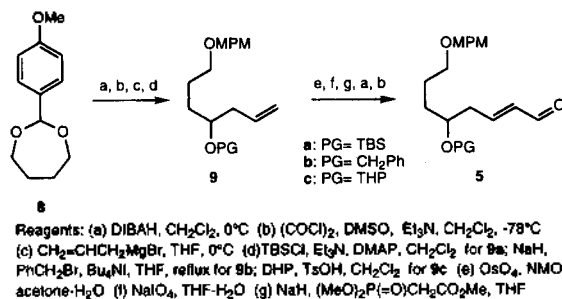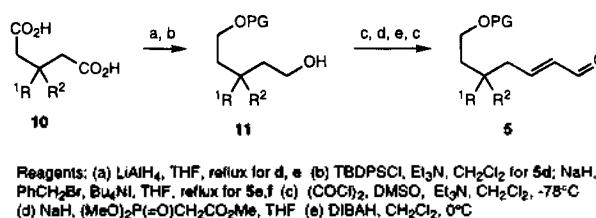3*E*)-diene, was also present and the diene assumed as (1*E*,3*Z*)-diene on the basis of the stereochemical outcomes from **5d-f**.

7. δ-Alkoxy-α,β-aldehydes **5a-c** were prepared as follows:

Reagents: (a) DIBAH, CH_2Cl_2, 0°C (b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78°C (c) CH_2=CHCH$_2$MgBr, THF, 0°C (d)TBSCl, Et$_3$N, DMAP, CH_2Cl_2 for **9a**; NaH, PhCH$_2$Br, Bu$_4$NI, THF, reflux for **9b**; DHP, TsOH, CH_2Cl_2 for **9c** (e) OsO$_4$, NMO, acetone·H$_2$O (f) NaIO$_4$, THF-H$_2$O (g) NaH, $(MeO)_2$P(=O)CH$_2$CO$_2$Me, THF

8. The coupling constants of ~6 Hz are observed for (Z)-siloxy olefins. See: House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

9. Enals **5d-f** were prepared as follows:

Reagents: (a) LiAlH$_4$, THF, reflux for d, e (b) TBDPSCl, Et$_3$N, CH_2Cl_2 for **5d**; NaH, PhCH$_2$Br, Bu$_4$NI, THF, reflux for **5e**,f (c) $(COCl)_2$, DMSO, Et$_3$N, CH_2Cl_2, -78°C (d) NaH, (MeO)$_2$P(=O)CH$_2$CO$_2$Me, THF (e) DIBAH, CH_2Cl_2, 0°C

Structure of 1,3,5-Tris(*p*-fluorophenyl)hexahydro-1,3,5-triazine[1]

Hyun-Joon Ha*, Young-Gil Ahn, Junghwan Do†, Hoseop Yun†*, Hun-Yeong Koh‡, Jung Chull Lee‡, and Kang-Bong Lee‡

Department of Chemistry, Hankuk University of Foreign Studies, Youngin, Kyonggi-Do 449-791, Korea
†*Department of Chemistry, Ajou University, Suwon, Kyonggi-Do 442-749, Korea*
‡*Korea Institute of Science and Technology, Cheongryang, Seoul 131-791, Korea*
Received December 7, 1996

1,3,5-Trisubstituted hexahydro-1,3,5-triazine as a source of N-methyleneamine equivalents in the presence of a Lewis acid were studied extensively in our laboratory.[2,3] Though the synthesis and utilities of 1,3,5-trisubstituted hexahydro-1,3,5-triazines were known for a long time little was revealed about their conformations.

The ample precedents can propose four possible conformers of **A-D** in the Figure 1 with different arrangements of three substituents on the chair form as the most stable conformer of the hexahydro-1,3,5-triazine. Crystal structure of 1,3,5-trinitro[4] and 1,3,5-triacetylhexahydro-1,3,5-triazines[5] showed the similar molecular structural features of the ring as a free cyclohexane geometry of chair from. Three nitro groups and three acetyl groups are inclined to the plane through the carbon ring atoms by approximately the angle of 18-62 °C and the similar angle of 48° respectively, *i.e.*
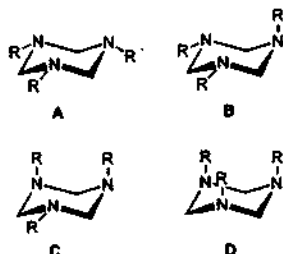

Figure 1. Four possible chair conformers of 1,3,5-trisubstituted hexahydro-1,3-5-triazine.

conformer **A**. 1,3,5-Trimethylhexahydro-1,3,5-triazines showed that three methyl groups are bonded equatorially to the hexahydro-1,3,5-triazine ring as a conformer **A**.[6] However, hexahydro-1,3,5-triazine bearing three neopentyl group has the similar ring structure of the chair form with one axial and two equatorial substituents in a crystal structure of the conformer **B**.[7]

With these attributes in mind we decide to study the conformation of the compound 1,3,5-tris(*p*-fluorophenyl)hexahydro-1,3,5-triazine, herein called TFPHT, synthesized from *p*-fluoroaniline and formaldehyde.[3a] This crystalline TFPHT is subjective for structural studies to answer the following questions, *i.e.* 1) What kind conformation the hexahydro-1,3, 5-triazine ring has in the crystalline state and in solution, 2) How the three phenyl rings were attached to the ring. We report herein the conformational studies of TFPHT based on the X-ray structure and the calculated stable conformers with the programs of PM3[8] and MMX.[9]

The ring configurations of the title compound TFPHT in the solid state is similar to free cyclohexane structure of undistorted chair conformation that was observed in the all reported crystalline products as shown in Figure 2. Especially TFPHT has a symmetry plane bisected through N5 and C6. Geometric configurations of substituents on TFPHT are different from the others that all three or at least two substituents are bonded equatorially to the carbon atom of ring shown in conformer **A** and **B**. Among three *p*-fluorophenyl substituents on the ring two of them are bonded axially and the other one is bonded equatorially like the conformer **C**.

This crystalline structure is quite similar to the ones observed with the other 1,3,5-triphenylhexahydro-1,3,5-triazenes.[10] The distance between C7 and its plane symmetry carbon, *i.e.* carbons bonded with nitrogen located at the axial phenyl, was 3.788 Å. This value is close to the effective van der Waals thickness of plane of aromatic hydrocarbon rings as 3.4 Å.[11] This indicates the possible interaction between two π-electron cloud attracts effectively to accommodate two phenyl ring bonded axially in the crystalline solid.[9]

The solution structure of 1,3,5-trisubstituted hexahydro-1, 3,5-triazine was not known[12] at all except one recent study[6] of 1,3,5-tris(neopentyl)hexahydro-1,3,5-triazine with ^{13}C NMR. This study reveals that the solution conformation is quite similar to the crystal structure of its own that two neopentyl groups are bonded equatorially to the hexahydro-1,3, 5-triazine ring with chair conformation. The same structure was also predicted by MM3 and MMX calculations. This brought us to study about the solution conformation of the title compound TFPHT. This compound has a great advantage for the study owing to the fluorine that the conformational change can be easily visualized in ^{19}F NMR. However we could not succeed to detect the conformational change in either ^{19}F or ^{13}C NMR at low temperature up to − 110 °C. PM3 calculation of the structure of the isolated

(a)   (b)

Figure 2. Chem 3D™ representation of crystal structure (I) of 1, 3,5-Tri-p-fluorophenylhexahydro-1,3,5-triazine along with the atom-labeling schme and thermal ellipsoids. (a) Top view of the molecule. (b) Side view of the molecule.

II   III

Figure 3. Chem 3D™ representation of two most stable conformation (II and III); PM3 calculation of the structure of the isolated molecule.

molecule showed two stable conformers **II** and **III** as shown in Figure 3 with energies of − 35.4 and − 34.7 Kcal/mol respectively. Conformer **II** has the chair ring conformation of hexahydro-1,3,5-triazine ring while a boat form of the ring was observed in conformer **III**. MM2 calculation of the molecule gives the lowest energy conformer similar to **III** with the minimized energy of 21.3 Kcal/mol. One interesting point to be cited is that the crystal structure of the conformer **I** also gave very low energy value of − 37.8 Kcal/mol by PM3 calculation.

Upto this moment it has not been allowed to draw any speculations about the solution conformation of the title compound TFPHT. There is a chance to have various possible conformers in solution. However the crystal structure we observed has some interesting features. There is a symmetry plane bisected through the hexahydro-1,3,5-triazine ring. The central ring has a free cyclohexane structure of undistorted chair conformation with two axial and one equatorial phenyl rings to accommodate the strong aromatic interactions.[13]

Experimental

Crystals of the title compound as a colorless single crystal (0.8×0.8×0.8 mm³), suitable for X-ray diffraction were obtained from $CHCl_3$ solution. Preliminary examination and data collection were performed on a Mac Science MXC3 diffractormeter equipped with graphite monochromatated MoK_α radiation. Cell constants and an orientation matrix for data collection were obtained from least-square refinements, using setting angles of 23 reflections in the range $26.0° < 2\theta < 30°$ that had been automatically centered. The orthorhombic cell parameters and calculated volume are a=14.418(4) Å, b=20.405(5) Å, c=12.109(3) Å and V=3562(2) Å.³ From the systematic absences (h+k=2n+1, h01:h,l=2n+1, hk0:h,k=2n+1,001:1=2n+1) are consistent with the centrosymmetric space group Cmca (No. 64). The data were collected at room temperature using the
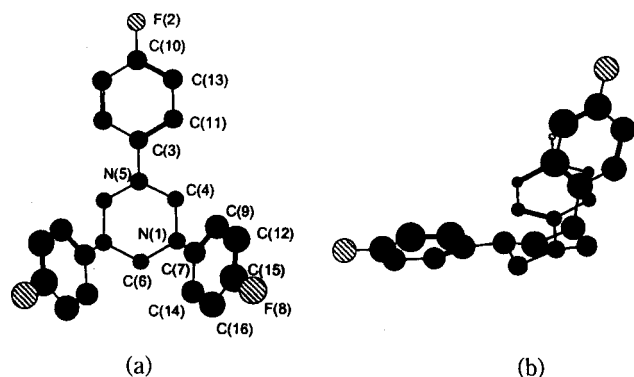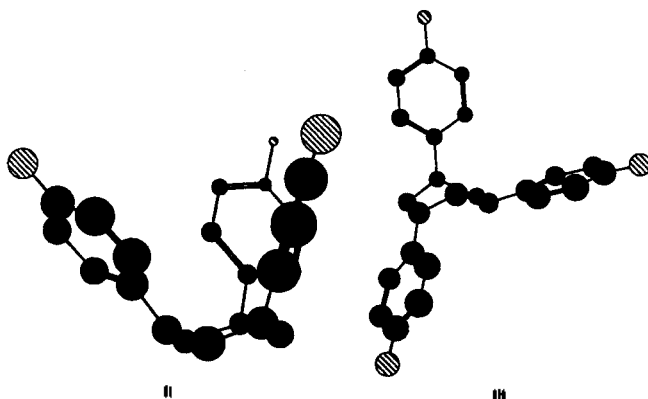
Table 1. Atomic cooridinates and equivalent isotropic thermal parameter for 1,3,5-Tri-*p*-fluorophenylhexahydro-1,3,5-triazine. U (eq) is defined as one third of the trace of the orthogonized Uij tensor

	x	y	z	U(eq)
N(1)	0.4156(1)	0.2716(1)	0.1280(1)	0.058(1)
F(2)	0.5	0.5496(1)	− 0.2951(2)	0.098(1)
C(3)	0.5	0.4007(1)	− 0.0626(2)	0.054(1)
C(4)	0.4166(1)	0.3361(1)	0.0782(2)	0.063(1)
N(5)	0.5	0.3465(1)	0.0100(2)	0.059(1)
C(6)	0.5	0.2619(1)	0.1930(2)	0.062(1)
C(7)	0.3861(1)	0.2183(1)	0.0610(1)	0.056(1)
F(8)	0.2896(1)	0.0607(1)	− 0.1192(1)	0.111(1)
C(9)	0.3665(1)	0.2242(1)	− 0.0504(1)	0.064(1)
C(10)	0.5	0.5006(1)	− 0.2186(2)	0.067(1)
C(11)	0.4184(1)	0.4278(1)	− 0.1029(2)	0.075(1)
C(12)	0.3337(1)	0.1713(1)	− 0.1107(2)	0.076(1)
C(13)	0.4182(2)	0.4771(1)	− 0.1807(2)	0.080(1)
C(14)	0.3721(1)	0.1576(1)	0.1095(2)	0.076(1)
C(15)	0.3224(1)	0.1129(1)	− 0.0595(2)	0.078(1)
C(16)	0.3410(2)	0.1045(1)	0.0499(2)	0.086(1)

Notes

Bull. Korean Chem. Soc. **1997**, Vol. 18, No. 3 **349**

Table 2. Bond distances (Å) and bond angles (°) for 1,3,5-Tri-*p*-fluorophenylhexahydro-1,3,5-triazine

N(1)-C(7)	1.423(2)	C(7)-C(14)	1.386(2)
N(1)-C(4)	1.446(2)	F(8)-C(15)	1.370(2)
N(1)-C(6)	1.463(2)	C(9)-C(12)	1.386(3)
F(2)-C(10)	1.362(3)	C(9)-H(9)	0.93
C(3)-C(11)*	1.389(2)	C(10)-C(13)*	1.354(2)
C(3)-C(11)	1.389(2)	C(10)-C(13)	1.354(2)
C(3)-N(5)	1.412(3)	C(11)-C(13)	1.379(3)
C(4)-N(5)	1.475(2)	C(11)-H(11)	0.93
C(4)-H(4A)	0.97	C(12)-C(15)	1.354(3)
C(4)-H(4B)	0.97	C(12)-H(12)	0.93
N(5)-C(4)*	1.475(2)	C(13)-H(13)	0.93
C(6)-N(1)*	1.463(2)	C(14)-C(16)	1.375(3)
C(6)-H(6A)	0.97	C(14)-H(14)	0.93
C(6)-H(6B)	0.97	C(15)-C(16)	1.362(3)
C(7)-C(9)	1.384(2)	C(16)-H(16)	0.93
C(7)-N(1)-C(4)	117.48(13)	C(7)-C(9)-C(12)	121.0(2)
C(7)-N(1)-C(6)	116.8(2)	C(7)-C(9)-H(9)	119.50(11)
C(4)-N(1)-C(6)	109.8(2)	C(12)-C(9)-H(9)	119.50(11)
C(11)*-C(3)-C(11)	115.8(2)	C(13)*-C(10)-C(13)	121.3(2)
C(11)*-C(3)-N(5)	122.04(11)	C(13)*-C(10)-F(2)	119.36(12)
C(11)-C(3)-N(5)	122.04(11)	C(13)-C(10)-F(2)	119.36(12)
N(1)-C(4)-N(5)	111.89(14)	C(13)-C(11)-C(3)	122.2(2)
N(1)-C(4)-H(4A)	109.24(9)	C(13)-C(11)-H(11)	118.98(11)
N(5)-C(4)-H(4A)	109.24(10)	C(3)-C(11)-H(11)	118.98(11)
N(1)-C(4)-H(4B)	108.24(9)	C(15)-C(12)-C(9)	119.1(2)
N(5)-C(4)-H(4B)	109.24(10)	C(15)-C(12)-H(12)	120.47(11)
H(4A)-C(4)-H(4B)	107.9	C(9)-C(12)-H(12)	120.47(11)
C(3)-N(5)-C(4)*	117.50(11)	C(10)-C(13)-C(11)	119.2(2)
C(3)-N(5)-C(4)	117.50(11)	C(10)-C(13)-H(13)	120.39(12)
C(4)*-N(5)-C(4)	109.3(2)	C(11)-C(13)-H(13)	120.39(11)
N(1)*-C(6)-N(1)	112.6(2)	C(16)-C(14)-C(7)	121.9(2)
N(1)*-C(6)-H(6A)	109.07(10)	C(16)-C(14)-H(14)	119.06(12)
N(1)-C(6)-H(6A)	109.07(10)	C(7)-C(14)-H(14)	119.06(10)
N(1)*-C(6)-H(6B)	109.07(11)	C(12)-C(15)-C(16)	122.1(2)
N(1)-C(6)-H(6B)	109.07(11)	C(12)-C(15)-F(8)	118.9(2)
H(6A)-C(6)-H(6B)	107.8	C(16)-C(15)-F(8)	119.0(2)
C(9)-C(7)-C(14)	117.5(2)	C(15)-C(16)-C(14)	118.5(2)
C(9)-C(7)-N(1)	123.3(2)	C(15)-C(16)-H(16)	121.75(13)
C(14)-C(7)-N(1)	119.12(14)	C(14)-C(16)-H(16)	121.75(13)

*Symmetry transformations used to generate equivalent atoms: − x, y, z.

ω-2θ scan technique. The intensities of three standard reflections measured every hundred reflection, showed no significant deviations during the data collection. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 0.105 mm^{-1} for MoK_α radiation. No absorption correction was applied. The structure was solved by the direct method with the SHELX-86 program[14] and refined with the use of the SHELX-93 program.[15] Positional and thermal parameters were refined using a full-matrix least-squires refinement procedure. In these refinements, anisotropic thermal parameters were used for all 16 non-hydrogen atoms. Atomic positions of hydrogen atoms were generated with the riding model technique of SHELX-93. The final cycle of refinement was performed on 2129 reflections. The final residual R1(Fo>4σ(Fo)) and wR2 are

0.0458 and 0.1505 respectively. A difference Fourier synthesis calculated with phases based on the final parameters contained no density outside the range − 0.15 eÅ^{-3} to +0.17 Å^{-3}, fluctuations consistent with the e.s.d. of the electron density 0.04 eÅ^{-3}. The anisotropic atomic displacement parameters (ADP) show no unexpected trends. Atomic coordinates and isotopic thermal parameters for non-hydrogen atoms are given in Table 1 and selected bond lengths and angles are listed in Table 2. Figure 2 shows the molecular geometry and atom labeling for the molecule using Chem 3D.

Calculation had been carried out with the semiemperical PM3 method available through MOPAC package[8] and MM2 through CSC Chem 3D program.[9]

References

1. This paper is part 7 in the series of *Lewis acid induced N-methyleneamine equivalents*; For part 6 see, Ha, H.-J.; Ahn, Y.-G. Synth. *Commun.* in press.

2. For comprehensive reviews see, (a) M. Tramontini and L. Angiolini, *Tetrahedron* **1990**, *46*, 1791. (b) E. F. Kleinman, In *Comprehensive Organic Synthesis*; ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 2, pp 893-973. (c) Tramontini M.; Angiolini L. *Mannich Bases Chemsitry and Uses*; CRC Press: Boca Raton, FL, 1994.

3. (a) Ha, H.-J.; Nam, G.-S.; Park, K. P. *Tetrahedron Lett.* **1990**, *31*, 1567. (b) Ha, H.-J.; Nam, G.-S.; Park, K. P. *Bull. Kor. Chem. Soc.* **1990**, *11*, 485. 9. (c) Ha, H.-J.; Nam, G.-S.; Park, K. P. Synth. *Commun.* **1991**, *21*, 155. (d) H.-J.; Ahn, Y.-G. *Synth. Commun.* **1995**, *25*, 969. (e) Ha, H.-J.; Ahn, Y.-G.; Chon, J.-K. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2631. (f) Ha, H.-J.; Kang, K.-H.; Ahn, Y.-G.; Oh, S.-J. *Heterocycles* in press. (g) Ha, H.-J.; Kang, K.-H.; Suh, J.-M.; Ahn, Y.-G. *Tetrahedron Lett.* **1996**, *37*, 7069.

4. Choi, C.-S.; Prince, E. *Acta Cryst.* **1972**, *B28*, 2857.

5. Choi, C.-S., Santoro, A.; Marinkas, P. L. *Acta Cryst.* **1975**, *B31*, 2934.

6. Lund, E. W. *Acta Chem. Scand.* **1958**, *12*, 1768-1776.

7. Anderson, J. E.; Casarini, D.; Ijeh, A.; Lunazzi, L.; Tocher, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 3054.

8. QCPE Program No 455 Ver 6.0 distributed by QCPE Bloomington IN U.S.A.. MOPAC program package have been developed by J. Stewart and coworkers.

9. Allinger, N. L. *Molecular Mechanics*; Burkert, J.; Allinger, N. L. Ed.; ACS: Washington DC, 1987.

10. (a) Crystal structure of 1,3,5-triphenylhexahydro-1,3,5-triazine, Giumanini, G.; Giumanini, A. G.; Modelli, A.; Poggi, G. *J. Prakt. Chem.* **1985**, *327*, 739. (b) Crystal structure of 1,3,5-tris(*p-t*-butylphenyl)hexahydro-1,3,5-triazine and 1,3,5-tris(*m*-fluorophenyl)hexahydro-1,3,5-triazine, Giumanini, A. G.; Verardo, G.; Zangrando, E.; Lassiani, L. *J. Prakt. Chem.* **1987**, *329*, 1087.

11. Gordon, A. J.; Ford, R. A. *The Chemist's Companion*;

John Wiley ans Sons: New York, 1972.

12. The extensive conformational analysis of 1,3,5-trialkylhexahydro-1,3,5-triazines with thermodynamic data predict the possible minimized energy conformer as B. R. P.; Jones, R. A. Y.; Katritzky, A. R.; Scattergoog, R.; Riddell, F. G. *J. Chem. Soc., Perkin Trans. II* **1973**, 2109: and references cited therein.

13. Noncovalent interactions between aromatic molecules,

see. (a) Jorgensen, W. L.; Severance, D. L. *J. Am Chem. Soc.* **1990**, *112*, 4768. (b) Hunter, C. A.; Sanders, J. K. M. *J. Am Chem. Soc.* **1990**, *112*, 5525. (c) Harmata, M.; Barnes, C. L. *J. Am Chem. Soc.* **1990**, *112*, 5655.

14. Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467.

15. Sheldrick, G. M. SHELXL 93, Program for the Refinement of Crystal Structure, University of Gottingen, 1993.

Morphology of Poly(tetramethylene succinate) Spherulites

E. S. Yoo, S. S. Im*, and K. J. Ihn**

Department of Textile Engineering, Hanyang University Seungdong-Ku, Seoul 133-791, Korea
**Department of Chemical Engineering, Kangwon National University Chunchon 200-701, Korea*
Received January 3, 1997

Some of the aliphatic polyesters have been reported to be decomposed relatively easily under natural environmental circumstances,[1-3] while many synthetic polymers create pollution problems because of difficulty in decomposition.[4-7] Poly(tetramethylene succinate) (PTMS) is a prominent one in the aliphatic biodegradable polyesters, but few reports about it's morphological features are available.

In our previous work,[8] PTMS were synthesized and electron micrographs of the single crystals were presented with the lattice parameters which were determined from electron diffraction pattern of the stretched films.

Lots of studies have been performed to investigate the structure of spherulites by the optical and electron microscopy. In 1950s Keller reported excellent studies on the structures of polymer spherulites. In the series of his works,[9-11] the morphological feature of spherulites of poly (ethyleneterephthalate) (PET), polyethylene and polyamides were presented. The major characteristic of PET spherulites between cross polars was the extinction cross pattern which referred as Maltese cross.

In the case of polyethylene, both of the Maltese cross and the closely spaced dark ring system are observed. As the crystallization temperature increase, Maltese cross becomes irregular and bushy like in appearance. All these extinction effects are understood on an optical level. And it is generally observed in ring structured spherulties that the ring spacing increase with crystallization temperature and may disappear altogether for crystallization at low supercoolings.

There are several arguments about the mechanisms of ring formation. Many people agree with Keller's idea[9] that the ring pattern under polarized light may originate from diffraction by phase grating in helicoidal structure. However Bassett[12] thought that the lamellae themselves form the ring structure, although he had not found any morphological evidence of twisted lamellar growth.

The concentric double ring structure in polymer spherulites is not a very common phenomenon, although the concentric double ring has been reported by other scientists. For example, Polyhexamethylene sebacamide[9] and polytrimethylene glutarate spherulites show the double rings between cross polars.[13] For the mechanism of this concentric double ring formation, either two theory which were mentioned above could be correct. But in general, it has been known that, in helicoidal structure model, double concentric rings may originate from the rotating of biaxial ellipsoid forming a helicoidal arrangement along the radius.

In this paper, the morphological changes of PTMS spherulites associated with the crystallization temperature were studied by Polarizing Optical Microscopy and Transmission Electron Microscope.

Experimentals

PTMS were fused between cover glasses on a hot plate for 5 minutes at 150 °C and subsequently immersed in a silicone oil-bath preheated to the crystallization temperature. The morphological features of PTMS spherulites were observed between crossed polars in optical microscope, OPTIPHOT-POL, Nikon.

In the above case, the material was crystallized between coverglasses. If the film crystallized with free surface, essentially similar spherulites were obtained. The surface morphology of that was investigated by Transmission Electron Microscope, JEOL-2000EX(II), using the replica method. And also the surface of samples grown between coverglasses was observed in the same way to compare with free standing one.

Results and Discussion

Straight Maltese cross is shown along the vibration directions of polarizer and analyzer in Figure 1. This spherulites was crystallized at 80 °C. The Maltese cross could be observed in the spherulites crystallized at the temperatures low-