## Mwd Measurements of Liquid Crystalline Aromatic Polyesters by Gpc-Lalls Using A Mixed Solvent

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# MWD MEASUREMENTS OF LIQUID CRYSTALLINE AROMATIC POLYESTERS BY GPC-LALLS USING A MIXED SOLVENT

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ABSTRACT

A GPC-LALLS method was developed to measure the molecular weight distribution(MWD) of liquid crystalline aromatic polyesters(LCPs). Pentafluolophenol and chloroform(35:65% by weight) as a mixed solvent was found to maintain the stability of LCPs solutions and to yild reliable GPC-LALLS curves for LCPs at room temperature.

## INTRODUCTION

A variety of LCPs have been synthesized[1, 2, 3, 4] and found to have many excellent physical and chemical properties, such as high strength, a high Young's modulus, low melt viscosity, a low expansion coefficient, high heat resistance, and high chemical resistance. Some of these polymers such as XYDER,[1] VECTRA,[2] and EKONOL,[3] have become of commercial to be used as raw materials

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in the field of plastics, fibers, and etc. Due to the insolubili-
ty of these polymers, it is very difficult to measurethe MWD.
Pentafluorophenol(PFP)[2] is the only solvent for LCPs yet fonnd.
Dilute solutions of LCPs in PFP were used for measurement of the
viscosity to estimate the molecular weights. PFP was also used
for the GPC method of polyethylene therephthalate.[5] We devel-
oped a specially designed high temperature GPC system operating
at 60℃ and reported a GPC method for LCPs using PFP.[6] As PFP
is solid at room temperature(m.p.=34~35℃), the method has some
weak points such as a gradual decrease of the column plate num-
ber, the necessity of a temperature controlled GPC instrument
(60℃), and complicated procedures, such as exchanging of the sol-
vent after every measurement to protect from cell cracks. The
solvent PFP is also too expensive to be used as a GPC solvent.
    In this investigation, we found that PFP and chloroform(35:65
% by weight)[7] are able to maintain the stability of LCPs in
solution, and that GPC-LALLS measurements using this mixed sol-
vent at room temperaturer(23℃) yield reasonable measurements of
the MWD and the average molecular weight.

### EXPERIMENTAL

Materials
    Commercial reagent PFP(99%, Ardrich Chemical Co.) and chloro-
form(99%, Kishida Chemical Co.) were mixed and passed through a
0.33μm Fluoropore filter(Sumitomo Electric Co.). LCP-A[2] (a co-
polyester of p-hydroxy benzoic acid and 2-hydroxy-6-naphthoic
acid, 3:1 molar ratio) and LCP-B[1] (a copolyester of p-hydroxy
benzoic acid, p, p'-dihydroxy biphenyl, terephthalic acid, 4:1:1
molar ratio) were synthesized. Five different molecular weight
polymers of LCP-A, listed in the Table 1 were obtained by hydroly-
sis of the original LCP-A in PFP to which was added 1% water and
2.5% acetic acid at 110℃ for 2~15 days.

Preparation of Sample Solutions
    A 20mg sample was dissolved in 7.0g of PFP at approx. 100℃
for LCP-A, and approx. 70℃ for LCP-B. 13.0g of chloroform was
added with stirring. Then 2ml of this solution was diluted by
8ml of mixed solvent(PFP:chloroform, 35/65% by weight). The solu-

tion was filtered with $0.45\mu$m Fluoropore filter(Sumitomo Elect-
ric Co.) to yield sample solutions of polymer at a concentration
of 0.0307%.

## GPC-LALLS
  A conventional type GPC,consisting of a model 510 pump,a
model U6K injector,and a model 410 differential refractometer
detector(RI)(Waters),was coupled with a model KMX-6 LALLS
(Chromatix),equipped with a $10\mu$l flow cell and a $0.1\mu$m Fluoro-
pore line filter. The operational conditions of the LALLS were
the scattering angle( $6\sim7°$ ) and the field stop(0.2mm). Two
Shodex KF-80M columns(Showa Denko Co.) were operated at 23℃.
The flow rate of the PFP/Chloroform (35:65% by weight) carrier
solvent was 0.8ml/minute. Sample solutions of 0.3ml at 0.03%
were injected and GPC-LALLS curves were obtained at the sensi-
tivity of 4x by the differential refractometer,and the sensi-
tivity of 350mV by the LALLS.
  The specific refractive index increment (dn/dc) of LCP-A was
calculated from GPC-LALLS curves of LCP-A and standard polysty-
rene(PST) SRM 706(National Bureau of Standards,the weight-aver-
age molecular weight: 260,000[8]) at the same conditions. At
small forward scattering angles $(6\sim7°$ ),the relationship be-
tween the excess Reyleigh factor $(R\theta )$ and the weight average
molecular weight (MW) is expressed as:

$$K \cdot c/R\theta = (1/MW)+2A_2 \cdot c \qquad (1)$$

where c is the solute concentration,$A_2$ is the second virial co-
efficient,$R\theta$ is the difference in the Ryleigh factor of the
solution and that of the pure solvent,and K is the polymer opti-
cal constant,defined as:

$$K=(2\pi^2 n^2/\lambda^4 N)(dn/dc)^2(1+\cos^2\theta ) \qquad (2)$$

where n is the refractive index of the solvent at the incident
wave length $\lambda$ (in vacuo), N is Avogadro's constant, $\theta$ is the
angle of scattered light collection,and dn/dc is the specific
refractive index increment. Because the concentration of solute
is very low in GPC measurement,the second term of Eq.1 is neg-
ligible small. Thus the dn/dc value is derived from Eq.1 and
Eq.2 by using the new constant $K_1$:

$$(dn/dc)^2=R\theta /MW \cdot K_1 \cdot c \qquad (3)$$

The value $R\theta/K_1 \cdot c$ can be expressed as:

$$R\theta/K_1 \cdot c = (A_{LS}/A_{RI}) \cdot K_2 \qquad (4)$$

where $A_{LS}$ and $A_{RI}$ are the peak area of LALLS and RI. From Eq.3 and Eq.4, the dn/dc value of standard PST in mixed solvent was determined using peak areas of LALLS and RI($A_{LS,PST}$, $A_{RI,PST}$).

$$(dn/dc)^2 \cdot {}_{PST} = (A_{LS \cdot PST}/A_{RI \cdot PST}) \cdot K_2/MW_{PST} \qquad (5)$$

where, $MW_{PST}$ is the weight-average molecular weight of standard PST. $K_2$ is the overall constant, including the optical constant, the instrument constant, and the refractive index of the solvent. In this experiment, no selective adsorption of PST was observed. The value dn/dc of PST SRM706 obtained is 0.162ml/g.

The dn/dc value(0.212ml/g) of LCP-A was determined by the experiment at the same concentration and the same conditions.

$$(dn/dc)_{LCP-A} = (A_{RI,LCP-A}/A_{RI,PST}) \times (dn/dc)_{PST} \qquad (6)$$

The refractive index (n=1.4306) of the mixed solvent at wave length 633nm and at the temperature 23℃ was determined by using a ATAGO ABBE refractometer(Atago Co.) and a monochrometer(Jobin Yvon).

## Intrinsic Viscosities

Intrinsic viscosities of five different molecular weight of LCP-A were determined in PFP at 50℃ using an Ubelohde type automatic viscometer(FICA).

## RESULTS AND DISCUSSION

## Stability of Solution

We obtained the mixed solvent solutions of LCPs by dissolving polymers in PFP followed by addition of chloroform with stirring at 23℃. The stability of each solution was tested by observation of the appearance and filtration. Results are summarized in Table 1. When the content of PFP is higher than 30%, the polymer solutions are stable. With 25% PFP or less, the solutions became impossible to filter or are cloudy. From these results, PFP and chloroform in a mixed solvent of 35:65% by weight is considered to be a good solvent for GPC-LALLS measurement.

Table 1

Solubility of Liquid Crystalline Aromatic Polyesters

| Solvent (weight ratio) PFP/Cnloroform | LCP-A Appearance | Filter[a] | LCP-B Appearance | Filter[a] |
|---|---|---|---|---|
| 30:70 | clear | possible | clear | possible |
| 25:75 | clear | possible | clear | impossible |
| 20:80 | clear | possible | clear | impossible |
| 15:85 | cloudy | impossible | micro gel | impossible |
| 10:90 | cloudy | impossible | cloudy | impossible |

[a] 0.45 $\mu$m Fluoropore filter(Sumitomo Electric Co.)

Table 2

Intrinsic Viscosity and Average Molecular Weight

| Sample | $[\eta]$ [a] | $Mn \times 10^{-4}$ | $Mw \times 10^{-4}$ | $Mz \times 10^{-4}$ | Mw/Mn |
|---|---|---|---|---|---|
| LCP-A1 | 6.80 | 1.43 | 4.42 | 9.53 | 3.1 |
| LCP-A2 | 4.75 | 1.03 | 3.04 | 6.20 | 2.9 |
| LCP-A3 | 3.25 | 0.79 | 2.20 | 4.20 | 2.8 |
| LCP-A4 | 2.30 | 0.51 | 1.44 | 2.89 | 2.8 |
| LCP-A5 | 1.60 | 0.37 | 1.05 | 2.45 | 2.8 |

[a] in pentafluorophenole at 50℃

## Concentration Effect in GPC Measurements

The effects of concentration on GPC measurement under optimal
conditions is shown in Fig.1,with a polystyrene gel column,a PFP
and chloroform (35:65% by weight) mixed solvent,a flow rate of
0.8 ml/min,and a temperature of 23℃. The chromatogram shape
changes abnormally at a polymer concentration of more than 0.05%.
Therefore,the measurement of GPC curves should be carried out at
a polymer concentration of less than 0.04%.

## Evaluation of GPC-LALLS Curves

Fig.2 shows an example of GPC-LALLS curve of LCP-A, and Fig.3
shows GPC curves of LCP-A at five different molecular weights.
The average molecular weights calculated from GPC-LALLS curves
and intrinsic viscosities are compiled in Table 2. The results
show a good relationship between the elution time,the intrinsic
viscosity $[\eta]$ ,and the average molecular weight. This suggests
that the PFP/chloroform mixed solvent system can be used for the
molecular separation of LCP-A based on the molecular size using
GPC. The signal intensity of LALLS in Fig.2 is strong enough to
calculate the absolute average molecular weight and the molecu-
lar weight distribution. This means that this mixed solvent has
as ideal n value to provide a high dn/dc value for polymers,such
as LCPs,with an aromatic structure. The stability of baseline is
excellent,because the difference of the refractive index between
PFP and chloroform is small.

## Molecular Weight - Intrinsic Viscosity Correlations

Measurement of the intrinsic viscosity measurement is essen-
tial to characterize a given polymer. We tried to determine the
coefficient K and the exponent a in the Mark-Houink-Sakurada
equation(Eq.7) of LCP-A in PFP at 50℃ by trial and error method
using the data on the five different molecular weight distribu-
tions obtained by the GPC-LALLS method and the five intrinsic
viscosities. The molecular weight to intrinsic viscosity corela-
tion for a polymer with monodispersity is defined as:

$$[\eta] = K M^a \tag{7}$$

where $[\eta]$ is the intrinsic viscosity, K is the coefficient,
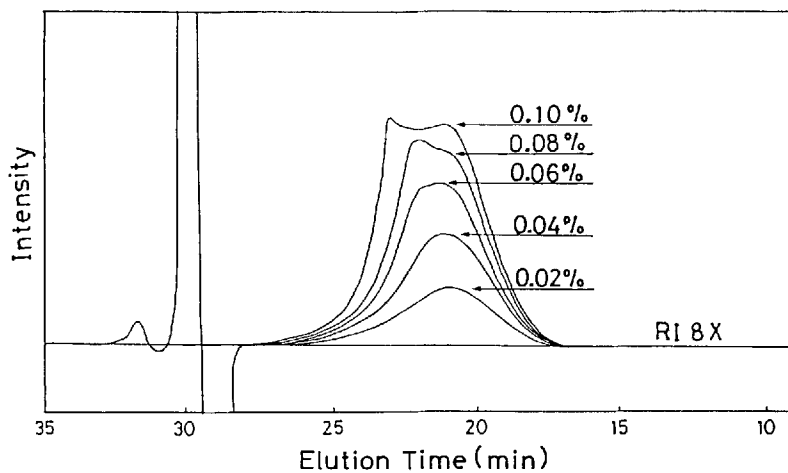and a is the exponent. The corelation for a polymer with poly-

Figure 1. GPC curves of LCP-A at five different concentrations
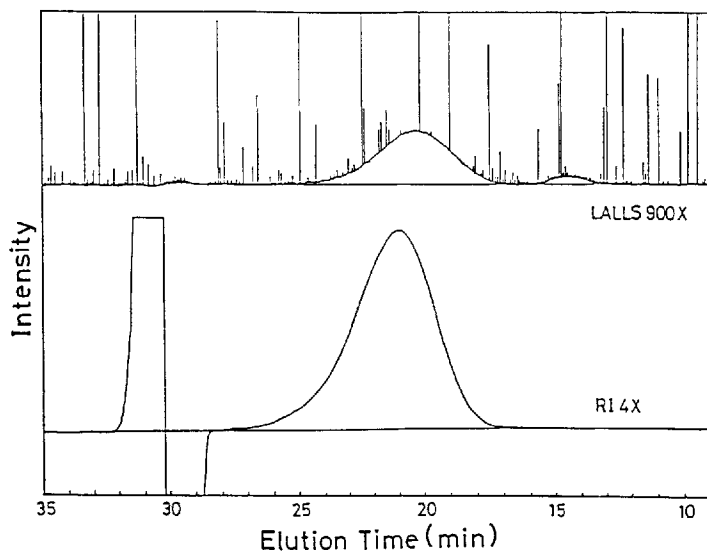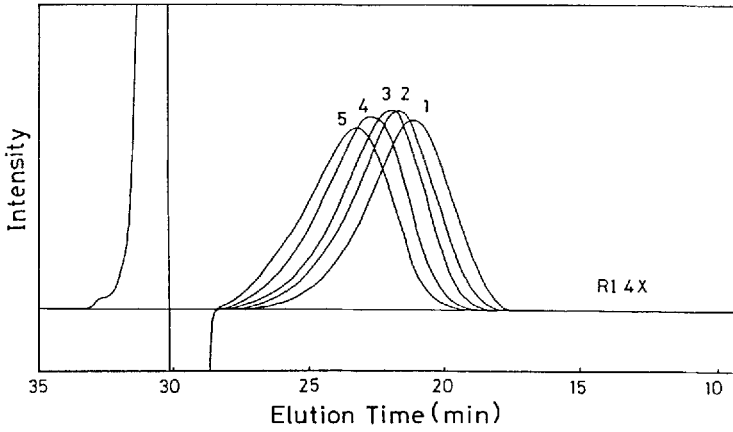


Figure 2. GPC-LALLS curve of LCP-A

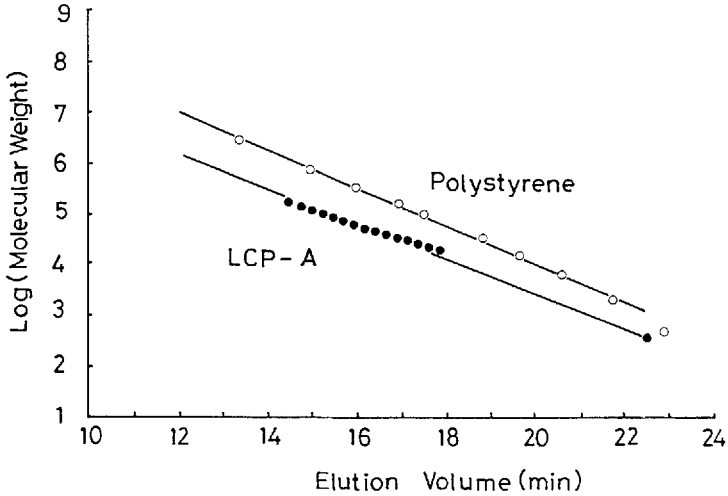Figure 3. GPC curves of LCP-A at five different molecular weight



Figure 4. Calibration curves of LCP-A and polystyrene

dispersity, $[\eta]$ is expressed as:

$$[\eta] = \Sigma Wi \cdot K (Mi)^a \qquad (8)$$

where Wi is the weight fraction of a molecule of i to the molecular weight $M_i$. Many exponent values corresponding to LCP-A were calculated using the given K values. We finally obtained a combination of K and a values (9) which yield each of five intrinsic viscosity values.

$$[\eta] = 9.205 \times 10^{-5} M^{1.05} \text{ (PFP at 50°C)} \qquad (9)$$

The exponent value obtained is much higher than the values for flexible polymers, such as polystyrene and polymethylmethacrylate. It can be considered that the molecules of LCP-A have a rather expanded shape in PFP, and have a large hydrodynamic volume.

Calibration Curves of LCP-A and Polystyrene

Fig. 4 shows two calibration curves obtained under the same chromatographic conditions using the mixed solvent system. The lower curve is the absolute MW calibration curve for LCP-A, and the upper curve is for polystyrene. Data points for LCP-A were absolute molecular weight values at each elution time calculated using the GPC-LALLS curve in Fig. 2. Diphenylisophthalate was used as a standard compound of molecular weight to estimate the elution time in the low molecular weight region. The calibration curve of polystyrene was constructed from the data of ten monodisperse standard materials. There is a large discrepancy in the two calibration curves. This suggests that the hydrodynamic volume of LCP-A in a mixed solvent is larger than that of polystyrene at the same molecular weight. A large discrepancy is olso observed in the result from experiments using pure PFP as a solvent. Judging from the solubility and the hydrodynamic volume in mixed solvent, the molecules of LCP-A are considered to have rod shape segments in the molecules, and are considered to be surrounded by selective adsorption of PFP at the equilibrium state.

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