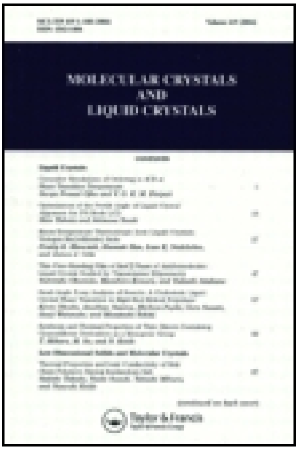

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# Electrorheological Properties of Liquid-Crystalline Materials containing Liquid-Crystalline Polymer of various Molecular Weights and Spacer Lengths

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# Electrorheological Properties of Liquid-Crystalline Materials containing Liquid-Crystalline Polymer of various Molecular Weights and Spacer Lengths

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Polymers with cyanobiphenyl groups (PCBAn) in their side-chains with different spacer lengths (n=2,6,11) and different molecular weights (Mw), were prepared. The phase behavior of the polymers and that of liquid-crystalline mixtures (LCMn) consisting of PCBAn and low-molecular weight liquid crystal, were observed. LCM2 and LCM6 showed liquid-crystalline property of nematic phase, while LCM11 showed liquid-crystalline property of smectic phase. The electrorheological properties of LCMn were investigated. The viscosity of LCMn increased upon application of a DC electric field, and the degree of increase was characteristic to each n value. LCM6 of different Mw showed nearly the same electrorheological behavior except for the LCM6 of lowest Mw, which displayed a large increase in viscosity upon application of the electric field.

*Keywords:* liquid-crystalline polymer; low-molecular weight liquid crystal; electrorheological properties; phase transition behavior; cyanobiphenyl group

## INTRODUCTION

Liquid crystals are materials which show strong anisotropy but retain liquid fluidity. Due to their interesting properties and wide application, the optical and mechanical properties of liquid crystals have been investigated. When an electric

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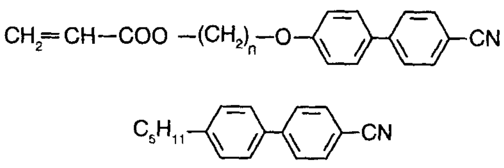
field is applied to liquid crystals, they show a remarkable increase in viscosity known as the electrorheological effect [1–3]. We previously demonstrated the electrical – mechanical energy conversion system using a thermotropic liquid-crystalline (LC) polymer gel which consisted of thermotropic liquid-crystalline elastomer and low-molecular weight liquid crystal [4]. We also reported the electrorheological effect of binary mixtures of poly(6-(4'-cyanobiphenyl-4-yloxy) hexylacrylate and 4-cyano-4'-pentylbiphenyl [5]. Polymers with the same cyanobiphenyl group in their side-chains but different lengths of the *n*-aliphatic substituent and different molecular weights, were prepared in order to investigate their electrorheological behavior in detail. The spacer length (n) of the *n*-aliphatic substituent would affects the stability of the alignment of the cyanobiphenyl groups, and differences in the molecular weight of polymers would result in a change in the viscosity of the binary mixtures (LCMn). In this paper, we studied the effect of structural factors, i.e., spacer length and molecular weight, on the electrorheological properties of LCMn.



(I)

(II)

FIGURE 1 Structure of monomer (I) where n varies as 2, 6, 11, and low molecular weight liquid crystal (5CB) (II)

## EXPERIMENTAL

### Materials

Figure 1 shows the structure of the LC materials used in this study. Liquid-crystalline polyacrylates carrying cyanobiphenyl groups in their side-chains with various spacer lengths (PCBAn, n=2, 6, 11) were prepared by radical polymerization of monomer (I). (I) was synthesized by the method reported by Sibaev, et al. [6]. The detailed method of the preparation of PCBAn was described in a previous report [5]. The prepared polymers were fractionated into several fractions by gel permeation chromatography (GPC). 4-cyano-4'-pentylbiphenyl (5CB) (II) was purchased from Merck, Inc. Each fractionated PCBAn was added to 5CB, and stirred at 80°C for several hours to obtain binary mixtures. The concentration of PCBAn in the mixture was 30 mol% with respect to the mesogenic unit.

### Measurements

The weight-average molecular weight (Mw) of each fractionated polymer was determined by GPC calibrated with polystyrene standards. The texture and phase transition of the LC materials were observed under an Olympus BH-2 polarizing microscope equipped with a hot stage. Thermotropic properties were determined with a SEIKO DSC-120 Differential Scanning Calorimeter at a heating rate of 5°C/min. The electrorheological properties of LCMn (n=2, 6, 11) were measured by a Nihon Rheology NRM-100EM Rotational Rheometer equipped with parallel plate electrodes. The temperature of the electrodes was controlled using an air thermostat. To compare the results of the viscosity measurements among LCMn, we used reduced temperatures, $T^*$ (where $T^*=T / T_{cl}$, T=measured temperature in Kelvin, $T_{cl}$ = clearing temperature in Kelvin), and all of the viscosity data were obtained at $T^*=0.903$.

## RESULTS AND DISCUSSION

### Phase behavior of LC materials

The molecular weight and phase transition temperature of each LC material are summarized in Table I. The Mw/Mn of most of the LC materials was less than 1.5. Since the Mw/Mn values before fractionation were over 2.5, the polymer became monodispersed by the fractionation. The glass transition temperature ($T_g$) of LCMn could not be detected by DSC measurement. Among each of the three PCBAn, both $T_g$ and $T_{cl}$ had little dependence on the Mw. The dependence of $T_g$ and $T_{cl}$ on spacer length showed the same tendency as that reported by Shibaev, et al. [6]. Because monomers of the corresponding polymer are crystalline substances but don't show LC properties, one can take 4-cyano-4'-alkoxybiphenyls to be low-molecular analogues of PCBAn [7]. The $T_{cl}$ of PCBAn is higher than that of the low-molecular analogue, and the $T_g$ is lower than the melting temperature of the low-molecular analogue for each n value. Therefore, "attachment" of a low-molecular liquid crystal to a polymer chain enhances the thermal stability of the resulting mesophase. Particularly in the case of PCBA2, one can see that the low molecular analogue does not display LC properties while PCBA2 does. It can be said that the mesophase of PCBA2 arises from the promotion of the alignment of cyanobiphenyl groups by attaching them to a polymer chain.

TABLE I Molecular weight and phase transition temperature of LC materials

| | *Spacer length* | *Mw* | *Mw/Mn* | *DP* | *Phase Transition Temperature / °C* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | *Polymer* | | | | | *Mixture* | | |
| PCBA2 | 2 | $1.5\times10^5$ | 1.5 | 520 | g | 67.3 | N | 92.9 | I | | – | |
| | | $1.0\times10^5$ | 1.7 | 340 | g | 69.4 | N | 93.5 | I | | – | |
| | | $5.1\times10^4$ | 1.6 | 180 | g | 72.2 | N | 95.1 | I | | – | |
| | | $2.7\times10^4$ | 1.6 | 90 | g | 74.1 | N | 98.9 | I | N | 69.4 | I |
| PCBA6 | 6 | $2.0\times10^5$ | 1.8 | 580 | g | 27.9 | N | 127.8 | I | N | 62.2 | I |
| | | $6.5\times10^4$ | 1.3 | 180 | g | 26.3 | N | 127.0 | I | N | 62.7 | I |
| | | $3.1\times10^4$ | 1.4 | 90 | g | 21.5 | N | 130.6 | I | N | 62.2 | I |
| | | $1.2\times10^4$ | 1.2 | 40 | g | 25.2 | N | 120.9 | I | N | 63.0 | I |
| PCBA11 | 11 | $5.4\times10^4$ | 1.3 | 130 | g | 9.2 | S | 140.2 | I | S | 76.7 | I |
| | | $3.2\times10^4$ | 1.3 | 80 | g | 11.9 | S | 139.1 | I | S | 78.0 | I |
| | | $1.8\times10^4$ | 1.2 | 40 | g | 7.0 | S | 129.5 | I | S | 69.4 | I |

Mw: The weight-average molecular weight, Mn: The number-average molecular weight.

DP: Degree of Polymerization was determined by dividing Mw by molecular weight of the monomer.

g: glass, N:nematic, I:isotropic

The phase behavior of binary mixtures consisting of PCBAn and 5CB was complicated. For PCBA2, the sample of Mw=$2.7\times10^4$ was completely miscible with 5CB, and a schlieren texture characteristic of the nematic LC phase was observed at room temperature. Samples with molecular weights greater than Mw=$2.7\times10^4$ separated from 5CB at room temperature, although they were miscible at 80°C. For PCBA6, all samples studied were miscible with 5CB, and showed a schlieren texture at room temperature. For PCBA11, all samples were miscible with 5CB, and showed a simple fan-shaped texture characteristic of the smectic LC phase. Taking into account the fact that PCBA11 displays the smectic phase while 5CB displays the nematic phase under these conditions, the cyanobiphenyl groups were predominantly aligned with the polymer rather than with 5CB in the mixture. Good miscibility was observed for polymers which had a longer spacer than the number of aliphatic chains in 5CB, upon mixing the two materials.

## Effect of the Molecular Weight of LCM6

Viscosity is plotted against the shear rate ($\dot{\gamma}$) of LCM6 containing PCBA6 of various Mw with no electric field in Figure 2. As the Mw of PCBA6 in LCM6

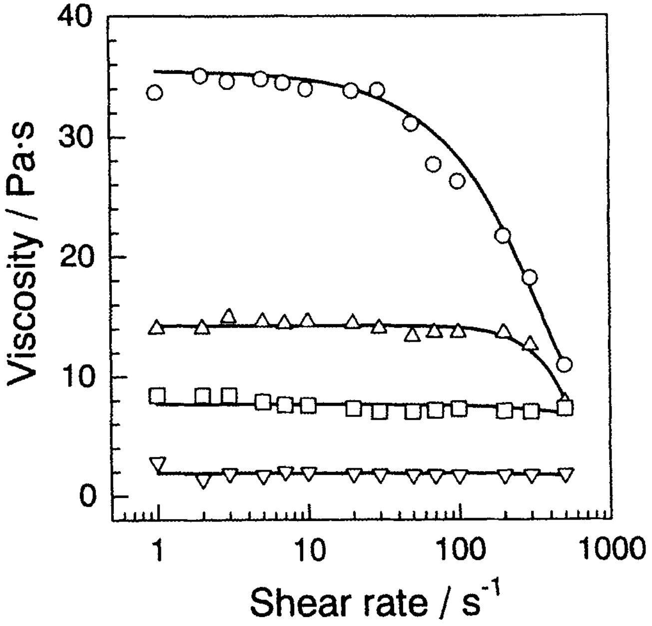


FIGURE 2 The dependence of viscosity on shear rate for LCM6 containing PCBA6 of various molecular weights. O: Mw = 2.0 × 10$^5$ , Δ : Mw=6.5×10$^4$, □: Mw=3.1×10$^4$, ∇: Mw=1.2×10$^4$

was increased, the viscosity increased by a greater degree. The viscosity of 5CB is very low, about 0.025 Pa·s at room temperature and the addition of PCBA6 brought about a remarkable increase in viscosity according to its molecular weight. The viscosity of LCM6 containing PCBA6 of Mw=1.2×10$^4$ and Mw=3.1×10$^4$ was nearly constant over the range of shear rate from 1 to 500 s$^{-1}$. Therefore, the orientation of mesogenic groups did not change in this range of shear rates, that is, the mesogenic groups oriented along flow direction even at the low shear rate of $\dot{\gamma} = 1$. The viscosity of LCM6 containing PCBA6 of Mw=6.5×10$^4$ and Mw=2.0×10$^5$ decreased in the higher shear rate region. It is difficult to attribute these decreases in viscosity to a change in the orientation of mesogenic groups. A conformational change in the polymer chain might take place in polymers of higher molecular weights. It may be considered that elongation of the polymer chain along the flow direction as a result of the increase in shear rate, led to the decrease in viscosity.

LCM6 displayed an electrorheological effect. Application of a DC electric field resulted in an increase in the viscosity of LCM6, and after the electric field

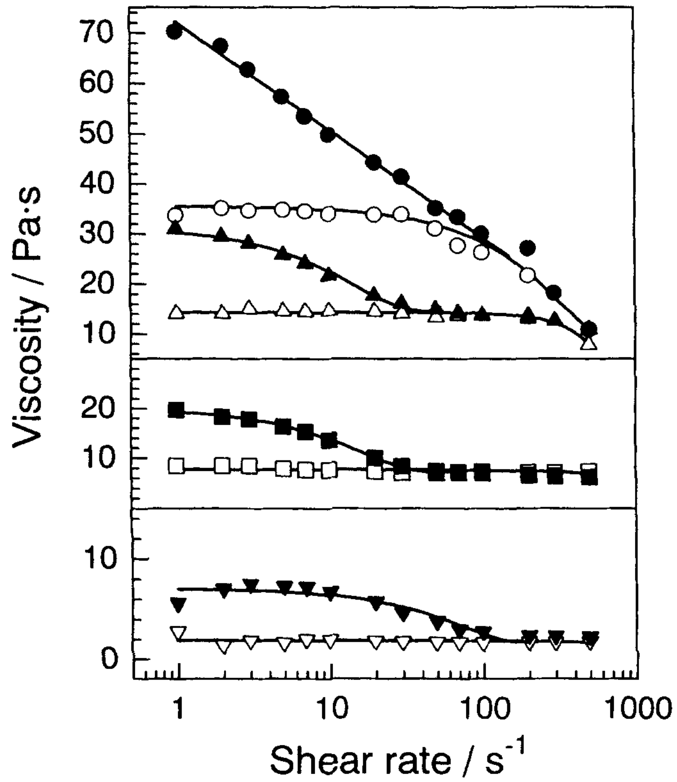


FIGURE 3 Electrorheological effect on LCM6 containing PCBA6 of various molecular weights. O: Mw=$2.0\times10^5$, Δ: Mw=$6.5\times10^4$, □: Mw=$3.1\times10^4$, ∇: Mw=$1.2\times10^4$. Open symbols, no electric field; filled symbols, electric field of 2kV/mm was applied

was turned off, LCM6 recovered its original viscosity. Figure 3 shows the electrorheological properties of LCM6 containing PCBA6 of various Mw when an electric field of 2 kV/mm was applied. The vertical axis in Figure 3 was divided in three so as to prevent the plots from overlapping. In the region of low shear rates, the increase in viscosity caused by the application of the electric field was significant, whereas the increase in viscosity was small in the region of higher shear rates. The electrorheological effect hardly appeared at shear rates above $\dot{\gamma} > 50s^{-1}$. It is suggested that the electrorheological effect results from a change in the orientation of mesogenic groups. Such orientation change might be hindered by shear. If due consideration including hydrodynamic theory was given on the hindrance of electrically induced orientation, a quantitative interpretation would be derived about the behavior of viscosities of LC mixtures. We, however, don't have enough explanation at present and further work must be done for this matter.

Figure 4 shows a graph of the relative viscosity ($\eta_{rel}$) of LCM6 vs. shear rate under an electric field of 2 kV/mm. Relative viscosity was defined as the ratio of the apparent viscosities with and without the electric field. LCM6 with different Mw showed nearly the same electrorheological behavior except for LCM6 of Mw = $1.2\times10^4$, which displayed larger values of $\eta_{rel}$ than the others. At shear rate 2 $s^{-1}$, the viscosity increased five-fold when the electric field was applied. Negita studied the increase in viscosity of 5CB alone upon application of an AC electric field, and reported that $\eta_{rel}$ =4 when an electric field of 2 kV/mm was applied [8]. Therefore, the viscosity of the material increases with the addition of PCBA6, whereas the addition doesn't lead to a significant increase in $\eta_{rel}$.

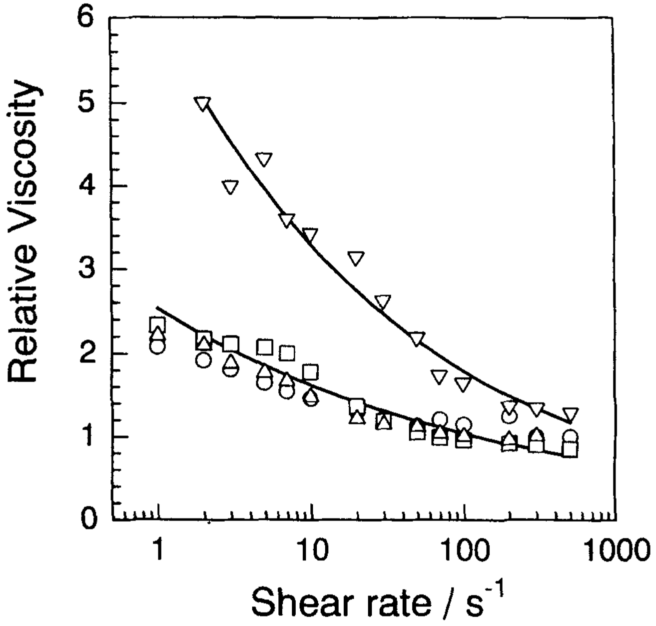


FIGURE 4 Relative viscosity plotted against shear rate for LCM6 containing PCBA6 of various molecular weights. Applied electric field is 2kV/mm. O: Mw=$2.0\times10^5$, Δ: Mw=$6.5\times10^4$, □: Mw=$3.1\times10^4$, ∇: Mw=$1.2\times10^4$

### Effect of spacer length

The electrorheological effect of LCMn was studied. For LCM2, PCBA2 of Mw=$2.7\times10^4$ showed miscibility with 5CB. Thus, PCBA6 of Mw=$3.1\times10^4$ and

PCBA11 of Mw=$3.2\times10^4$ were chosen and mixed with 5CB to make the degree of polymerization nearly uniform for viscosity measurements.

Figure 5 shows the change in the viscosity of LCMn with the application of 2 kV/mm. Since LCM2 and LCM6 are in nematic phase and LCM11 is in smectic phase, the viscous behavior of these LC materials will be different. Regarding the electrorheological effect of smectic LC materials, a decrease in viscosity by application of a DC electric field has been reported for the low-molecular weight liquid crystal, 4'-octyl-4-cyanobiphenyl, which is an analogue of the mesogenic group of PCBAn [9]. However, a slight increase in viscosity was observed for LCM11 when an electric field was applied. Although it has been proposed that the electrorheological effect of smectic LC materials is due to realignment of the domains and form of the layered structure [10], further investigation is necessary to interpret the increase in viscosity of LCM11.

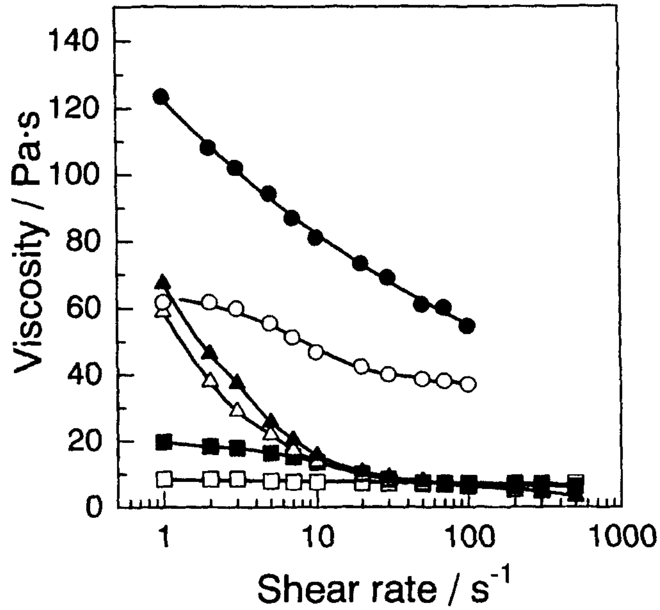


FIGURE 5 Electrorheological effect on LCM containing PCBA of various spacer lengths. O: LCM2 (Mw of PCBA2 = $2.7\times10^4$), □:LCM6 (Mw of PCBA6 = $3.1\times10^4$), Δ: LCM11 (Mw of PCBA11 = $3.2\times10^4$). Open symbols, no electric field; filled symbols, electric field of 2kV/mm was applied

The viscosity of LCM2 was larger than that of LCM6. It can be considered that the polymer chain in LCM2 is more rigid than the polymer chain in LCM6 due to steric hindrance between cyanobiphenyl groups as a result of the shorter spacer length. The viscosity of LCM6 was nearly constant under the shear rate range studied, while the viscosity of LCM2 decreased as the shear rate was increased. The polymer chain of PCBA6 elongates along the flow direction even at low shear rates. The more rigid chain of PCBA2 cannot elongate at low shear rates; as the shear rate is increased polymer chain elongation occurs, resulting in a decrease in viscosity.

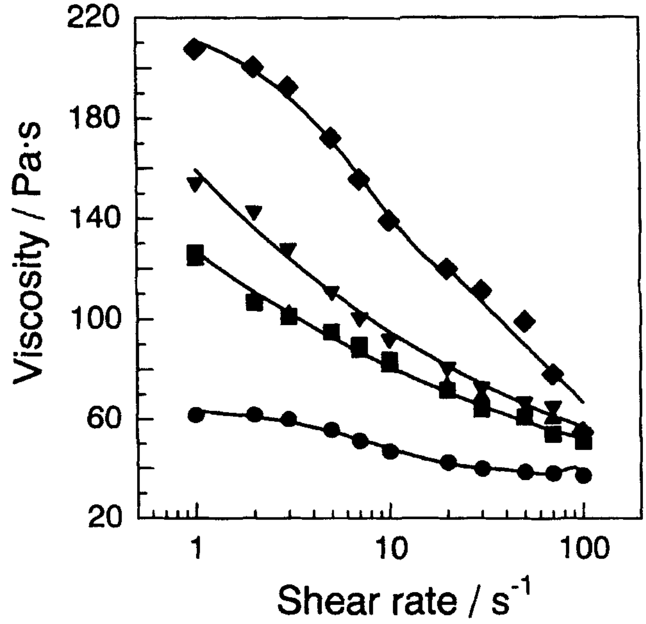


FIGURE 6 Electrorheological effect of LCM2, Mw of PCBA2 is $2.7\times10^4$. Electric field, ●: OFF, ■: 3kV/mm, ▼: 4kV/mm, ♦: 5kV/mm

The viscosity of both LCM2 and LCM6 increased approximately two-fold in the low shear rate region when 2 kV/mm was applied. As the electric field strength was increased, the viscosity of LCM2 and LCM6 increased by a significantly greater degree, as shown in Figures 6 and 7. At each electric field strength, a consistent decrease in viscosity with increasing shear rate was measured for LCM2 as shown in Figure 6. For LCM6 when 3 or 5 kV/mm was applied, a plateau region was observed in the lower shear rate region ($\dot{\gamma} < 10s^{-1}$). These results suggest that the alignment of mesogenic groups in LCM6 is more stable against shear than the alignment of mesogenic groups in LCM2.

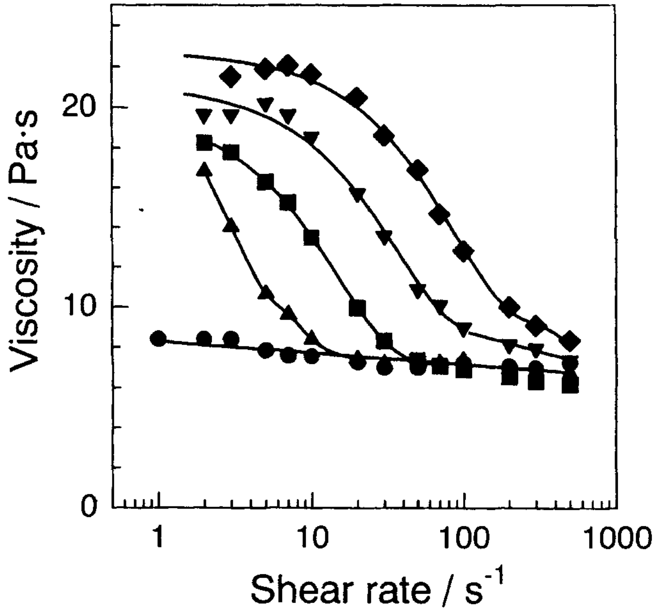


FIGURE 7 Electrorheological effects of LCM6, Mw of PCBA6 is $3.1\times10^4$. Electric field, ●: OFF, ▲: 1kV/mm, ■: 2kV/mm, ▼: 3kV/mm, ◆: 5kV/mm

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