(Form4-2)

JOINT RESEARCH PROJECT

FINAL REPORT
For Japan-Korea Joint Research Project

AREA	1. Mathematics & Physics ②. Chemistry & Material Science 3. Biology 4. Informatics & Mechatronics 5. Geo-Science & Space Science 6. Medical Science 7. Humanities & Social Sciences

1. Research Title:

Basic Study for the Development of Novel Polyester Materials with Long Methylene Segments

2. Term of Research: From **July 1st, 2009** To **June 30th, 2011**

3. Total Budget

a. Financial Support by JSPS: Total amount: 2,400 thousand yen

1st Year 624 thousand yen 2nd Year 1,200 thousand yen

3rd Year 576 thousand yen

b. Other Financial Support : Total amount: 0 thousand yen

4. Project Organization

a. Japanese Principal Researcher	
Name	Dr. Kohji Tashiro
Institution / Department	Toyota Technological Institute, Graduate School of Engineering, Department of Future Industry-oriented Basic Science and Materials
Position	Professor
b. Korean Principal Researcher	
Name	Dr. Hyun Hoon Song
Institution / Department	Hannam University College of Life Science and Nanotechnology Department of Advanced Materials
Position	Professor

c. List of Japanese-side Participants (Except for Principal Researcher)

Name	Institution/Department	Position
Dr. Makoto Hanesaka	Toyota Technological Institute, Graduate School of Engineering, Department of Future Industry-oriented Basic Science and Materials	Post Doctoral Fellow
Dr. Hiroko Yamamoto	as above	Post Doctoral Fellow
Dr. Tran Hai Ninh	as above	Post Doctoral Fellow
Dr. Thontree Kongkhlang	as above	Post Doctoral Fellow
Dr. Kummetha Raghunatha Reddy	as above	Post Doctoral Fellow
Dr. Taiyo Yoshioka	as above	Post Doctoral Fellow

d. List of Korean-side Participants (Except for Principal Researcher)

Name	Institution/Department	Position
Dr. Hye-Jin Jeon	**Hannam University**	**Post Doctor Fellow**
Thi Cuc Do	as above	PhD student
Hak Seung Jeong	as above	PhD student
Dr. Moonhor Ree	**Pohang University of Science and Technology**	Professor

5. Number of Exchanges during the Final Fiscal Year*

a. from Japan to Korea *Japanese fiscal year begins April 1.

Name	Home Institution	Duration	Host Institution
Kohji Tashiro	Toyota Technological Institute	2011.4.6 - 9	Hannam University Pohan University of Science and Technology
For Final Fiscal Year(FY2011) Total: 1 persons		For Final Fiscal Year(FY2011) Total: 4 man days	
Numbers of Exchanges during the past fiscal years			
FY2009: Total 3 persons x 4 days = 12 man days FY2010: Total 5 persons x 6 days = 30 man days			

b. from Korea to Japan

Name	Home Institution	Duration	Host Institution
For Final Fiscal Year(FY2011) Total: 0 persons		For Final Fiscal Year(FY2011) Total: 0 man-days	
Numbers of Exchanges during the past fiscal years			
FY2009: Total 3 persons , 24 man days FY2010: Total 5 persons, 317 man days			

6. Objective of Research

Polyesters, as represented by poly(ethylene terephtalate) (PET), have been utilized in the wide fields in the various ways. The amount of usage of these compounds has been still increasing every day, but the trials to improve the properties may be almost saturated. We may expect an appearance of novel polyesters with more excellent physical properties.

There have been synthesized a series of arylate-type polyesters with the chemical formulae $-[(CH_2)_mOCOC_6H_4COO-]-$ in recent years. For example, 3GT with m = 3 and 4GT with m = 4 have been applied as the excellent polyester materials with high elasticity and/or high toughness. The polyesters with m = 5, 6, and 7 were also synthesized, which have not yet been applied to the practical usage. It is now a new challenge to synthesize novel polyesters with much longer methylene segments and to clarify how the properties change from the conventional polyesters. In our previous collaborative works between Japan and Korea, we had already studied the crystal structure and crystallization behavior of polyesters with m = 9 on the basis of X-ray diffraction technique and so on. Our interest in this research theme is to know the changes in structure, crystallization behavior and physical properties of these polyesters when the methylene sequential length m is increased to 20, 40, and more. Unfortunately, however, we cannot find any literatures about this research theme. From the viewpoint of pure basic science, also, these new polyesters may give us various new concepts about the interrelation between the polyester parts and long methylene segmental parts including the phase separation between them as well as the chain folding scheme around the methylene parts in the crystalline lamellae.

In the present project we have been challenged to synthesize a series of polyesters with quite long methylene segments and to study the molecular conformation and packing mode of these chains in the crystal lattice, the higher-order structure and the crystallization behavior from the melt on the basis of X-scattering, infrared spectroscopy, and thermal analysis as well as the computer simulation technique by focusing into the role of long methylene segments in the development of physical properties of these new polyesters.

7. Methodology

(1) Synthesis of a series of new polyesters with various methylene segmental lengths

The model compounds $CH_3(CH_2)_{m-1}OCOC_6H_4COO(CH_2)_{m-1}CH_3$ (mGT) and the corresponding polyesters $-[(CH_2)_m-OCOC_6H_4COO-]_n-$ (PmGT) have been synthesized by condensation reactions of the corresponding methylene diol and terephthalic acid chloride. The methylene diols with m = 9 – 20 were obtained commercially or by modifying the corresponding ester compounds, which were supplied to the condensation reactions. The diol compounds with m = 40 and more are now being synthesized in the laboratory.

(2) Analysis of molecular conformation and crystal structure of model compounds and polyesters

The molecular conformation and packing structure of the thus obtained compounds were analyzed using the X-ray diffraction method. The low-molecular-weight model compounds mGT were dissolved into the solutions, from which the single crystals were prepared and supplied to the X-ray structure analysis. The polymer substances were melted and quenched into the ice water bath to prepare the amorphous samples, which were stretched several times the original length followed by the heat treatment at high temperatures to get the uniaxially-oriented samples.

The X-ray diffraction measurements of the single crystals of the low-molecular-weight compounds mGT were performed using a Rigaku R-axis Rapid-2 X-ray diffractometer with a cylindrical camera of 2D imaging plate detector, where a graphite-monochromatized Mo-Kα line was used as an incident X-ray beam. The X-ray structure analyses were made using a software "Crystal Stucture". As the methylene segmental length became longer, it was more difficult to prepare the single crystals without any damages. For example, the mGT compounds of m = 12 – 20 showed quite often the platelet crystals with highly rounded or bent shape. The perfectly flat and relatively thick platelet crystals of high quality could be obtained after many trials of crystal growth using the different types of solvent.

The X-ray structure analysis of uniaxially-oriented polyesters PmGT has been performed for the 2D X-ray diffraction patterns taken by the above-mentioned Rapid-2 diffractometer. The data analysis was carried out by evaluating the position and integrated intensity of all the observed reflections by means of a home-made software.

(3) Temperature dependent measurement of X-ray diffraction and FTIR spectra

The temperature dependence of X-ray diffraction patterns was measured for a series of low-molecular-weight compounds mGT and also for the unoriented polyester films of PmGT by using a Rigaku TTR-III X-ray powder diffractometer with Cu-Kα line as an incident X-ray source. The temperature dependence of infrared spectra was measured using KBr disks of these compounds as well as the polymer films, where the temperature of the sample was changed using a Linkam optical microscopy cell with heating equipment.