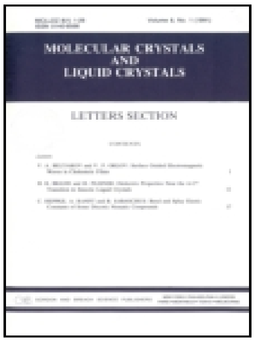

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The Electro-Optical Properties of Doping Polycyclic Aromatic Hydrocarbon Liquids in Twisted Nematic Liquid Crystals

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In this paper, doping liquid materials to enhance the electro-optical (EO) properties of twisted nematic liquid crystals (NLCs) was presented. Two polycyclic aromatic hydrocarbon (PAH) liquids, toluene and 1-methylnaphthalene, were chosen as dopants in order to lower the driving voltage and response time of the NLCs. We find that the main reason of this phenomenon is due to a large amount of reduction in the rotational viscosity of PAH liquids doped NLCs. Without the drawbacks of aggregation that the solid nanoparticles could have, the method of doping liquids provides a more reliable choice for applications in various LC display systems.

Keywords: nematic liquid crystals; polycyclic aromatic hydrocarbon liquids; rotational viscosity; visco-elastic coefficient

Introduction

Liquid crystals (LCs) are currently one of the most used materials for electro-optical (EO) applications. A very wide range of commercialized display devices, such as mobile phones, televisions, monitors, or touching panels, are utilizing the techniques of liquid crystal displays (LCDs). In order to obtain better electro-optical characteristic of LCDs, it is a quite important task to decrease the response time and lower the driving voltage in LCD applications. Recent years, doping nanoparticles into NLCs has been of magnificent interest to improve the EO properties of NLC devices. Many kinds of conducting nanomaterials, such as gold nanorods [1], gold nanoclusters [2], carbon nanotubes (CNTs) [3] etc. were dispersed into NLCs. However, it was found that, because of the ion drift of conducting particles, these doped nano-materials might not be able to maintain voltage-holding ration (VHR) in the LC cells [4]. The low VHR condition may lead to image sticking and poor display contrast, further influences the quality of LCDs.

In order to maintain high VHR in LCDs, many researchers developed an alternative way to dope insulating nanoparticles such as diamond powders, ZnO, TiO_2, and Ce_3O_4 etc. to mix with LCs. A variety of valuable effects has been observed including lowering the threshold voltage, suppressing the screen effect, or reducing the

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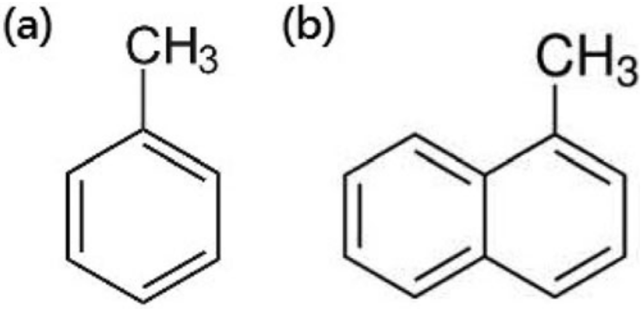

Figure 1. Chemical structures of (a) toluene and (b) 1-methylnaphthalene.

transient currents [5–7]. Moreover, it has also been reported that that these insulating nanoparticles used as dopant can maintain high VHR for display applications [8]. However, these nanoparticles might easily precipitate or aggregate to cause topological defects to increase the response time and break the phase of LCs [9, 10]. To overcome the drawbacks of using nanoparticles, we develop a much simpler method to avoid the disadvantages of nanoparticles doping and can successfully obtain compatible results.

Since solid nanomaterials could improve the EO properties of NLCs by simply doping without chemical reactions, we expect that liquid materials might induce the similar effects. To date, some surfactants were doped into polymer dispersed LCs (PDLCs) to decrease the driving voltage [11–13]. These studies showed that doping liquids into PDLCs could be a feasible way to change the EO properties of PDLCs compared with doping nanoparticles. We tried to dope some common and simple liquids into NLCs to replace nanoparticles as dopants. As long as the liquid can dissolve uniformly with NLCs, the disadvantages of doping nanoparticles mentioned above can be avoided.

In this study, two polycyclic aromatic hydrocarbon (PAH) liquids, toluene and 1-methylnaphthalene (the structures are shown in Figure 1), were doped into NLCs for properties modification. The NLCs modified by the PAH liquids exhibit fantastic EO properties in the ways of lowering the driving voltage and the response time. The PAH liquids are completely miscible with NLCs because they are comprised of simple aromatic rings. After the PAH liquids were doped into NLCs, lower driving voltage and faster response time were observed in twisted nematic (TN) cells. In experiments, we measured the rotational and flow viscosity of NLC mixtures and demonstrated the relationship between the viscosity and the EO properties. Since toluene and 1-methylnaphthalene are both low-viscosity liquids (0.59 cP and 3.26 cP at 20°C, respectively) relative to NLCs, the viscosity of NLCs could be greatly reduced by doping these two PAH liquids. We successfully optimized the performance of NLCs in TN cells through doping PAH liquids, which provides a more reliable method than the use of solid nanoparticles doping. Here our results demonstrate a new feasible choice of doping liquid materials into NLCs, especially the variety of liquids is much wider than nanoparticles. The PAH liquids are potentially used in different LC systems that open a simple and efficient way to enhance the performance of LC electro-optical devices for display applications.

Experimental

Toluene (purity 99.8%, TEDIA) and 1-methylnaphthalene (purity >94%, Merck) were doped into NLC (DF-7538A, $\Delta n = 0.095$, $\Delta\varepsilon = 7.25$, Daily Polymer Corp.) separately with doping concentrations at weight ratios of 2.5, 5.0, 7.5, and 10.0 wt.%. The mixtures were then stirred at room temperature for one day. After the solutions were well-mixed, the mixtures with various doping concentrations were injected into empty cells of glass substrates coated with indium tin oxide (ITO) electrodes. On the top of ITO, the surfaces were covered with rubbed polyimide alignment layer. The unidirectional aligned substrates were fabricated in antiparallel direction with cell gap 15 μm and in twisted 90° direction with cell gap 4 μm for the measurement of phase retardation and EO properties, respectively.

The normally-white TN NLC cells were set up for the EO measurement of voltage-transmittance (V-T) curve and response time characteristics with various PAH doping concentrations. NLC cells were placed between mutually perpendicular polarizer and analyzer. A square wave (1 kHz) with amplitude from 0 V to 8 V was applied to NLC cells by a function generator (DS360, Stanford Research System). A He-Ne laser ($\lambda = 632.8$ nm) provided the incident laser light which was directed into the NLC cells, and the transmitted light intensity was measured with a photodiode. The NLC cells were also observed by a polarizing optical microscope (POM) and its charge-coupled device (CCD) camera to verify whether there were local defects generated by the doped liquid materials in NLC mixtures. The flow viscosity was measured by rheometer (AR2000, TA instruments) with temperature from −5°C to 80°C. And the capacitances of NLC cells with antiparallel and vertical alignment were measured by LCR meter (4284A, Agilent), and the dielectric constant was derived from the capacitance normalized by the empty cell capacitance [14].

Results and Discussion

The POM images of NLC mixtures are shown in Figure 2. Figure 2(a) is the result of pure undoped NLCs and Figure 2(b)-(c) are the results of NLCs doped with toluene and 1-methylnaphthalene with various concentrations, respectively. Each set of pictures contains the bright states (voltage off) on the left side and dark states (voltage applied) on the right. From these pictures, there were no noticeable differences between the undoped NLCs and the PAH liquids doped NLCs. Only the mixture with 10 wt.% 1-methylnaphthalene presents a little weak dark state. Therefore, we did not proceed the following experiments at PAH liquids doping concentrations beyond 10 wt.%.

The V-T characteristics of various doping concentrations were measured and shown in Figure 3. The driving voltage (V_d) is defined as the voltage required to achieve 10% of the maximum transmittance. The driving voltage of undoped NLC was 2.46 V, and it decreased as PAH liquids doping concentration increased. Toluene doped NLCs exhibited a larger impact on the descending of the driving voltage, as shown in Figure 3(a). It was reduced by 18% to 2.02 V at 10 wt.% toluene doped in NLCs. The driving voltage of 1-methylnaphthlene doped NLCs (Figure 3(b)) was also reduced by 12% to 2.17 V at the concentration of 10 wt.%, roughly equal to the result of 5 wt.% toluene doped in NLCs. Figure 3(c) shows the measured driving voltages of PAH liquids doped NLCs with various doping concentrations.

The results of response time measurements were shown in Figure 4. Response time is defined as the addition of rise time and decay time. Rise time and decay time are evaluated as the time intervals required to reach 10% and 90% of the transmittance by the application and removal of voltage (8 V), respectively. Figure 4(a)-(b) show the performances of rise

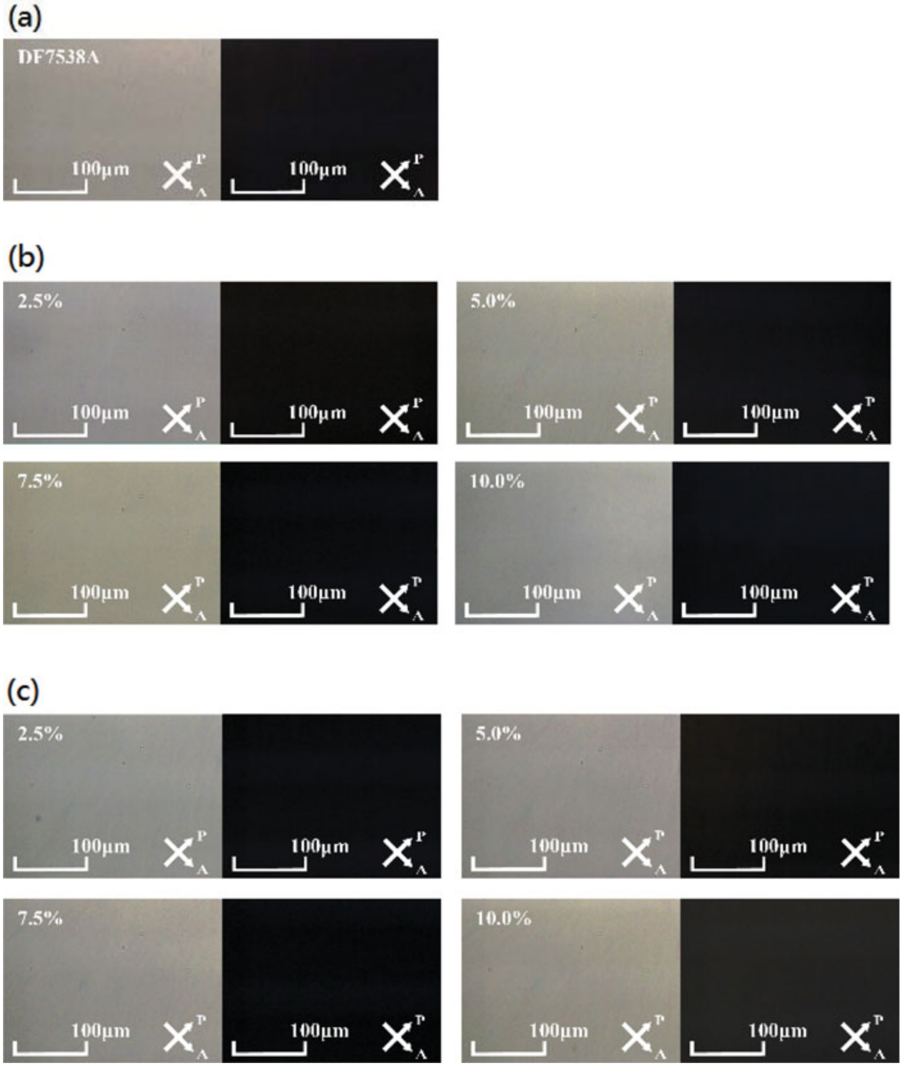

Figure 2. Polarizing optical microscopy (POM) pictures of (a) NLCs, (b) doping toluene, and (c) doping 1-methylnaphthalene. Doping concentrations are listed on the pictures. POM images show the bright states (voltage off) on the left side and dark states (voltage applied) on the right side for each group of pictures. A and P show the directions of analyzer and polarizer.

time and decay time of NLCs doped with toluene and 1-methylnaphthalene, respectively. Rise time was decreased with doping toluene into NLCs, but showed no dependence on the doping concentrations. The 1-methylnaphthalene, on the other hand, had no affects on reducing the rise time. However, both toluene and 1-methylnaphthalene dopings were capable to reduce the decay time of NLCs, and the decay times were decreased when the doping concentrations increased. According to the equations of response time [15],

$$T_{rise} = \frac{\gamma_1 d^2}{K_{11}\pi^2 \left|V^2 - V_d^2\right|} \tag{1}$$

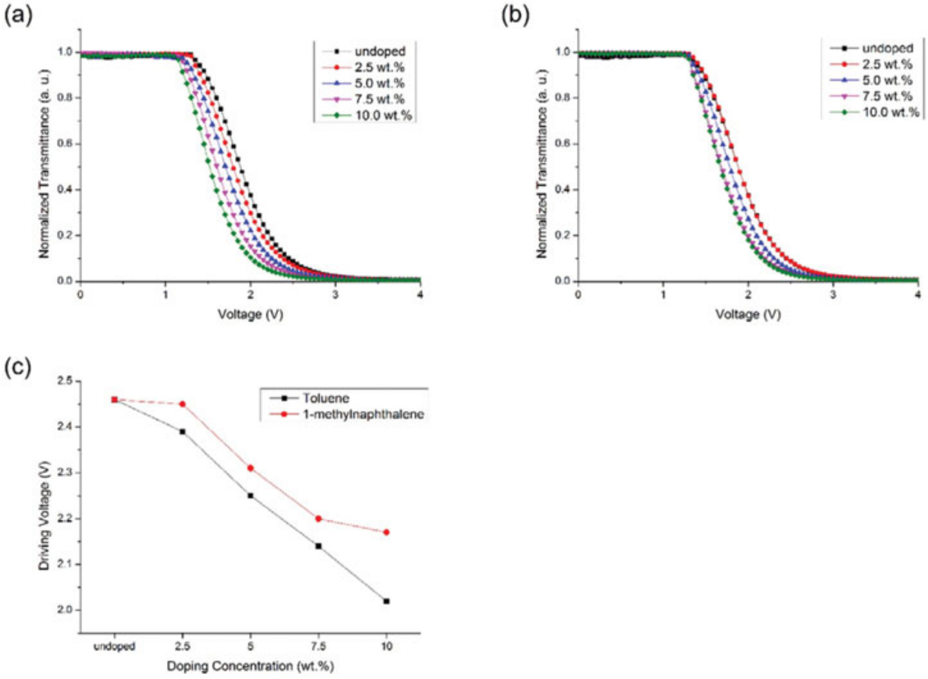

Figure 3. Voltage-transmittance curves with various doping concentrations of (a) toluene and (b) 1-methylnaphthalene. (c) The change of driving voltages with various doping concentrations of toluene and 1-methylnaphthalene dopants.

$$T_{decay} = \frac{\gamma_1 d^2}{K_{11}\pi^2} \tag{2}$$

where γ_1 is the rotational viscosity, K_{11} is the splay elastic coefficient, and d is the cell gap, rise time is inversely proportional to the square of applied voltage. Therefore, toluene decreased the rise time of NLCs, but the concentration dependence was suppressed by the stronger influence of applied voltage. On the contrary, since the decay time was measured after the applied voltage was turned off, the concentration dependence comes out obviously without the voltage influence. As the result shown in Figure 4(c), the response time (rise time + decay time) of NLCs was ultimately decreased by 18% and 15% from 22.8 ms to 18.6 ms and 19.4 ms by doping 10 wt.% toluene and 1-methylnaphthalene, respectively.

Within all the parameters that influence the response time and driving voltage, viscosity (γ_1) and elastic constant (K_{11}) are significant intrinsic parameters of NLCs. Viscosity is proportional to response time and the driving voltage while the elastic constant is inversely proportional to them, so reducing the viscosity or raising the elastic constant are effective to improve the EO properties of NLCs. In some previous studies, the nanoparticles tended to enlarge the elastic constant by raising the dielectric anisotropy ($\Delta\varepsilon$) of NLCs [7]. Although the viscosity of NLCs might increase slightly, the visco-elastic coefficient (γ_1/K_{11}) was decreased. Therefore, the slight increase of viscosity could be negligible to treat it as a constant during doping nanoparticles. In our work, we consider viscosity should be the main reason to improve the EO properties of NLCs since toluene and 1-methylnaphthalene

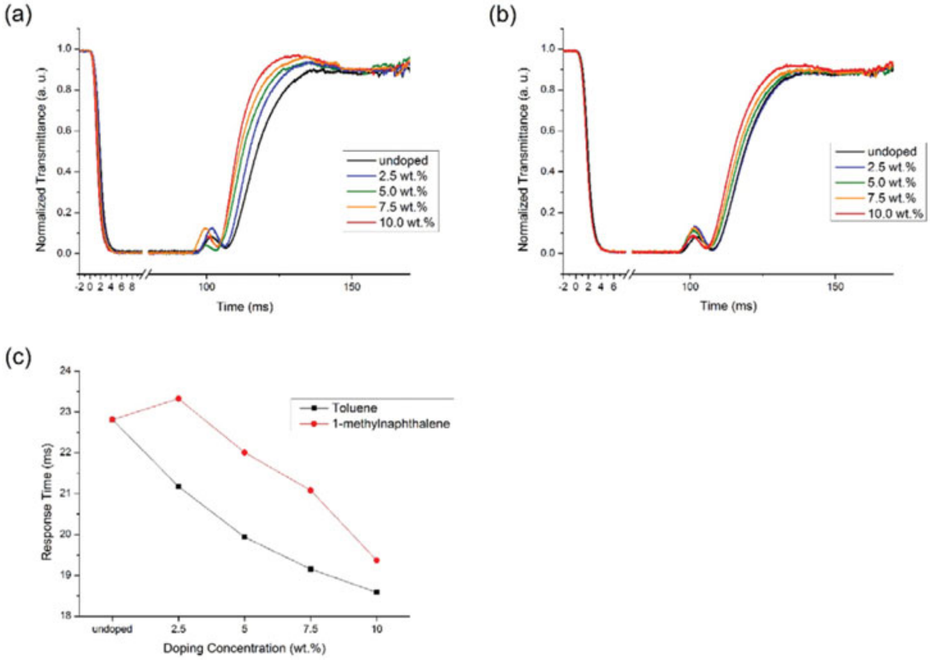

Figure 4. (a) & (b) The performances of rise time and decay time of doping toluene and 1-methylnaphthalene into NLCs, respectively. (c) The change of response times with various doping concentrations of toluene and 1-methylnaphthalene dopants.

are both extremely low-viscosity materials compared with NLCs. As long as the variation of dielectric anisotropy or elastic constant (K_{11}) is smaller than that of viscosity, the visco-elastic coefficient will definitely decrease and improve the EO properties of NLCs as we observed [16, 17].

The viscosity parameter of LCs can be separated to flow viscosity and rotational viscosity. For the rotational motion of LCs under electric fields, rotational viscosity gives more influence than flow viscosity. Several experimental methods had been developed to measure the rotational viscosity [18–23], and we used the phase decay time measurement [21] to obtain the rotational viscosity as well as some other useful parameters of NLC mixtures. In this study, antiparallel aligned cells were used to measure the phase retardation and the birefringence. A small bias voltage (V_b), which was usually chosen at the first maximum or minimum transmittance occurred in the phase retardation figure, was then applied to cells so that the LC directors were deformed by a small angle. After the bias voltage was cut off, the intensity of transmittance I (t) and the phase decay time δ (t) can be expressed as [21]

$$\delta\,(\mathrm{t}) = \delta_0 \exp\left(-\frac{2t}{\tau_0}\right) \tag{3}$$

$$\mathrm{I}\,(\mathrm{t}) = I_0 sin^2\left(\frac{\Delta_{tot} - \delta\,(t)}{2}\right) \tag{4}$$

Table 1. The significant measured parameters for rotational viscosity

		Doping toluene (wt.%)				Doping 1-methylnaphthalene (wt.%)			
	NLCs	2.5	5.0	7.5	10.0	2.5	5.0	7.5	10.0
Δn	0.092	0.088	0.083	0.080	0.078	0.091	0.090	0.089	0.086
τ_0 (ms)	588.24	506.33	377.36	330.58	303.03	506.33	487.80	481.93	476.19
$\Delta\varepsilon$	7.22	6.82	6.67	6.51	6.45	6.98	6.63	6.38	6.03

where δ_0 represents the initial relative phase retardation; I_0 is the initial transmittance at t = 0; Δ_{tot} and τ_0 are the total phase retardation and the phase relaxation time, respectively. τ_0 is determined from the slope of the curve of $\ln(\frac{\delta(t)}{\delta_0})$ versus time t.

The relevant parameters are listed in Table 1. From the total phase retardation, birefringence (Δn) was derived for $\lambda = 632.8$ nm. Due to the PAH liquids doping, it had some disturbs to decrease the order parameter of NLCs. Therefore, the birefringence, which is proportional to order parameter [24], slightly decreased with the increasing of doping concentrations. However, the decrease of order parameter caused by PAH liquids doping did not have negative impact to NLCs, but lowered the phase relaxation time. The decrease of the phase relaxation time implies that PAH liquids doped NLCs need less time to return the original phase compared with undoped NLCs.

After the derivation of τ_0, the following equations express the rotational viscosity:

$$\gamma_1 = \frac{\tau_0 K_{11} \pi^2}{d^2} \tag{5}$$

$$K_{11} = \left(\frac{V_{th}}{\pi}\right)^2 \Delta\varepsilon\varepsilon_0 \tag{6}$$

V_{th} is the Fréedericksz threshold voltage, which was determined from the phase retardation curve, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ is the dielectric anisotropy, and the other parameters are the same as previous equations.

$\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ were measured from the normalized capacitance of vertical and antiparallel aligned NLC cells, respectively. As listed in Table 1, both doping toluene and 1-methylnaphthalene slightly decreased their dielectric anisotropy, so the relevant elastic constants were also decreased in a small amount. However, the rotational viscosity of NLCs (Figure 5) decreased to nearly half of its maximum when 10 wt.% PAH liquids were doped. Therefore, the visco-elastic coefficient (Figure 6) also decreased with the rise of doping concentrations, and it explains the improvement of EO properties of NLCs doped with PAH liquids. Moreover, the Equation (5) shows that the visco-elastic coefficient is just proportional to the phase relaxation time (τ_0), so the descending of τ_0 already implies the higher response speed of NLCs. From the above derivations and calculations, we unambiguously proved the viscosity was the main role to decrease the visco-elastic coefficient in this study.

Through the series of measurements and calculations, we concluded that doping PAH liquids into NLCs was effective to decrease the viscosity of NLCs, and this improvement made the driving voltage and response time lower and faster with no local defects observed in POM pictures.

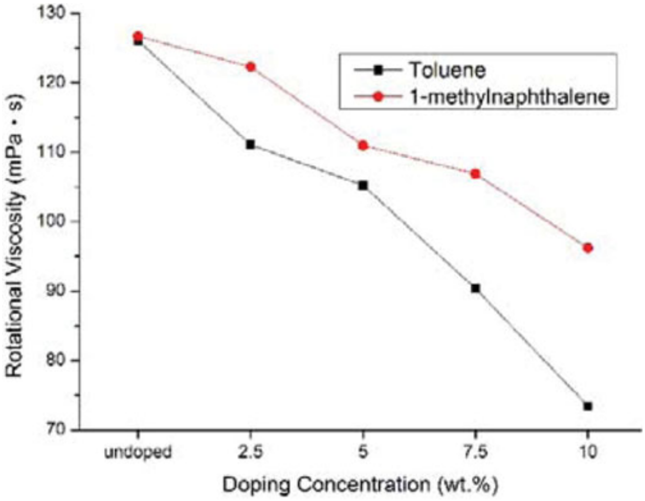

Figure 5. The rotational viscosity of NLCs with different doping concentrations.

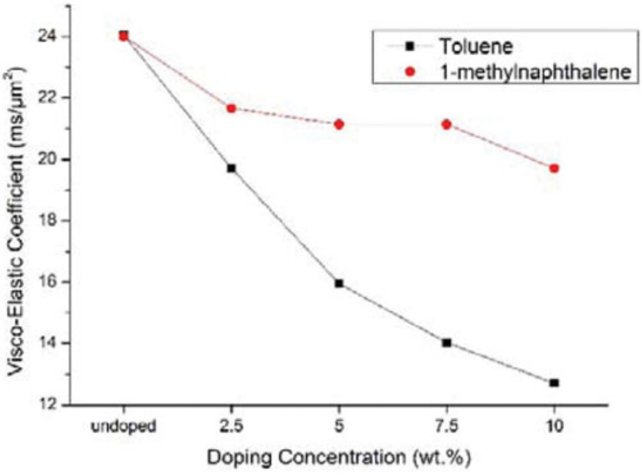

Figure 6. The visco-elastic coefficient of NLCs with different doping concentrations.

Conclusion

In this study, we present a simple and efficient way to improve the performance of the TN LC device by doping LCs with a small amount of PAH liquids. The electro-optical properties of TN device can be optimized by adjusting the PAH doping concentrations. When doping concentrations were increased, the PAH liquids doped NLCs exhibited the lower driving voltage and faster response time. We found that the main reason of this phenomenon is due to the low viscosity of PAH liquids which lowers the viscosity of NLC mixtures. In this work, our results demonstrate a new feasible choice of doping liquid materials into NLCs, especially the variety of liquids is much wider than nanoparticles. To sum up, without the drawbacks that doping solid nanoparticles could have, the PAH liquid doping method provides a more promising opportunity for applications not only in various LC display systems but also other fields in similar aspect in the future.

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