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PHYSICO-CHEMICAL STUDIES OF POLYAMIDES III

Isomorphism in Copolyamides of Long Chain Units Containing Oxa- and Thia-Alkylene Linkages

BY HIROSHI KOMOTO

Various copolyamides of long repeating chain units were prepared from *p*-xylylenediamine (PXD) with aliphatic dicarboxylic acids of three structural type; *α*, *ω*-alkanedioic, *α*, *ω*-oxaalkanedioic, and *α*, *ω*-thiaalkanedioic acids. These copolyamides having the same number of chain atoms with the diamine afforded highly crystalline copolyamides. In the cases of all these copolymers, the plots of the melting points and the densities *versus* the compositions are expressed by linear relations. From X-ray examination it is ascertained that the lattice spacing of each copolyamide are unchanged by the composition. These results show that methylene, ether, and thioether linkages are in the relation of isomorphous replacement for each other in these copolyamide systems. Moreover, the linear relationship between the melting point and the composition is explained by assuming that the entropy of fusion in these copolyamides changes linearly according to the change of the composition.

Introduction

Since Edgar and Hill[1] first observed a linear relationship between the melting points and the composition in the copolyamides of hexamethylenediamine with adipic and terephthalic acids, this relationship has been accepted as a criterion for isomorphous replacement. Cramer and Beaman[2] found a better linearity of the melting points *versus* the composition in the copolyamides of heptamethylenediamine and bis-3-aminopropyl ether with dicarboxylic acids. Isomorphous replacement between the benzene ring and a four-methylene sequence was also investigated by Yu and Evans[3][4]. Levine and Temin[5] observed that there is good linearity of the melting points *versus* the composition in the copolyamides of *ε*-caprolactam with *p*-aminomethylcyclohexylcarboxylic acid. Tranter[6] pointed out from X-ray examination of the copolyamides of hexamethylenediamine with several dicarboxylic acids that the shape of the melting point *versus* the composition curve is not a reliable criterion for isomorphous replacement. This paper deals with isomorphous replacement in the copolyamides of long repeating chain units containing oxa- and thia-alkane linkages.

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1) O. B. Edgar and R. Hill, *J. Polymer Sci.*, **8**, 1 (1952)
2) F. B. Cramer and R. G. Beaman, *J. Polymer Sci.*, **11**, 237 (1956)
3) A. J. Yu and R. D. Evans, *J. Am. Chem. Soc.*, **81**, 5361 (1959)
4) A. J. Yu and R. D. Evans, *J. Polymer Sci.*, **42**, 249 (1960)
5) M. Levine and S. C. Temin, *J. Polymer Sci.*, **49**, 241 (1961)
6) T. C, Tranter, *J. Polymer Sci.*, **2**, 4289 (1964)

Experimentals

The melting points, glass transition temperatures, the reduced viscosities and the densities were measured according to the same methods as described in part I[7]. The melting points, glass transition temperature and some X-ray analysis were carried out according to the same method as described in part I[7]. A mixture of each nylon salt was polymerized in the same way as described in part II[8] for the preparation of homogeneous polyamides.

Results

Copolyamides of binary system: In order to investigate the isomorphous replacement of methylene, ether and thioether linkages, various copolymers of several different compositions were prepared in binary systems, each containing two different acid residues; alkylene/oxaalkylene, alkylene/thiaalkylene, or oxaalkylene/thiaalkylene groups. The melting points and the reduced viscosities are listed in Tables 1～3. In the notation used the polyamide is X–Y, X representing diamine and Y dicarboxylic acid. PXD denotes *p*-xylylenediamine and simple numerals denote aliphatic dicarboxylic acid, while mOn and mSn show oxa- and thiaalkanedioic acids of the following formulas: $HOOC(CH_2)_{m-1}O(CH_2)_{n-1}COOH$ and $HOOC(CH_2)_{m-1}S(CH_2)_{n-1}COOH$.

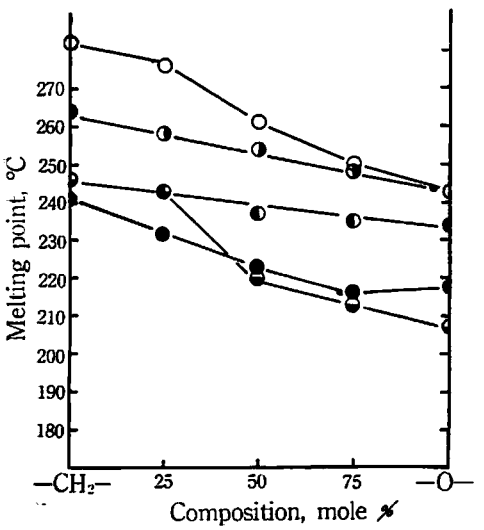

Fig. 1 Melting points *vs.* composition in copolyamides having oxaalkane groups
○ PXD-9/PXD-4O4,
◑ PXD-11/PXD-5O5,
◐ PXD-13/PXD-6O6,
◒ PXD-13/PXD-5O7,
● PXD-15/PXD-5O9

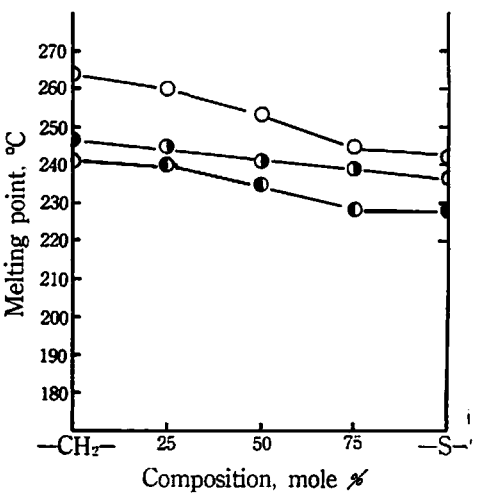

Fig. 2 Melting points *vs.* composition in copolyamides having thiaalkane groups
○ PXD-11/PXD-5S5,
◑ PXD-13/PXD-6S6,
◐ PXD-15/PXD-7S7

7) H. Komoto, *This Journal*, **37**, 105 (1967)
8) H. Komoto, *This Journal*, **37**, 112 (1967)

The relations between the melting points and the compositions of the copolyamides which contain two different acid residues of the same number of chain atoms are plotted in Figs. 1～3. Linear relations between the densities and the compositions are also obtained in the following copolyamides; PXD-11/PXD-5O5, PXD-11/PXD-5S5 and PXD-5O5/PXD-5S5 (Fig. 4).

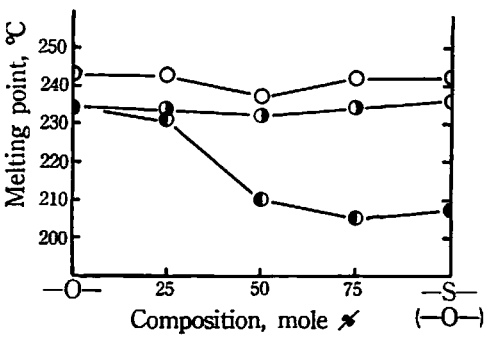

Fig. 3 Melting points *vs.* composition in copolyamides having both ether and thioether linkages and two different ether linkages
○ PXD-5O5/PXD-5S5,
◑ PXD-6O6/PXD-6S6,
◐ PXD-6O6/PXD-5O7

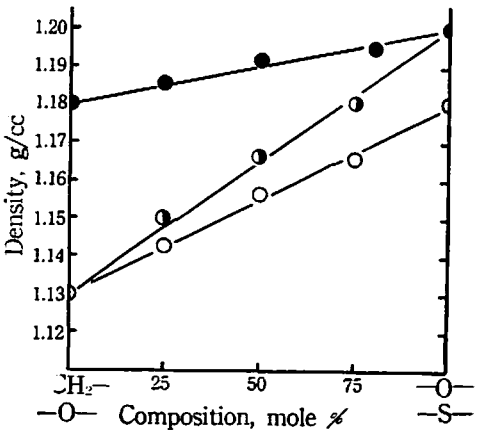

Fig. 4 Densities *vs.* composition in binary copolyamides
○ PXD-11/PXD-5O5,
◑ PXD-11/PXD-5S5,
● PXD-5O5/PXD-5S5

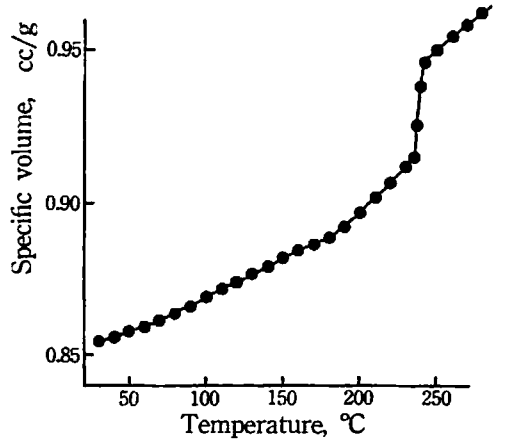

Fig. 5 Temperature-specific volume curve for PXD-5O5

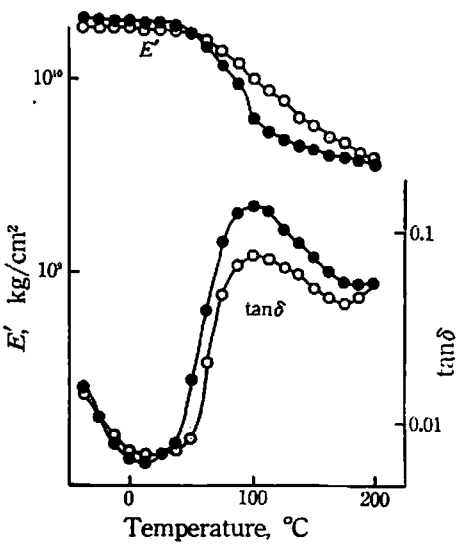

Fig. 6 Dynamic viscoelasticity of PXD-5O5 (undrawn)
○: Heat treated at 180°C

Table 1 Melting point and viscosity of copolyamides containing ether linkages

Copolyamide	Composition mole %	Copolyamide mp °C	η_{sp}/C
PXD-9	100	282	1.15
PXD-9/PXD-4O4	75/25	276	0.86
〃	50/50	261	0.73
〃	25/75	250	0.78
PXD-4O4	100	243	0.72
PXD-11	100	264	1.36
PXD-11/PXD-5O5	75/25	258	0.86
〃	50/50	254	0.91
〃	25/75	249	0.88
PXD-5O5	100	243	1.35
PXD-13	100	247	1.30
PXD-13/PXD-6O6	75/25	243	1.00
〃	50/50	237	0.98
〃	25/75	235	0.97
PXD-6O6	100	234	0.88
PXD-13	100	247	1.30
PXD-13/PXD-7O5	75/25	243	0.83
〃	50/50	220	0.84
〃	25/75	213	0.85
PXD-7O5	100	207	0.93
PXD-15	100	241	1.01
PXD-15/PXD-9O5	75/25	232	0.92
〃	50/50	223	0.88
〃	25/75	216	0.88
PDX-9O5	100	217	0.75

Table 2 Meltimg point and viscosity of copolyamides containing thioether linkages

Copolyamide	Composition mole %	Copolyamide mp °C	η_{sp}/C
PXD-11/PXD-5S5	75/25	260	0.82
〃	50/50	253	0.81
〃	25/75	245	0.83
PXD-13/PXD-6S6	75/25	245	0.92
〃	50/50	241	0.85
〃	25/75	239	0.75
PXD-15/PXD-7S7	75/25	240	0.95
〃	50/50	235	0.98
〃	25/75	228	0.80

The glass transition temperature of PXD-5O5 is shown in Figs. 5 and 6. The glass transition temperature is depressed significantly by the introduction of ether linkage (Table 4).

X-ray examination of copolyamides: X-ray diffraction patterns of standard polyamides ar

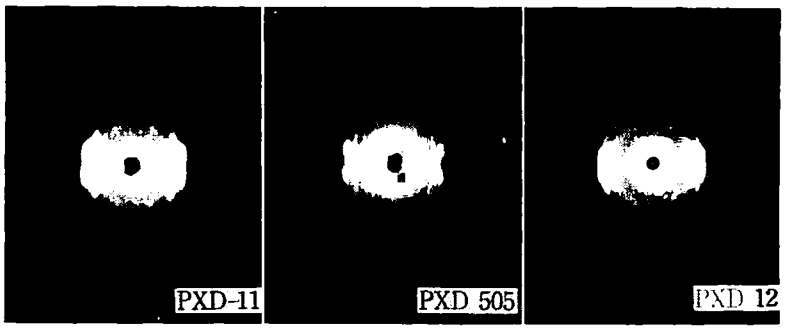

Fig. 7 X-ray fiber diagrams of polyamides

shown in Fig. 7. X-ray diffraction pattern of PXD-11 is identical with that of PXD-5O5. Their crystalline forms could not be obtained.

Table 3 Melting point and viscosity of copolyamides containing both ether and thioether linkages or containing two different ether linkages

Copolyamide	Composition mole %	Copolyamide mp °C	η_{sp}/C
PXD-5O5/PXD-5S5	75/25	243	0.89
//	50/50	238	0.78
//	25/75	242	0.90
PXD-6O6/PXD-6S6	75/25	234	0.85
//	50/50	232	0.78
//	25/75	234	0.83
PXD-6O6/PXD-7O5	75/25	231	0.99
//	50/50	210	0.81
//	25/75	205	0.75

Table 4 Glass transition temperatures of copolyamides

Copolyamide	Composition mole %	T_g °C
PXD-11	100	110
PXD-11/PXD-5O5	75/25	85
//	50/50	75
//	25/75	74
PXD-5O5	100	70

PXD-12, however, has similar X-ray patterns to PXD-10[9], differing only in the fiber identical period. From the bulk polymer samples, pieces about 1 mm thick were cut and photographed with Ni-filtered CuKα radiation. The lattice spacings were calculated from the diameters of the Debye-Scherrer rings. The lattice spacings of several copolyamides of different compositions made from PXD

9) D. C. Vogelsong, *J. Polymer Sci.*, **57**, 895 (1962)

Table 5 Lattice spacings of copolyamides

Copolyamide	Composition mole %	Lattice spacings Å						
PXD-11/PXD-5O5	100/0	3.9	—	4.5	5.1	—	9.0	18.0
〃	75/25	3.8	4.1	4.5	5.1	—	8.9	18.0
〃	50/50	3.7	4.1	4.4	5.1	—	8.8	18.0
〃	25/75	3.8	4.2	4.5	5.0	5.5	8.8	18.0
〃	0/100	3.7	4.2	4.5	—	5.5	8.9	17.6
PXD-11/PXD-5S5	100/0	3.9	—	4.5	5.1	—	9.0	18.0
〃	75/25	3.8	4.1	4.4	5.0	5.6	9.1	17.5
〃	50/50	3.8	4.0	4.5	5.0	5.5	9.1	17.6
〃	25/75	3.7	4.1	4.5	5.0	5.5	9.0	17.9
〃	0/100	3.6	4.0	4.6	4.9	5.4	—	18.0
PXD-5O5/PXD-5S5	100/0	3.7	4.2	4.5	—	5.5	8.9	17.6
〃	75/25	3.7	4.1	4.4	5.0	5.5	8.7	17.6
〃	50/50	3.7	4.0	4.4	5.0	5.5	8.7	17.5
〃	25/75	3.7	4.0	4.5	5.0	5.5	8.8	17.6
〃	0/100	3.6	4.0	4.6	4.9	5.4	—	18.0

and dicarboxylic acids of 11 chain atoms involving ether or thioether linkage are shown in Table 5.

Infrared absorption spectra: The polarized infrared spectra of stretched and oriented crystalline specimens of PXD-11 and PXD-5O5 are shown in Figs. 8 and 9. The intense band at 1639 cm^{-1} is associated to the amide I vibration which mainly involves the C=O stretching mode, and the bands at 1545 and 1250 cm^{-1} are assigned to the amide II and III vibrations which are associated with the coupled N-H in-plane deformation and C-N stretching mode, respectively. The band at 3297 cm^{-1} is assigned to the N-H stretching mode and the weak band at 3074 cm^{-1} to the first overtone of the amide II vibration. The amide V mode which is primarily due to the N-H out-of-plane deformation is the most sensitive to the crystalline form and the crystallinity of the specimen among all the amide cha-

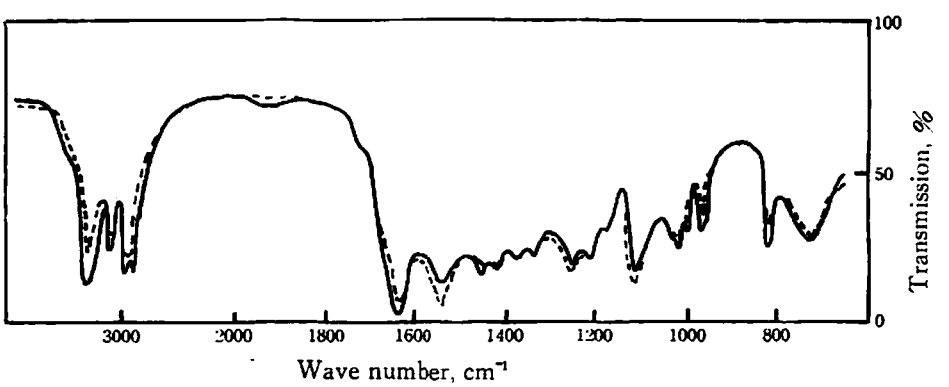

Fig. 8 Infrared spectrum of stretched and annealed PXD-11
(———) electric vector perpendicular to stretching direction
(·····) electric vector parallel to stretching direction

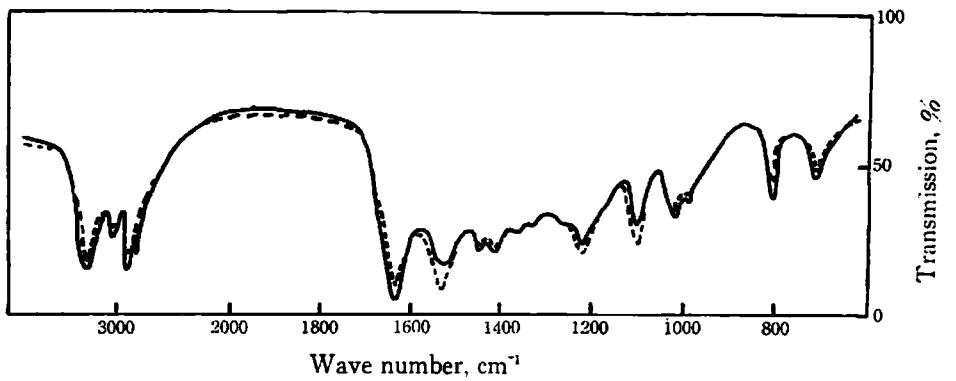

Fig. 9 Infrared spectrum of stretched and annealed PXD-5O5
(———) electric vector perpendicular to stretching direction
(·····) electric vector parallel to stretching direction

racteristic vibrations. In the cases of aliphatic polyamides it has been established that the amide V bands appear at around 690 cm^{-1} for α-form and at around 720 cm^{-1} for γ-form[10]. In the cases of PXD-11 and PXD–5O5, the band at 720 cm^{-1} is assigned to the amide V band. There was no clear difference in intensity of amide V band between these isomorphous copolyamides and homogeneous polyamide. Although the specimens are highly oriented, the observed dichroism of the characteristic bands are much lower than those of PXD–12 (Fig. 10). This may indicate that the transition moment

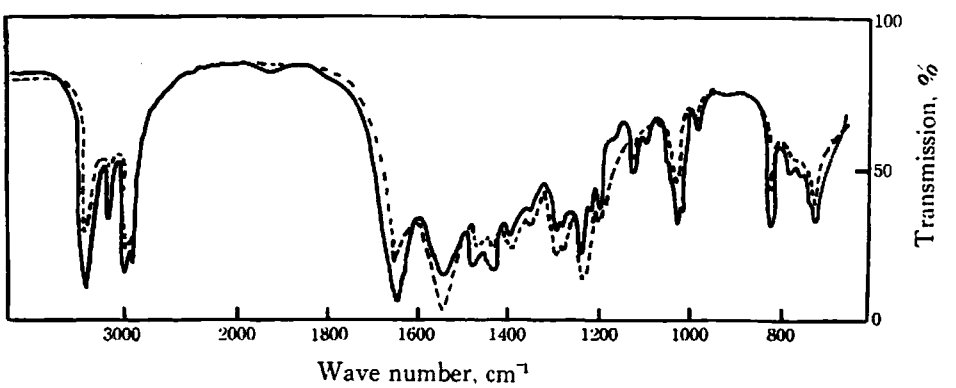

Fig. 10 Infrared spectrum of stretched and annealed PXD-12
(———) electric vector perpendicular to stretching direction
(·····) electric vector parallel to stretching direction

of these vibrations is inclined to the orthogonal direction of the chain axis to a considerable extent to make the pleated sheets structure[11]. This is the reason why it is difficult to make clear the crystalline form of PXD–11 and PXD–5O5.

10) A. Miyake, *J. Polymer Sci.*, **44**, 223 (1960)
11) L. Pauling and R. B. Corey, *Proc. Nat. Acad. Sci. U.S.*, **39**, 253 (1953)

Considerations

The similarity in the length of a repeating chain unit has been said to be the most important requisite for the occurrence of isomorphous replacement in the crystal lattice or the interchange of different repeating units within the crystal lattice without reduction in crystallinity. The copolyamides investigated in this work have the following chain units: $-HNCH_2-C_6H_4-CH_2NHCO-(CH_2)_m-Y-(CH_2)_nCO-$. In Y we take the C–C–C angle as 110° and the length of the bond as 1.53Å.; the C–O–C angle (in diethyl ether) is 108° and the bond length is 1.43 Å.; the C–S–C bond is taken as 1.82 Å[12]. Tranter[6] investigated the isomorphous relationship in copolyamides containing *p*-phenylene linkages. In a series of binary copolymers based on homopolymers prepared from hexamethylenediamine and several dicarboxylic acids containing *p*-phenylene linkage, such as *p*-phenylenedipropionic (3P3), 3-(*p*-carboxymethyl) phenylbutyric (2P4), 2-(*p*-carbomethoxy)-phenylpropionic (3PO2), hydroquinonediacetic (2OPO2), and terephthalic acids, he found that only the 6–3P3/6–3PO2 system showed a linear relationship between the softening points and the compositions. From X-ray examination and infrared and density measurements, he pointed out that the form of the softening point *versus* composition curve is not a reliable criterion for isomorphous replacement, and it seems likely that this conclusion applies equally to the melting point *versus* composition curve. There is no evidence in the criterion that a linear melting point *versus* composition relationship indicates isomorphous replacement in copolymers. Isomorphous replacement should be decided from the following observations; no difference is observed in the X-ray diagrams between the copolymer and the homopolymers and no large depression of crystallinity is observed in the copolymer. In part I, from the comparison of the densities of the aliphatic polyamide having long methylene chains with that of polymethylene, we pointed out that polyamide molecules are more loosely packed than polymethylene molecules in the crystal lattice. Therefore, it may be considered that there is enough space remaining in the polyamide crystal lattice for different repeating chain units with similar dimensions to interchange isomorphously. As shown in Table 5, the differences in lattice spacings among the homopolymers PXD–11, PXD–5O5, and PXD–5S5 are very small irrespective of the fact that the C–S bond length is longer by 0.4 Å than that of C–O. Perhaps, the lengths of the repeating chain units of PXD–11, PXD–5O5 and PXD–5S5, are equalized through the arrangement of the bond angles in long sequences of the atoms of these copolyamides. No practical differences in the lattice spacings and crystallinity are found among these copolyamides with different compositions. A good linear relationship is observed between the densities and the compositions. For all the copolyamide systems investigated in this work, the relations between the melting points and the compositions show a good linearity. No minimum melting point can be found in any case. It is surprising that the melting points are practically unchanged in the whole range of composition in such copolyamides as PXD–5O5/PXD–5S5 and PXD–6O6/PXD–6S6.

The polymer melting points are expressed by:

$$T_m = \Delta H / \Delta S$$

12) R. B. Corey and L. Pauling, *Proc. Roy. Soc.* (London), **B 141**, 10 (1953)

where ΔH is the heat content of fusion and ΔS the entropy of fusion.

The value of the heat of fusion is related to the value of the cohesion energy. The cohesion energies of the ether, thioether and methylene groups were shown in part II These differences are small enough to be neglected for the whole repeating chain unit. At least, ΔH may be estimated as a linear function against the polymer compositions. Taking the values in the case of the methylene linkage as the standard, ΔH and ΔS can be expressed as:

$$\Delta H=(\Delta H)_c+(\Delta' H)_y,$$
$$\Delta S=(\Delta S)_c+(\Delta' S)_y$$

where y represents the mole fraction of the ether or thioether linkages as the replacing groups.

Since $(\Delta' S)_y$ is considered to be very small compared with $(\Delta S)_c$, and $(\Delta' H)_y$ is very small compared with $(\Delta H)_c$ and if $(\Delta' S)_y$ can be expressed by ky, proportional to the composition, T_m is written as:

$$T_m=\frac{\Delta H}{(\Delta S)_c}\cdot\frac{1}{1+k'y}=\frac{\Delta H}{(\Delta S)_c}(1-k'y)$$

where $k'=k/(\Delta S)_c$.

This relation expresses a straight line which passes through both the melting points of homopolymers and corresponds well with the experimental results. As a matter of fact, there is no substantial evidence that the entropy of fusion is expressed as a linear relation with the copolyamide compositions. However, it may be concluded from the above explanation that the entropy of fusion in these copolyamides increases steadily as the mole fraction of the hetero-atom linkages, such as ether and thioether groups, increases, which was shown in part II.

Acknowledgement

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