

This article was downloaded by: [Tomsk State University of Control Systems and Radio]

On: 21 February 2013, At: 10:50

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954

Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

Relation Between TN-Cell Response Time and Transition Temperatures Liquid Crystal Materials

Akio Mukoh^a, Hidetoshi Abe^a, Teruo Kitamura^a,
Norimasa Kamezawa^a & Mikio Satoh^a

^a Hitachi Research Laboratory Hitachi, Ltd., Hitachi, Ibraki, 319-12, Japan

Version of record first published: 21 Mar 2007.

To cite this article: Akio Mukoh, Hidetoshi Abe, Teruo Kitamura, Norimasa Kamezawa & Mikio Satoh (1983): Relation Between TN-Cell Response Time and Transition Temperatures Liquid Crystal Materials, *Molecular Crystals and Liquid Crystals*, 94:1-2, 155-165

To link to this article: <http://dx.doi.org/10.1080/00268948308084254>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to

date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Relation Between TN-Cell Response Time and Transition Temperatures of Liquid Crystal Materials

AKIO MUKOH, HIDETOSHI ABE, TERUO KITAMURA,
NORIMASA KAMEZAWA and MIKIO SATOH

Hitachi Research Laboratory, Hitachi, Ltd., Hitachi, Ibaraki 319–12, Japan

(Received September 16, 1982)

The relation between the transition temperature of typical nematic liquid crystal mixtures and the dynamic properties of twisted nematic (TN) cells are presented. The extrapolated response time at nematic-isotropic transition temperature is of use as a relative response time in the comparison of liquid crystal materials with each other. The glass transition temperature of liquid crystal mixtures is one of the best indicators of the dynamic properties of TN-cells. The linear relation between the reciprocal ΔT_g and the logarithm of the reciprocal response time led us to believe that we could improve the response time of TN-cells by producing liquid crystal materials with lower T_g 's. We assumed that the lower limit for the response time of TN-cells at 25°C is about 10–20 ms from the above relation.

INTRODUCTION

Twisted nematic (TN) liquid crystals have been used as displays for wrist watches and electronic calculators, and improved TN-liquid crystals are beginning to be used as displays for information systems and automobiles. Before such liquid crystals can be used more widely, however, their response time must be shortened considerably. Accordingly, many research groups are conducting physicochemical investigations to isolate new parameters that might be useful in the design of liquid crystal molecules with a short response time.

Jakeman and Raynes established the dependence of the response time of TN-cells on twist viscosity.¹ This viscosity is approximated by the bulk viscosity² which can be rather easily measured. Consequently, we decided to attempt to estimate the bulk viscosity of the nematic phase from the

chemical structure of liquid crystal compounds,³ using the evaporation energies observed by Eyring *et al.*,⁴ but this method of estimating the bulk viscosity is not adequate for molecular design of chemical structures with a low viscosity. If the glass transition temperature is known, it can be used in the design of a chemical structure with a low viscosity, because glass transition temperature is well known as a temperature with a strong correlation to the viscosity in macromolecular chemistry.⁵ Furthermore, much information about the relation between glass transition temperature and chemical structure can be found in macromolecules.⁶

In this paper, a study of the relation between the transition temperature, especially glass transition temperature of liquid crystal mixtures and the response time of TN-cells is presented. The discovery of new parameters for the dynamic properties of TN liquid crystals and the use of these parameters in the design of molecules for liquid crystals with a short response time is also described.

THEORY OF ELECTRO-OPTICAL RESPONSE

A theoretical equation for the turn on (T_{on}) and turn-off (T_{off}) times of TN-cells has been given by Jakeman and Raynes as follow:¹

$$T_{\text{on}} = \frac{\eta d^2}{\Delta \epsilon E - K \pi^2} \quad (1)$$

$$T_{\text{off}} = \frac{\eta d^2}{K \pi^2} \quad (2)$$

Where $K = K_{11} + (K_{33} - 2K_{22})/4$, K_{11} , K_{22} and K_{33} are the splay-, twist- and bend elastic constants, $\Delta \epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$, ϵ_{\parallel} and ϵ_{\perp} are dielectric permittivities parallel and perpendicular to the director, η is the twist viscosity, E is the electric field, and d is the thickness of the liquid crystal layer.

According to our experiments, the influence that ηd^2 exerts on T_{off} is less than the influence that it exerts on the T_{on} . Because the theoretical value for the thickness of the liquid crystal layer in Eq. (2) is d^2 , but the actual value was found to be d .^{1,6} Therefore, when we calculate the standard response time at $d = 10 \mu\text{m}$, we use the corrected value for thickness d ,^{1,6} as shown in Eq. (3)

$$T_{\text{off}} = \frac{\eta d^{1.6}}{K \pi^2} \quad (3)$$

EXPERIMENTAL

Experiments were carried out with various liquid crystal mixtures which consisted of from two to seven components. Table I lists the liquid crystal mixtures, their transition temperatures, and the temperature ranges that response times were measured in.

SB-2, ES-4 and PPY-5 are from Hoffman-La Roche (TN-200, TN-101 and TN-403); BP-4 is from British Drug House (E-7); and PCH-3, PCH-4, and PCH-6 are from E. MERCK (ZLI-1083, ZLI-1132 and ZLI-1565). AZ-5 is prepared by adding 5% by weight of 4-cyanophenyl 4-*n*-butylbenzoates to an azoxy mixture from E. MERCK (NP-5). The ratio of components in the remaining mixtures is equivalent. The code numbers indicate the number of components in the liquid crystal mixtures.

The glass transition temperature (T_g) and phase transition temperature, for example, the crystal-nematic phase transition temperature (T_{CN}) and the nematic-isotropic phase transition temperature (T_{NI}), are measured in a differential thermal analysis, as shown in Figure 1. After heating to the isotropic phase, samples were cooled with liquid N_2 , and then differential thermal analysis was measured at a rate of about $1^\circ\text{C}/\text{min}$.

Experimental liquid crystal cells were made of two glass plates, each of which had a thin, transparent, electrically conductive layer. Glass beads of $10\ \mu\text{m}$ in diameter were used as a gap control between the two glass plates and epoxy adhesives were used as peripheral sealants. The inner surface of the plates to which the polyimide thin film was applied were treated by rubbing. The gap was measured before the cell was filled with a liquid crystal material.

Electro-optical measurements were carried out with the apparatus shown in Figure 2. An alternating square wave voltage (1 kHz) was applied to the liquid crystal cell.

In this paper, T_{on} and T_{off} are defined as shown in Figure 3. T_{on} is defined here as the time required for transmission to reach 90% after the driving voltage (V_o) is turned on, whereas T_{off} is the time required for the transmission to reach 10% after the V_o is turned off, as shown in Figure 3. Ordinarily, a V_o that is twice the threshold voltage (V_{th}) is applied to each cell.

RESULTS AND DISCUSSION

Temperature dependence of dynamic properties of TN-cells

The results obtained in the experiments are shown in Figures 4 to 6. The response times for all the liquid crystal mixtures shown in Table I are

TABLE I
Transition temperature of liquid crystal mixtures

Structure of main components	Code	Transition temperature $T_g/^\circ\text{C}$	$T_{\text{CN}}/^\circ\text{C}$	$T_{\text{NI}}/^\circ\text{C}$	$T_o - T_g$ $\Delta T_g/^\circ\text{C}$	$T_o - T_{\text{CN}}$ $\Delta T_{\text{CN}}/^\circ\text{C}$	$T_o - T_{\text{NI}}$ $\Delta T_{\text{NI}}/^\circ\text{C}$
	SB-2	-61.5	6	63.5	71.5 ~ 101.5	-6 ~ 34	-23.5 ~ -63.5
	AZ-5	-74.5	-13	70	74.5 ~ 134.5	13 ~ 73	-10 ~ -70
	ES-2	-54	37	60	54 ~ 94	-37 ~ 3	-20 ~ -60
	ES-4	-54	16	70	54 ~ 94	-16 ~ 24	-30 ~ -70
	ECH-7	-66	0	60	66 ~ 106	0 ~ 40	-20 ~ -60
	BP-2	-71	1	39	71 ~ 111	-1 ~ 39	-1 ~ -39
	BP-4	-67	-1	60.5	67 ~ 107	1 ~ 41	-20.5 ~ -60.5
	PPY-5	-59	9	82	59 ~ 99	-9 ~ 40	-42 ~ -82
	PCH-2	-74	-4	54	74 ~ 114	-4 ~ 36	-14 ~ -54
	PCH-3	-70	-5	51	70 ~ 110	5 ~ 45	-11 ~ -51
	PCH-4	-69	-4	71.5	69 ~ 109	4 ~ 44	-31.5 ~ -71.5
	PCH-6	-82	-21	87	54 ~ 122	-7 ~ 61	-47 ~ -115

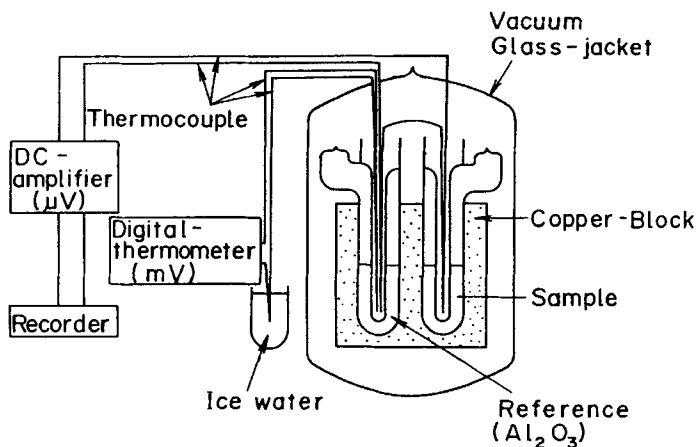


FIGURE 1 Apparatus used in thermal analysis.

plotted as a function of ΔT_{NI} , ΔT_{CN} and ΔT_g without regard to material type or the number of components. Where $\Delta T_{NI} = T_o - T_{NI}$, $\Delta T_{CN} = T_o - T_{CN}$ and $\Delta T_g = T_o - T_g$, and T_o is the temperature at which the response time of TN-cells was measured.

Figures 4 to 6 show the tendency of the relation between response time and the reference temperature in the T_{NI} , T_{CN} , T_g sequence. It is clear from the figures that response time is more correlative to ΔT_g than ΔT_{NI} and ΔT_{CN} . The relation between response time and ΔT_g is independent of material type and the number of components in a mixture. The patterns observed for T_{on} and T_{off} in the above case are quite similar to each other. However, the chemical structures of the liquid crystal materials can be

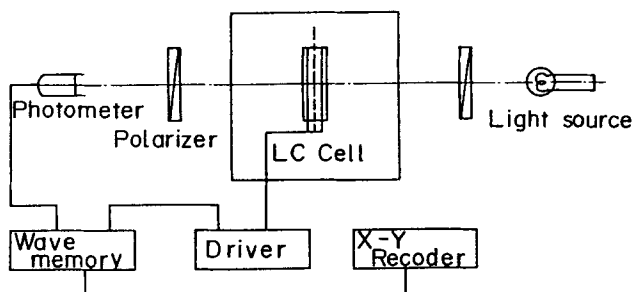


FIGURE 2 Block diagram of apparatus used to measure the response characteristics of liquid crystals.

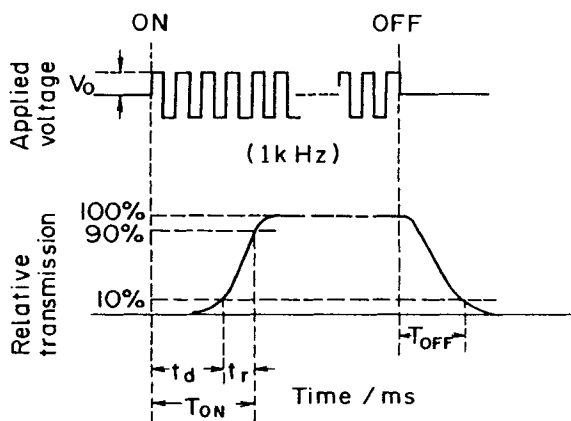


FIGURE 3 Definition of response time.

divided into two types, A and B. Type A (○) has direct bonds between its ring systems and Type B (●) has central bond groups as azomethine, azoxy and ester groups between its ring systems.

Consequently, the relation between T_g and response time depends on the chemical structure of the liquid crystal materials.

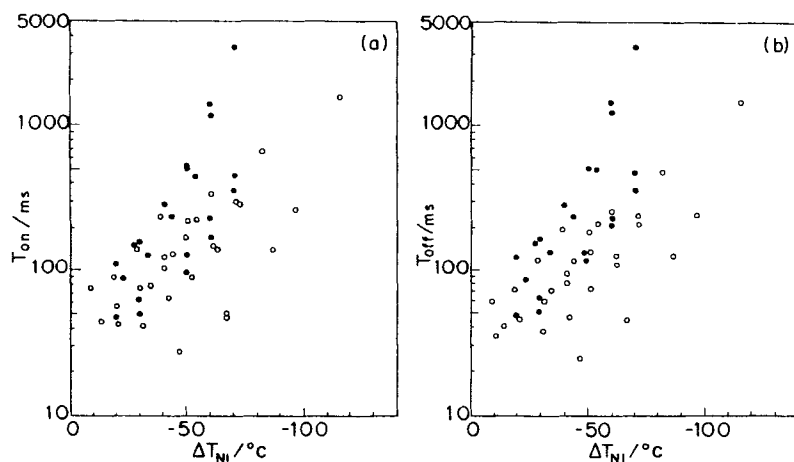


FIGURE 4 (a) T_{on} and (b) T_{off} for liquid crystal mixture is plotted as a function of ΔT_{NI} . ○ and ● represent chemical structure, and ○ (Type A) has direct bonds and ● (Type B) has central bond groups between its ring systems.

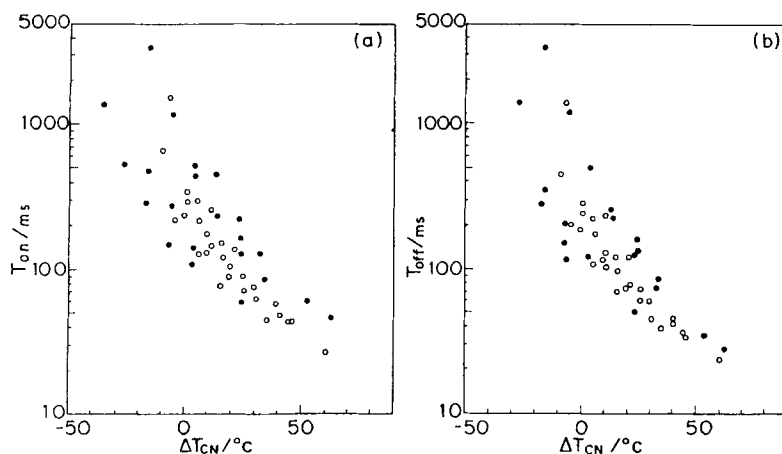


FIGURE 5 (a) T_{on} and (b) T_{off} for liquid crystal mixture is plotted as a function of ΔT_{CN} . \circ and \bullet represent chemical structure, and \circ (Type A) has direct bonds and \bullet (Type B) has central bond groups between its ring systems.

Extrapolated dynamic properties at T_{NI}

Obviously the relation between the dynamic properties of TN-cells and ΔT_{NI} in Figure 4 is not recognized, but it becomes clear when the response time for each liquid crystal mixture is plotted as a function of ΔT_{NI} , as

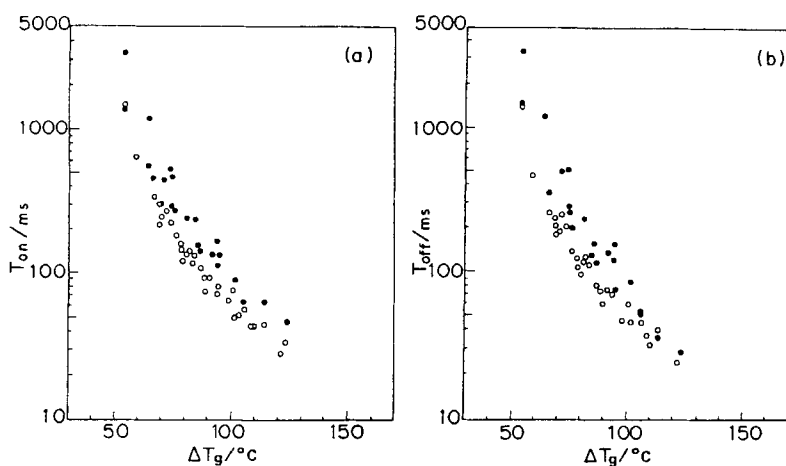


FIGURE 6 (a) T_{on} and (b) T_{off} for liquid crystal mixture is plotted as a function of ΔT_g . \circ and \bullet represent chemical structure, and \circ (Type A) has direct bonds and \bullet (Type B) has central bond groups between its ring systems.

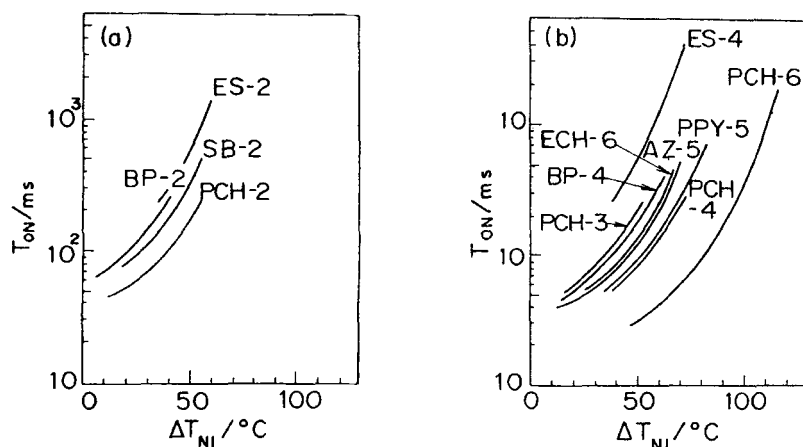


FIGURE 7 T_{on} of liquid crystal mixtures with (a) two components and (b) more than two components as a function of ΔT_{NI} .

shown in Figure 7. In the figure, note that none of the curves intersect over the wide temperature range of 10°C – 120°C . Therefore, the extrapolated response time at T_{NI} can be used as the relative response time for nematic liquid crystal materials in comparisons of liquid crystal mixtures. Only T_{on} is shown, because T_{off} is quite similar to T_{on} .

Relation between ΔTg^{-1} and reciprocal response time

The temperature dependence of the dynamic properties of TN-cells shown in Figure 6 can be rewritten in terms of ΔTg^{-1} and reciprocal response time, as shown in Figure 8. This relation is rewritten for Type A chemical structures in Figure 6(a) and 6(b). A good linear relation is obtained between the ΔTg^{-1} and the logarithm of the reciprocal response time. This linear relation can also be seen in cases of another voltage applied, shown in Figure 9. Furthermore, if T_{on} is divided into two components; that is, delay time (t_d) and rise time (t_r), as shown in Figure 3. These can also be obtained from the above linear relation, as shown in Figure 10.

These results demonstrate that the parameter represents the temperature at which the dynamic properties of TN-cells become manifest. Furthermore, when the Tg of liquid crystal mixtures can be obtained, the temperature dependence of the dynamic properties of TN-cells can be determined over a relatively wide temperature range, using Figures 8 to 10. The most important result of this work is the discovery that it is possible to develop liquid crystal mixtures with a short response time by searching for liquid crystal materials with Tg 's that are lower than those for known materials.

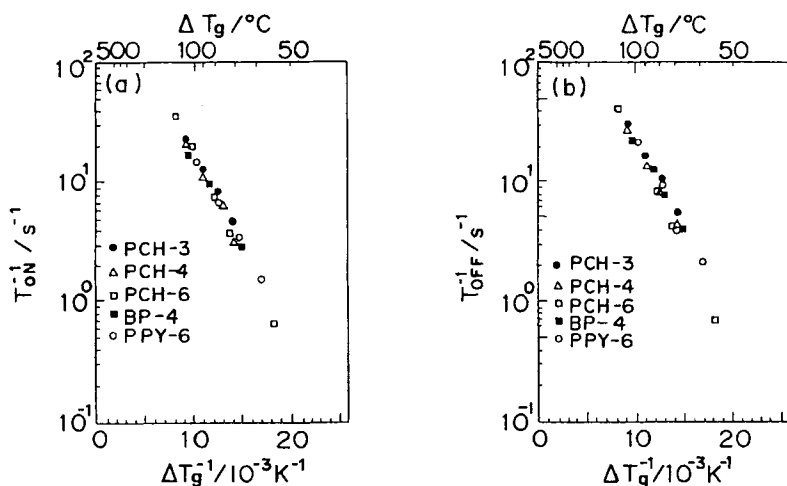


FIGURE 8 Relation between reciprocal of (a) T_{on} and (b) T_{off} , and ΔT_g^{-1} .

Limitation of response time of TN-cells

It is of interest to be able to estimate the limits of the response time of TN-cells. If the T_g of a liquid crystal mixture is considered the sum of the T_g 's for the liquid crystal materials in the mixture in molar or volume ratio, the limits of the response time of TN-cells can be estimated from Figures 8 to 10.

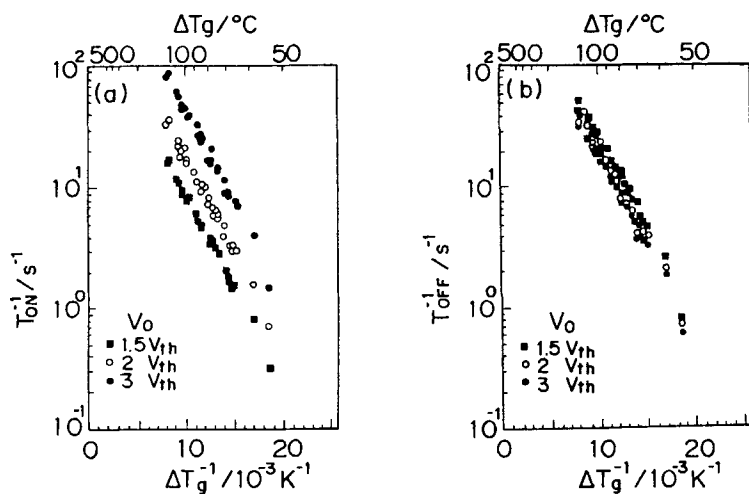


FIGURE 9 Dependence of applied voltage on (a) $T_{on}^{-1} \sim \Delta T_g^{-1}$ and (b) $T_{off}^{-1} \sim \Delta T_g^{-1}$ characteristics.

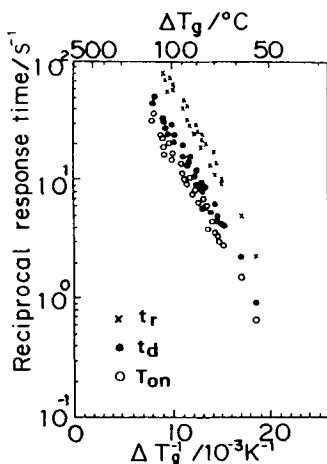


FIGURE 10 Relation between reciprocal response time and ΔT_g^{-1} .

Generally, it is difficult to measure the T_g of a single material. But, Seki, Suga and Sorai have succeeded in measuring the T_g 's of water,⁷ ethyl alcohol⁸ and azo methine type nematic liquid crystals.⁹ Their T_g 's were 135 K, 90 K and 204 K, respectively. Furthermore, the T_g 's of a typical nematic liquid crystal mixture are without exception above 190 K, as shown in Table I.

These results indicate that one of the limits of the T_g of nematic liquid crystals is about 150 K. Consequently, a response time of about 20 ms for TN-cells ($d = 10 \mu\text{m}$) at 25°C can be obtained from $T_g = 150$ K, using the relation in Figure 8. When a V_o of $2V_{th}$ is applied to a liquid crystal layer the values for T_{on} and T_{off} became nearly the same. These results indicate that it is not now possible to achieve a response time below 10 ms at 25°C with TN display devices.

CONCLUSIONS

We have attempted to clarify the relation between the transition temperature of typical nematic liquid crystal mixtures and the dynamic properties of TN-cells. We found that the extrapolated response time at T_{NI} can be used as a standard response time in comparisons of liquid crystal materials with each other. We also found that the T_g of liquid crystal mixtures is one of the most useful parameters indicating the dynamic properties of TN-cells.

The linear relation that holds between the reciprocal ΔTg and the logarithm of the reciprocal response time indicated to us that TN-cells with a shorter response time could be obtained by searching for liquid crystal materials with a Tg lower than that of known materials.

The results presented in this paper demonstrate that Tg is one of the most important indicators of molecular behavior, not only in macromolecules, but also in liquid crystal molecules. It seems that the correlation between the response time of TN-cells, and the viscosities of nematic liquid crystal materials, and the Tg 's of those materials can be understood with the well known WLF (Williams-Landel-Ferry)¹⁰ equation. Investigation that attempts to prove the validity of this assumption is the subject of future publications.

Acknowledgments

The authors wish to thank Prof. S. Seki of Kwansei Gakuin University, and Prof. H. Suga and Dr. M. Sorai of Osaka University for simulated discussions on the transition temperature of liquid crystals.

References

1. E. Jakeman and E. R. Raynes, *Phys. Lett.*, **39A**, 69 (1972).
2. M. Schadt and F. Muller, *IEEE Transactions on Electron Devices*, **ED-25**, 1125 (1978).
3. T. Watanabe, R. Sudoh, and A. Mukoh, *Mol. Cryst. Liq. Cryst.*, in contribution.
4. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill Book Company, New York and London, 1941.
5. M. L. Williams, *J. Appl. Phys.*, **29**, 1395 (1958).
6. R. F. Boyer, *Rubber Chem. & Technol.*, **36**, 1303 (1963).
7. M. Sugisaki, H. Suga, and S. Seki, *Bull. Chem. Soc. Japan*, **41**, 2591 (1968).
8. H. Haida, H. Suga, and S. Seki, *Proc. Japan Acad.*, **48**, 683 (1972).
9. M. Sorai and S. Seki, *Bull. Chem. Soc. Japan*, **44**, 2887 (1971).
10. J. D. Ferry, *Viscoelastic Properties of Polymer*, Wiley, New York, 1961, Ch. 11.