unit
● n-T, ○ n-BDP, ● n-BDA

9) Y. Kinoshita, *Makromol. Chem.*, **33**, 1 (1959)

chain units, are plotted against the methylene numbers in a repeating chain unit in Figs 6 and 7. Parallel relationships are observed between the melting points and the densities against the methylene numbers in a repeating chain unit. The densities of polyterephthalamides agree with those of the corresponding poly-benzene-1,4-dipropionamides. On the other hand, the densities of poly-benzene-1,4-diacetamides lie below those of poly-benzene-1,4-dipropionamides. The depressions, both of the melting point and of density, for poly-benzene-1,4-diacetamides in Figs. 2 and 7 may be attributed to the odd-numbered methylene chain joined directly to the benzene ring. The fact that no practical differences in the melting points and densities are observed between the polyterephthalamide and their isomeric poly-benzene-1,4-dipropionamides is considered to indicate the absence of the conjugation of the carbonyl group with the benzene ring in polyterephthalamides. Perhaps, the conjugation between the carbonyl and the benzene ring is interfered with by the intermolecular hydrogen bond with the amide groups. This is quite different from poly alkylene terephthalate, in which the resonance between the carbonyl and the benzene ring causes its melting point to increase anomalously¹⁰⁾.

The same relationships between the melting points and cohesion energies are observed in the polyamides prepared from PXD and BDP with α , ω -thiaalkanedioic acids as shown in Fig. 3. Ether and thioether bonds which are more rotatable than the methylene bond cause a depression of melting points of polyamides, although the cohesion energy of ether and thioether groups are larger than that of the methylene group.

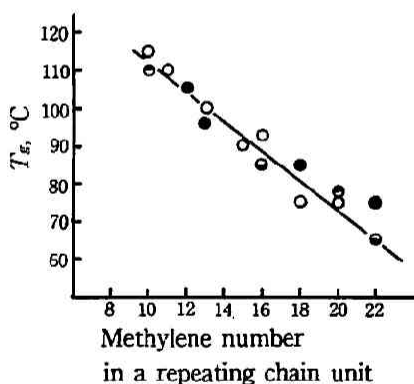


Fig. 8 Glass transition temperatures vs. methylene number in a repeating chain unit
 ○ PXD-n, ● PBE-n,
 ◐ n-BDA, ◑ n-BDP

The linear relationship between the glass transition temperatures and the methylene numbers in a repeating chain unit for these aromatic polyamides is plotted in Fig. 8. The effect of the benzene ring on the glass transition temperatures is conspicuous, since those of most aliphatic polyamides are between 40 and 50°C, irrespective of their methylene chain length.

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

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*Technical Research Laboratory,
Asahi Chemical Industry Co., Ltd.,
Itabashi-ku, Tokyo, Japan.*