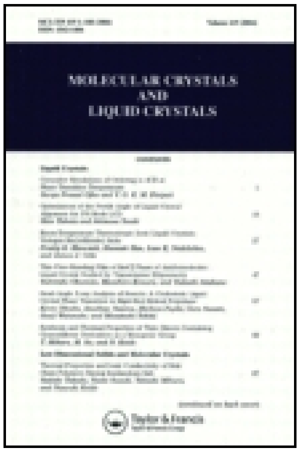

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# A New High Performance Liquid Crystal Polyester by Controlling Molecular Structures

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# A New High Performance Liquid Crystal Polyester by Controlling Molecular Structures

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A new liquid crystal polyester with improved moldability (high flowability and high thermal stability) was developed by controlling molecular structure. This new chemical structure enabled the commercialization of this material in the field of precision electronic parts particularly for the surface mount technology (SMT).

Keywords: liquid crystal polyester; weldline strength; DTUL;
surface mount technology; flowability; copolymerization

## INTRODUCTION

Polyester base liquid crystal polymer (LCP) is one of the most attractive materials in the field of engineering thermoplastics because of its superior heat resistance, stiffness, accuracy of dimensions, moldability and the excellent balance of these properties.[1]-[4] LCP is recently expanding its applications, in particular, those for the precision electronic parts appropriate for surface mount technology (SMT). However, because of the further demands for smaller and more highly integrated electronic devices, improvement of flowability, thermal stability during injection molding, and weldline strength of LCP materials has been also strongly demanded by the users. We have investigated LCP materials fit for the demands for a long time, and we have made more than 200 patent applications on the materials. Finally, we succeeded in the development of our novel high performance LCP “SIVERAS” with a unique formula, and we started sample work from

February 1994.[5] Fortunately, as a consequence of the sample work, the properties such as moldability and weldline strength of our material have been recognized as the highest level in the world. We started up our new commercial plant (1000 t/y capacity) in Ehime, Japan in April 1997.[6]

## BACKGROUND

Commercially available LCPs are classified into three types by the deflection temperature under load (DTUL) of the molded articles: Type I (DTUL >270°C), Type II (270°C > DTUL > 240°C), and Type III (240°C > DTUL).

TABLE I Milestones of the three types of LCP

|  | Thermotropic LCP |  |  |
|---|---|---|---|
|  | I | II | III |
| 1960 |  |  |  |
| 1970 | 1972 EKKCEL<br>(Carborundum)<br>1979 EKONOL<br>(SUMIIKA SUPER LCP)<br>(Sumitomo Chem.) |  | 1974 X-7G<br>(Eastman) |
| 1980 | 1984 XYDAR<br>[Dartco(Amoco)]<br>1985 EKONOL FIBER<br>(EKF)<br>(Sumitomo Chem.)<br>1987 HAG,HBG<br>(Tosoh Susteel)<br>1988 GRANLAR<br>(Granmont) | 1984 VECTRA<br>[Celanese(Hoechst)]<br>1986 ULTRAX (BASF)<br>1987 VICTREX SRP (ICI)<br>1988 RHODESTER (Rhone-Poulenc)<br>HX (DuPont)<br>UENO-LCP(Ueno Fine Chem.)<br>VECTRAN(Fiber)(Kuraray)<br>1989 K-LCP (Kawasaki Steel) | 1985 RODRUN<br>(Unitika)<br>EPE(NOVACCURATE)<br>[Mitsubishi Kasei<br>(Mitsubishi Chem.)]<br>1986 POLYSTAR(Bayer)<br>1987 IDEMITSU-LCP<br>(Idemitsu Petrochem.) |
| 1990 |  | 1990 MGC-LCP(Mitsubishi Gas Chem.)<br>1994 SIVERAS (Toray)<br>ZENITE (DuPont) |  |

A chronological table of development of these three types is shown in Table I. However, recently the greatest application of LCP was revealed to be that for molded electronic parts appropriate for the SMT, which demands as high heat resistance as that of Type II LCP. From the trend of the demands of LCPs, research and development of the Type II LCP with improved moldability (flowability) have been actively pursued by many companies by suppressing the heat resistance of Type I LCP.

On the other hand, generally Type III LCP has a structure derived from p-hydroxybenzoic acid and poly(ethyleneterephthalate) (HBA/PET), and it has been insufficient for the SMT applications due to its low DTUL, though it has an advantage of low cost starting materials.

We started the research on our own ultimate LCP which has both the Type II comparable heat resistance and the Type III competitive cost, not starting from the Type I LCP, but from the Type III LCP by improving the heat resistance of it. In addition, we had paid great attention to the flowability appropriate for the precision molding. Finally, we set up our goal as an LCP with DTUL of 250°C, improved flowability, and superior cost performance as shown in Fig. 1.

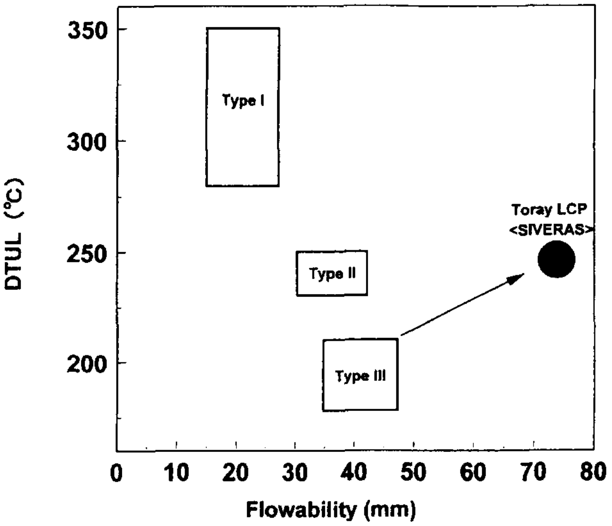


FIGURE 1 Target of Toray LCP <SIVERAS>

## RESULTS AND DISCUSSION

### Molecular Design

Type III LCP is synthesized by the reaction of p-acetoxybenzoic acid (ABA) and poly(ethyleneterephthalate) (PET). Fig. 2 shows the relation between DTUL versus PET content of Type III LCP. Commercially available Type III LCPs contain normally more than 20 mol % of PET repeating units in all ester repeating units. Fig. 2 indicates that the DTUL of 250°C should be achieved by reducing the amount of PET units of Type III LCP to less than 20 mol %. However, a small amount of PET units such as less than 20 mol % in the whole ester repeating units causes the difficulty in homogeneous melt polymerization. In a typical case, solidification of polymer was observed during the polymerization. By observing the solidified polymer using a polarized microscope, there existed polymer with highly block sequence of HBA, which was infusible even at 400°C. Nicely et al.[7] reported that the Type III LCP even with 20 mol % of PET repeating units

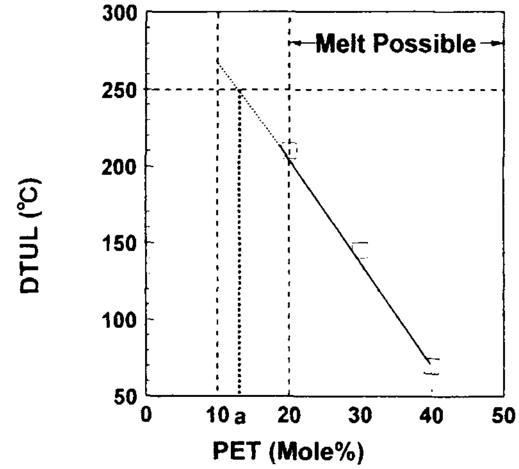
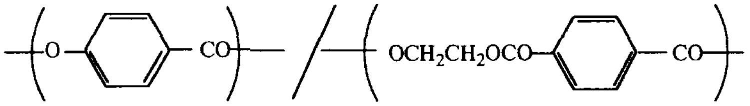


FIGURE 2 DTUL as a function of PET content in HBA/PET



had blocky sequences of HBA.

From a series of kinetic studies, the rate constant $k_1$ and $k_2$, corresponding to (1) the reaction between ABA and PET, and (2) the self-condensation of ABA, respectively were determined. The rate constant $k_2$ was much larger than $k_1$ as shown in Fig. 3. This means the self-condensation of ABA is a predominant reaction at the beginning of the polymerization of Type III LCP. We suppose this is the main reason why the infusible HBA block formed during the polymerization in the case of Type III LCP with a high HBA content.

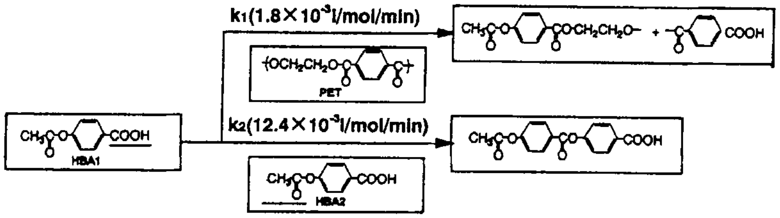


FIGURE 3 Reaction mechanism of HBA/PET and the rate constants

The average repeating number ($\overline{N}$) of HBA units at a certain reaction time t can be calculated from the concentration of acetoxy group of ABA at the initial stage and at the desired reaction time of t (Eq. (1)). In fact, the $\overline{N}$ of HBA units in the polymer at the time of emerging infusible polymer was 6.8.

$$\overline{N} = \frac{[HBA_2]_0}{[HBA_2]_t} \qquad (1)$$

In order to avoid this self-condensation reaction of ABA, we have investigated the reactions which are competitive to the self-condensation. By exploring varying acetates of aromatic dihydroxy compounds and terephthalic acid to add to the HBA/PET system as the third component of polyester, we finally found that the addition of certain amount of dihydroxy compound (DHC) and terephthalic acid (TPA) could derive the homogeneous polymer free from the infusible polymer even at the lower content of PET units than 20 mol %.

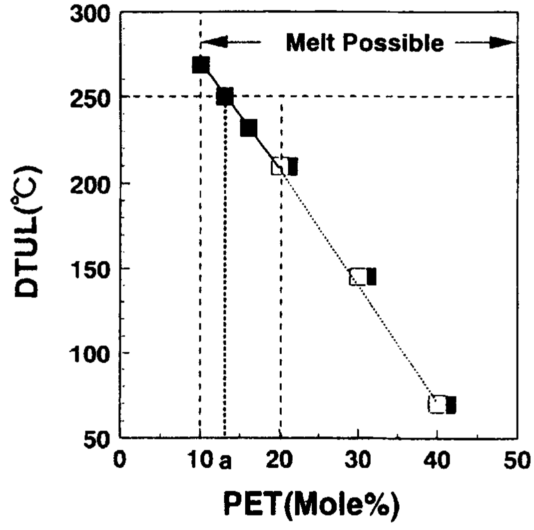


FIGURE 4 DTUL as a Function of PET Content in HBA/PET (□) and Toray LCP (■)

Fig. 4 shows the relation between DTUL and PET content in the copolymers of Type III LCPs both with and without copolymerized DHC/TPA units as the third component. Fig. 4 indicates that the Type III LCPs with DHC/TPA (shown as solid squares) and the Type III LCPs without DHC/TPA (shown as open squares) have the same linear relation between DTUL and PET content. From this result, we assume that DHC/TPA units formed crystals having the same characteristics as those of HBA crystals.

As the reaction between DHC/TPA units and HBA units was confirmed by a HPLC study, we determined the rate constant $k_3$ corresponding to (3) the reaction between ABA and DHC, and the average repeating number ($\overline{N}$)

of HBA units. The rate constant $k_3$ was much larger than $k_1$, and the $\overline{N}$ of HBA units was smaller than that of the reaction without copolymerizing DHC/TPA units (Figs. 5 and 6). This competitive reaction to the reaction (1) could completely avoid the formation of the infusible polymer.

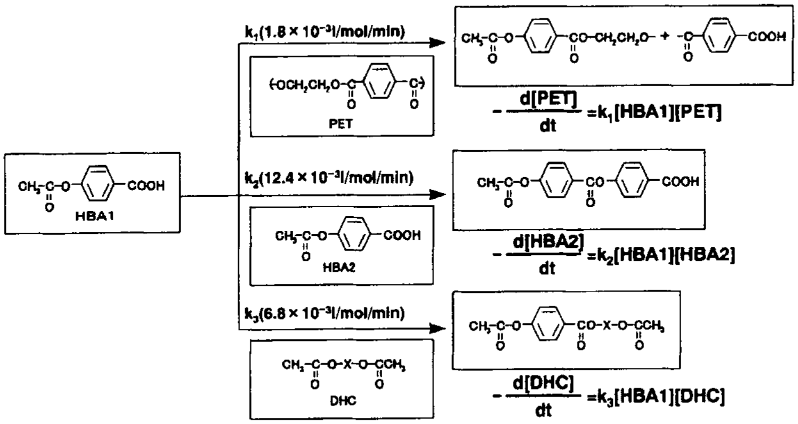


FIGURE 5 Reaction of the comonomer and rate constants $k_1$, $k_2$ and $k_3$

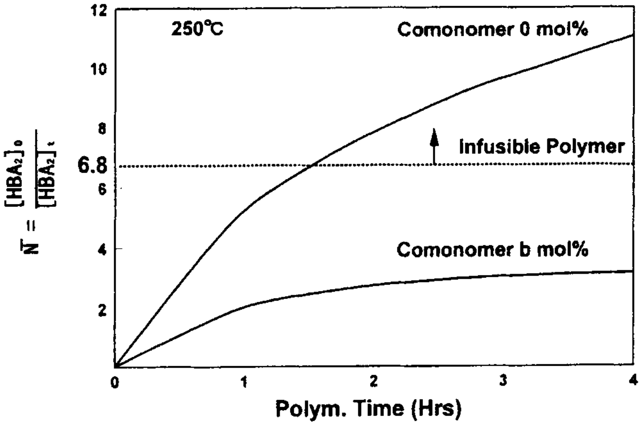


FIGURE 6 Average repeating number ($\overline{N}$) of HBA units

In addition to the improvement in homogeneity, the heat of fusion of the polymer, which indicates the crystallinity, dramatically increased in spite of the copolymerization of the third component. Fig. 7 shows the melting point (Tm) of HBA/PET copolymerized with the third component as a function of the content of comonomer. Though the certain amount of comonomer reduced Tm and enabled melt processing of the polymer as shown in Fig. 7, it is very interesting that the heat of fusion (ΔH) takes a maximum value within the reduced Tm range. This means that the crystallinity of the polymer was peculiarly improved by copolymerizing appropriate amount of the third component (Fig. 8). This phenomenon was also supported by wide angle X ray diffraction (WAXD).

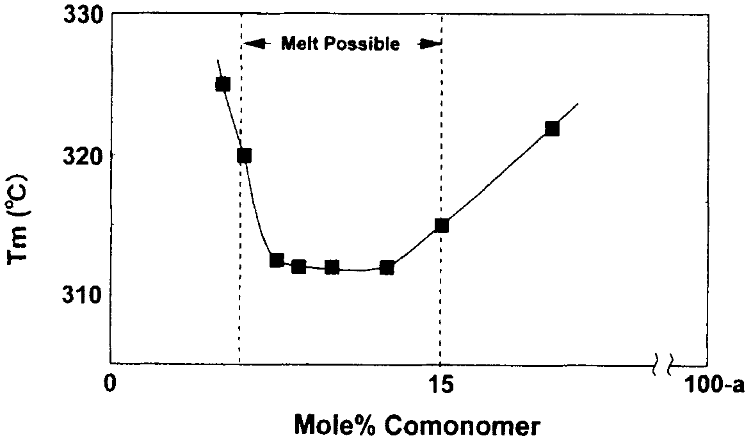


FIGURE 7 Melting point (Tm) vs. content of comonomer

The reason for the improvement of crystallinity by copolymerization of the third component seems to be a contribution of the formation of non-periodical layer (NPL) crystal as discussed by Donald.[8] We concluded that the improvement of crystallinity was resulted by the formation of mixed crystals with well-aligned molecular chains, which were induced by sufficient molecular movement of the copolymer.

Using that unique copolymerization method, we first realized the improvement of heat resistance of Type III LCP, and obtained the new LCP with a DTUL as high as 250°C. This is the basic formula of our novel LCP "SIVERAS" based upon our new concept of controlling molecular structures.

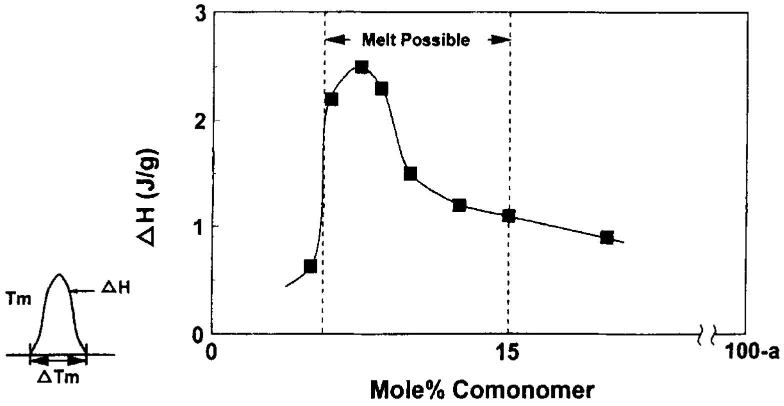


FIGURE 8 Heat of fusion (ΔH) vs. content of comonomer

## Polymerization

In general, Type III LCP is polymerized by the following procedure: Previously isolated ABA, which is derived from HBA and acetic anhydride, is allowed to react with PET over 250°C. Reaction of ABA and PET at a temperature between 150°C and 250°C may cause the formation of the self-condensed product of HBA as mentioned above. In other words, costly processes such as independent acetylation of HBA and subsequent isolation and purification of ABA were unavoidable for the synthesis of Type III LCP. On the other hand, in the case of our "SIVERAS", copolymerizing DHC/TPA units could reduce the repeating number ($\bar{N}$) of HBA units and resulted in the formation of no infusible polymer consisting of the self-condensate of HBA. We were strongly encouraged at this result, and tried to pursue the acetylation of HBA by acetic anhydride in the presence of PET and the consecutive copolymerization with PET and DHC/TPA in one pot by heating gradually. The polymerization can be carried out by a uniform melt condensation process, and the infusible polymer was not observed in the product. And a $^{13}$C-NMR study supported that the resulted polymer had complete random sequence. We finally established a new process for "SIVERAS", which is more feasible than the process for Type III LCP.

## Properties of Polymer

Fig. 9 shows DTUL versus crystallinity of "SIVERAS" and other commercial Type III LCPs determined by WAXD using $Al_2O_3$ internal standard. The values of crystallinity represent relative crystallinity to $Al_2O_3$

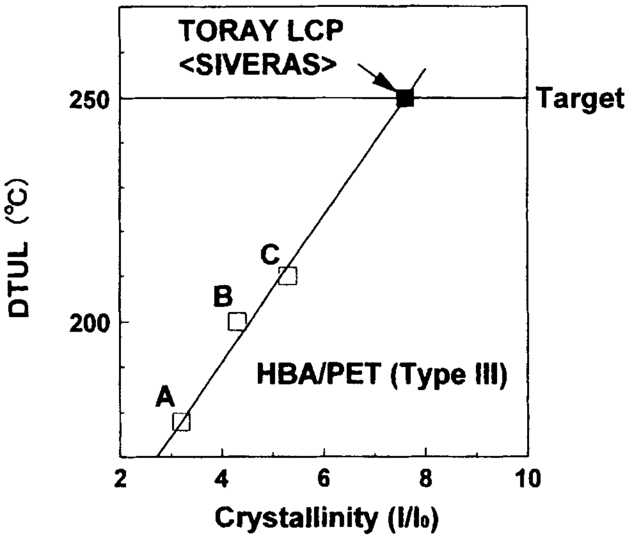


FIGURE 9 DTUL vs. crystallinity of Toray LCP <SIVERAS> The values of relative crystallinity ($I/I_0$) were determined by the following manner: In the WAXD pattern of each mixture of LCP and internal α-$Al_2O_3$ standard with a constant proportion observed at 250°C, the peak intensity (I) corresponding to the LCP ($2\theta$ = 20°) was divided by the peak intensity ($I_0$) corresponding to the α-$Al_2O_3$ ($2\theta$ = 43.4°). A, B and C were prepared according to the patents and literatures.

($I/I_0$). The observed values of DTUL were linearly dependent upon the relative crystallinity. "SIVERAS" shows high DTUL and high relative crystallinity, which corresponds to high value of heat of fusion (ΔH).

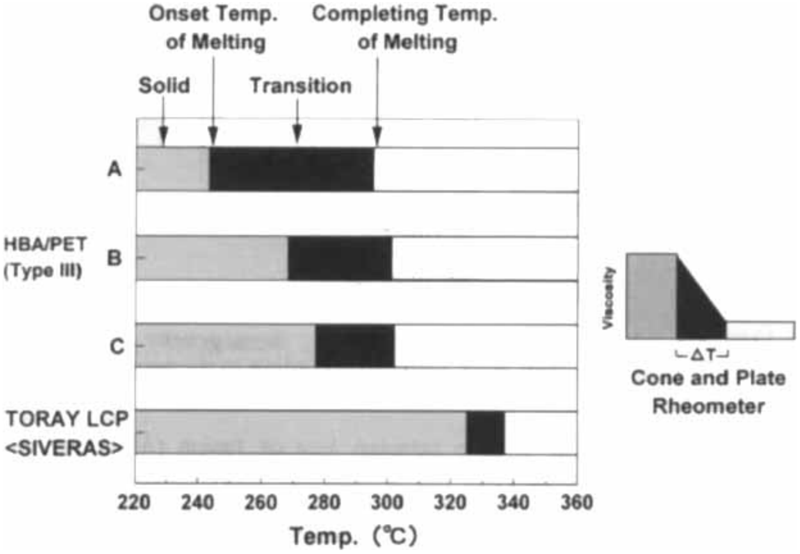


FIGURE 10 Phase transition temperature determined by dynamic viscoelasticity. A, B and C were prepared according to the patents and literatures.

In order to evaluate the homogeneity of polymers, the phase transition behavior was investigated by the measurements of dynamic viscoelasticity dependent on the temperature using a cone-plate type dynamic viscoelastometer. The difference between onset and completing temperatures of melting for each sample is shown in Fig. 10. "SIVERAS" has narrower transition range than those of any Type III LCPs on the market as shown in Fig 10. This result shows good agreement with the melting temperature range (ΔTm) which is represented by the peak width of Tm, observed by DSC (Fig 11). Both two studies support the superior homogeneity of "SIVERAS".

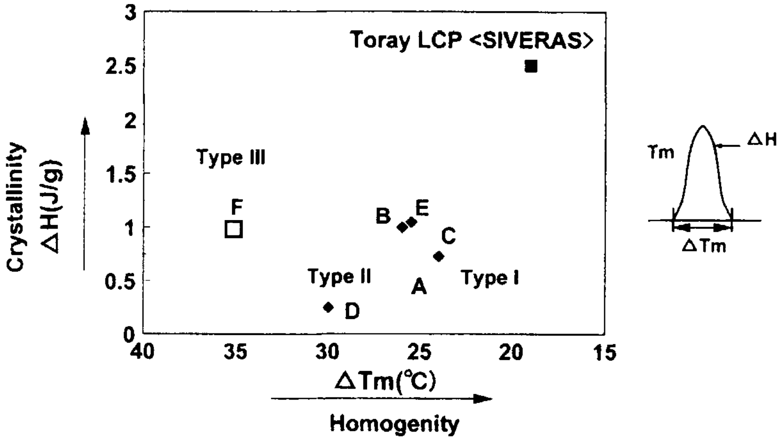


FIGURE 11 Crystallinity (ΔH) vs. homogeneity (ΔTm) measured by DSC. A~F were prepared according to the patents and literatures.

Fig 11 shows the relation between heat of fusion (ΔH) and melt transition range (ΔTm) of LCPs on the market. "SIVERAS" shows the highest ΔH value and the lowest ΔTm among these LCPs, which means the highest crystallinity and the highest homogeneity, respectively.

### Properties of Injection Molded Articles [9]-[11]

"SIVERAS" has an excellent heat resistance which is appropriate for the SMT applications. Here we present several important properties superior to the typical commercially available LCP materials for the SMT applications.

(1) Moldability (Flowability)

Flowability of several commercial LCPs in the thin wall mold is shown in Fig. 12. "SIVERAS" shows the highest flowability among all, which is reflecting its excellent homogeneity. Flowability was determined by flow lengths of injection molded test pieces using a test mold shown in Fig. 12. Applied injection temperature and pressure were 10°C higher than Tm, and 100 MPa, respectively.

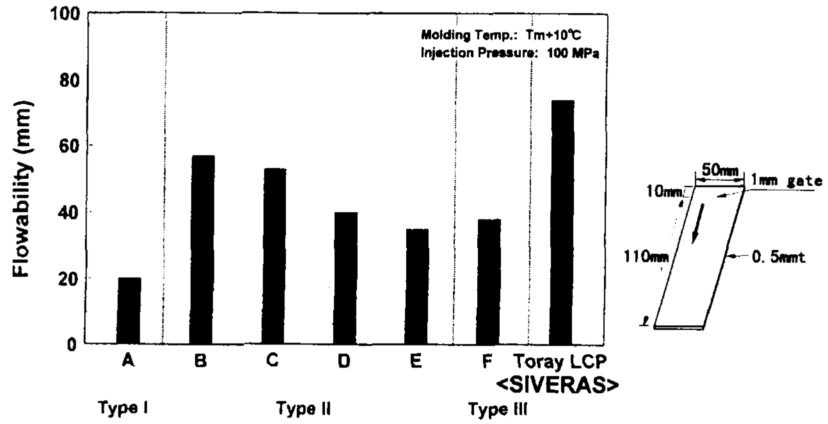
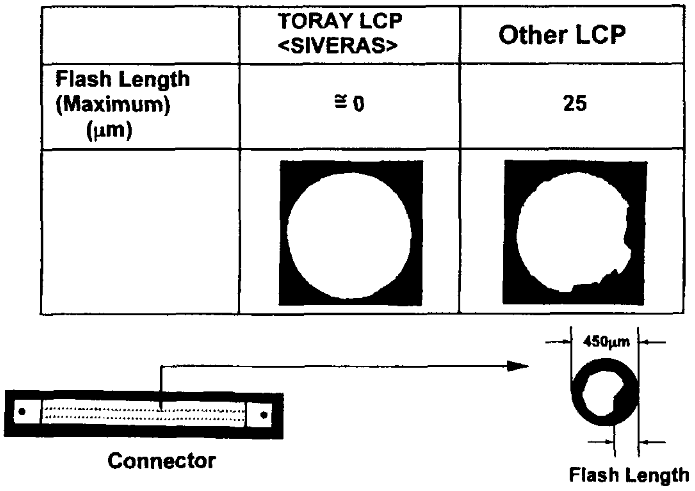


FIGURE 12 Flowability of LCPs in the thin wall mold. A~F were prepared according to the patents and literatures.



| | TORAY LCP <SIVERAS> | Other LCP |
|---|---|---|
| Flash Length (Maximum) (μm) | ≅0 | 25 |

FIGURE 13 Flash length of molded connector. Other LCP was prepared according to the patents and literatures.

(2) Flash properties

In general, LCP materials generate low flash during injection molding compared to other engineering thermoplastics. "SIVERAS" can realize the much lower level of flash than other Type II LCPs on the market because of its low injection pressure brought by its excellent flowability (Fig. 13).

(3) Mechanical properties

"SIVERAS" has the highest level of mechanical properties among commercial LCPs, in particular, it has the world highest weldline strength, which is the most desired property of LCP materials to be improved (Fig. 14).

| | **TORAY LCP <SIVERAS>** | **Other LCPs** |
|---|---|---|
| **Flexural (MPa)** | **56** | **35-48** |

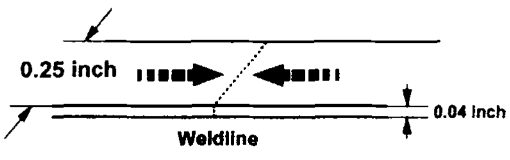


FIGURE 14 Weldline strength of injection molded article. Other LCPs were prepared according to the patents and literatures.

## CONCLUSION

As described above, "SIVERAS" has the well-balanced heat resistance for the SMT applications and mechanical properties, and in particular, it has the world highest level of moldability (flowability and low flash capability) and weldline strength. Consequently, it is the most appropriate material which can meet the demands for downsizing and high density integrating in the fields of electric and electronic devices, and mechanical parts for computer peripherals, audio-visual equipment, and cellular devices. Here shows some examples of applications of "SIVERAS" in Figs. 15 and 16.

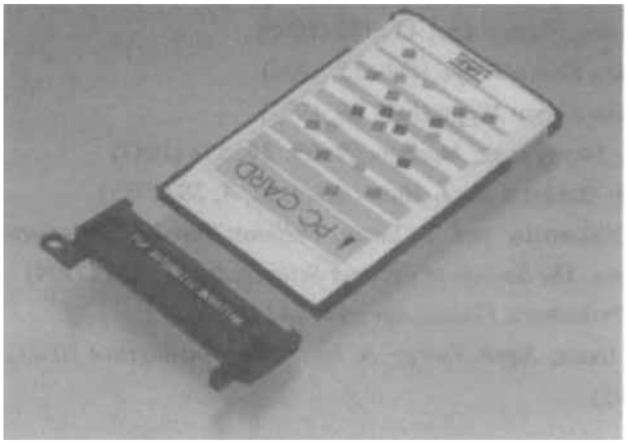


FIGURE 15 PC card connector

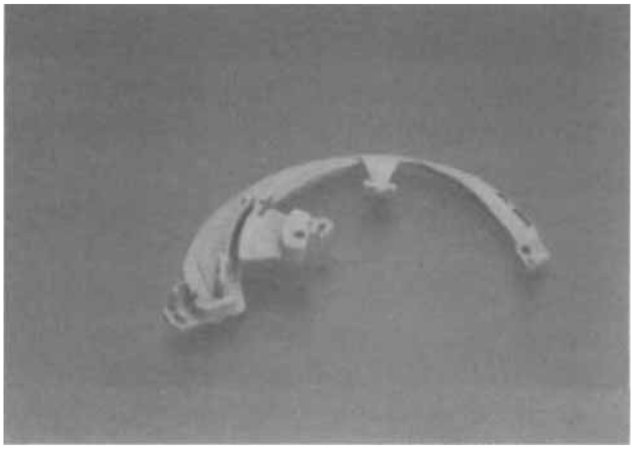


FIGURE 16 Video parts

## References

[1.] T. Inoue, *Plastic Age Encyclopedia*, 176 (1987)

[2.] T. Inoue, *Kagaku-Kogaku*, **58**, 374 (1994)

[3.] T. Inoue, *Kobunshi, High Polymers, Japan*, **43**, 730 (1994)

[4.] T. Inoue, *Plastics Age*, **41**, 132 (1995)

[5.] *Kagaku Kogyo Nippo* (Feb. 15, 1994)

[6.] *Kagaku Kogyo Nippo* (Feb. 25, 1997)

[7.] V. A. Nicely et al., *Macromolecules*, **20**, 573 (1987)

[8.] A. M. Donald et al., *J. Mater. Sci. Lett.*, **4**, 58 (1985)

[9.] K. Nakamura, and T. Inoue, *Preprints for 3rd. Polymeric Material Forum*, *The Society of Polymer Science, Japan* , 237 (1994)

[10.] K. Nakamura, *Plastics Age*, **42**, 142 (1995)

[11.] T. Inoue, *Japan Energy & Technology Intelligence (JETI)*, **43**, 21, (1995)