Elastic Properties of Liquid Crystalline Mixtures in Relation to Their Molecular Composition

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The ratios of the bend and splay elastic constants k_{33}/k_{11} as a function of the reduced temperature $t_r = T[K]/T_{N-1}[K]$ are reported for binary mixtures of different liquid crystalline classes. A distinct change in k_{33}/k_{11} between the various classes has been observed. The elastic constants of 4-n-alkylphenyl 4-n-alkanoyloxybenzoates, comprising one of these binary mixtures, are influenced considerably by adding appropriate liquid crystal compounds. Absolute values of k_{33}/k_{11} down to 0.64 at low reduced temperatures have been obtained. It is shown that the significant lowering in k_{33}/k_{11} is due to an interaction between a terminal CN—group of the added liquid crystal and the ester mixture. However, alkyl chain length, conjugation, and overall molecular length of the additive play a minor role. For certain mixing ratios of the esters with components containing terminal polar groups, an induced smectic phase is observed.

INTRODUCTION

The information content which can be shown by a twisted nematic liquid crystal matrix display (TN—LCD) depends on its multiplexing level. One restriction on the maximum number of multiplexable lines in a TN—LCD is the steepness of the electro-optical response. The influence of cell and material parameters on the electro-optical response has been investigated in several numerical calculations based on different models.[1-6] From these calculations we know that improvements in the multiplexing capability require among other things thin cells, a low pre-tilt, a low birefringence, and a high threshold voltage. Above all, not the absolute values of the elastic constants, but their ratios are of importance. Both the ratio of bend and splay elastic constants k_{33}/k_{11} and the ratio of twist and splay elastic constants k_{22}/k_{11} should be as

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†Presented at the Eighth International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

low as possible. The main influence on the steepness of the transmission characteristic results from the ratio k_{33}/k_{11}.

It is possible to match most of the material and cell parameters to the theoretically calculated optimum, but it is still difficult in the case of the elastic constants. In order to influence the elasticity of single components, the relationship between molecular structure and elastic properties should be known. For multi-component mixtures, as required for industrial use, the situation is even more complicated, because their elastic behavior is governed in addition by the interaction of the different liquid crystal compounds. Only a few systematic studies of this problem have been made: some measurements on homologous series,[7-12] a first step towards correlating elasticity with molecular dimensions,[9,12,13] and measurements on various classes of liquid crystals.[14]

In this paper we shall present data on binary mixtures of various liquid crystalline classes. The main purpose of our paper is to show one possible way of influencing the elasticity of one of these binary mixtures, the ester system NP 1008, by adding appropriate liquid crystals. First of all we have investigated ternary mixtures of NP 1008 with 7.5% by weight of additive, altering either the alkyl chain length, the cyclic systems, the terminal polarity, or the overall molecular length of the added liquid crystal. Subsequent to these experiments, we have carried out measurements on mixtures of NP 1008 containing different proportions of 4-n-octyl-4'-cyanobiphenyl (CB 8) or 1-n-octyl-4-(4'-cyanophenyl) cyclohexane (PCH 8). Furthermore we report data on a mixture of NP 1008 with two different additives at the same time.

EXPERIMENTAL

All measurements have been done with a guard-ring cell and homogeneous planar surface orientation. The planar orientation was obtained by oblique evaporation of SiO at an angle of about 50° to the normal to the glass and has been checked for each cell by a magnetic null method. Cell thickness d has been determined interferometrically to ±0.2% and is typically 50 μm. The optical phase difference δ between the ordinary and extraordinary light ray is recorded as a function of a deforming magnetic field H which is carefully adjusted perpendicular to the director of the undistorted layer. For reasons of comparison and in order to obtain the absolute values of the splay and bend elastic constants an electric field V/d instead of a magnetic field has been used. To get quasi-static conditions, the change in the magnetic field (electric field) near the Fréedericksz threshold is chosen to be not greater than 8 0e/min (3 mV/min). The field strengths are determined to ±0.5%. From a non-linear least squares fit of the whole deformation curve, we obtain the ratio of the elastic constants k_{33}/k_{11} as defined by Frank.[15] It is shown in previous papers,[16,17] that fitting the optical path difference δ to

$$1 - \delta(f_r)/\delta(0) = \frac{n_e}{n_e - n_0} \left(1 - \frac{\int_0^{\pi/2} (F_\kappa F_\gamma/F_{-1}F_\nu)^{1/2} \, d\psi}{\int_0^{\pi/2} (F_\kappa F_\gamma/F_{-1})^{1/2} \, d\psi} \right) \qquad (1)$$

is the only adequate way to determine k_{33}/k_{11} from the described experimental arrangement. In Eq. (1)

$$f_r = \begin{cases} H/H_c - 1 \text{ with } H_c = \pi/d \cdot \left(\dfrac{k_{11}}{\mu_0 \Delta\chi} \right)^{1/2} \\[3mm] V/V_c - 1 \text{ with } V_c = \pi \cdot \left(\dfrac{k_{11}}{\epsilon_0 \Delta\epsilon} \right)^{1/2} \end{cases} \qquad (2)$$

$\mu_0 = 4\pi \cdot 10^{-7} \text{ Hm}^{-1}$; $\epsilon_0 = 8.85 \cdot 10^{-12}$ Fm^{-1}

$\Delta\chi$ = diamagnetic anisotropy

$\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$; $\epsilon_\parallel$, $\epsilon_\perp$ = static dielectric constants

$\kappa = \dfrac{k_{33}}{k_{11}} - 1$

$\nu = \left(\dfrac{n_e}{n_0} \right)^2 - 1$; n_e, n_0 = refractive indices $\qquad (3)$

$\gamma = \begin{cases} 0 & \text{for magnetic deformation} \\[2mm] \epsilon_\parallel/\epsilon_\perp - 1 & \text{for electric deformation} \end{cases}$

with

$$F_x = 1 + x \cdot \sin^2\theta_m \cdot \sin^2\psi \qquad (x = -1, \kappa, \nu, \text{ or } \gamma) \qquad (4)$$

In the last equation θ_m is the tilt angle in the middle of the layer and is related to f_r by

$$f_r = -1 + \frac{2}{\pi} \cdot (1 + \gamma \sin^2\theta_m)^{1/2} \int_0^{\pi/2} \left(\frac{F_\kappa}{F_{-1}F_\gamma} \right)^{1/2} d\psi \qquad (5)$$

A modified version of Deuling's program[18] has been used for the fit procedure. Fit parameters are the threshold field H_c or the threshold voltage V_c, respectively, and κ. For magnetic field induced deformations we need n_e and n_0, which are determined by an Abbé-refractometer to an accuracy of $\pm 0.01\%$. For electric field induced deformations, we also have to measure $\epsilon_\parallel$ and $\epsilon_\perp$.
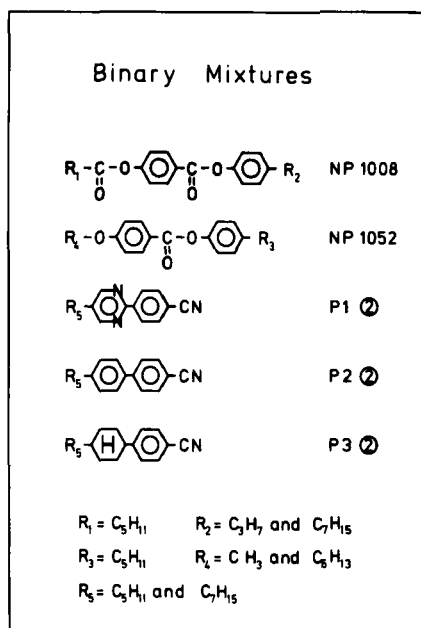
FIGURE 1   Chemical compositions of five binary mixtures.
NP 1008: propyl:heptyl = 55%:45% by weight (wt)
NP 1052: methyl:hexyl = 66.7%:33.3% wt
P1, P2, and P3: pentyl:heptyl = 40%:60% (molar proportions)

This has been done with a capacitance bridge (Gen. Radio 1621) to $\pm0.5\%$. Both magnetic and electric field induced deformations result in k_{33}/k_{11} values which coincide within experimental error. The error in k_{33}/k_{11} is estimated to $\pm1.5\%$, in k_{11} to $\pm1.5\%$, and in k_{33} to $\pm3\%$.

RESULTS AND DISCUSSION

Several measurements on homologous series have shown that the ratio k_{33}/k_{11} decreases with increasing alkyl chain length[8-12] and at this point it seemed to be worthwhile to have a look at various classes of liquid crystals. In order to obtain larger nematic phase ranges we have used binary mixtures whose chemical compositions are given in Figure 1. Besides the two ester systems—4-n-alkylphenyl 4-n-alkanoyloxybenzoates (NP 1008) and 4-n-alkylphenyl 4-n-alkyloxybenzoates (NP 1052), we have investigated a cyanophenylalkylpyrimidine-mixture (P1 ②), an alkylcyanobiphenyl-mixture (P2 ②), and a cyanophenylcyclohexane-mixture (P3 ②). A distinct change in k_{33}/k_{11} between the different classes could be observed, though the molecular dimensions of P1, P2, and P3 are almost identical. The highest
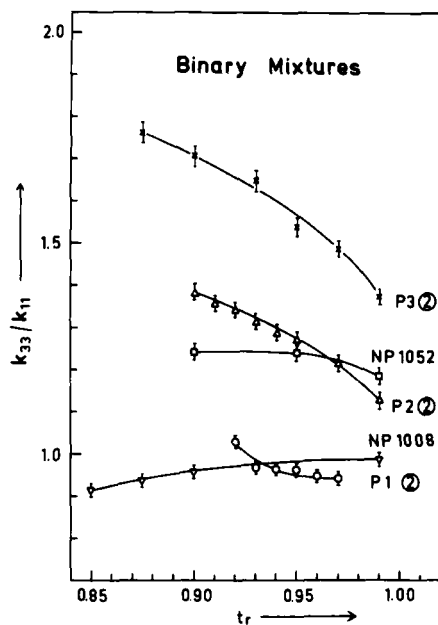
FIGURE 2   Ratio of the bend and splay elastic constants k_{33}/k_{11} of five binary mixtures as a function of the reduced temperature $t_r = T[K]/T_{N-I}[K]$.

values of k_{33}/k_{11} are found for the phenylcyclohexane and the lowest values of about 1.0 for the phenylpyrimidine and for the ester mixture NP 1008 (Figure 2).

In order to obtain a steeper electro-optical response, we have tried to lower the ratio k_{33}/k_{11} of the ester mixture NP 1008, firstly by adding several liquid crystalline compounds and secondly by studying different mixing ratios of NP 1008 and CB 8 or PCH 8, respectively. In the experiments with various additives NP 1008 always contains 7.5% by weight of dopant. This portion gives no induced smectic phase or at most only at low reduced temperatures.

The influence of the alkyl chain length of the added liquid crystal on the ratio k_{33}/k_{11} of NP 1008 is shown in Figure 3. We observe a decrease in the k_{33}/k_{11} values of the mixture in going from pentylcyanobiphenyl (CB 5) to octylcyanobiphenyl (CB 8) as dopant. For CB 9 there seems to be no further decrease, and for CB 10 even a slight increase. But in all cases the change in the ratio k_{33}/k_{11} of the mixture containing low or high homologues is rather small. Figure 2 and Figure 3 show in addition that a small temperature dependence of k_{33}/k_{11} results only for values of about one. For k_{33}/k_{11} ratios smaller than one, an increase, and for ratios greater than one, a decrease with increasing temperature could be observed. The influence of the polarizability of dopants with a terminal CN—group is shown in Figure 4. For a fixed alkyl
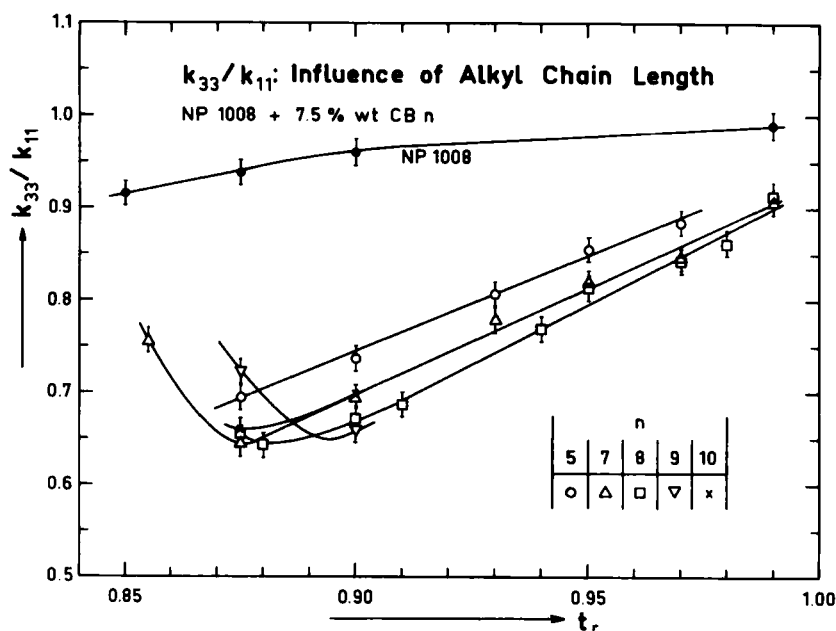
FIGURE 3   Ratio k_{33}/k_{11} versus t_r for NP 1008, and NP 1008 containing 7.5% wt CB n. Parameter n is the number of carbon atoms in the alkyl chain (n = 5, 7, 8, 9 or 10).
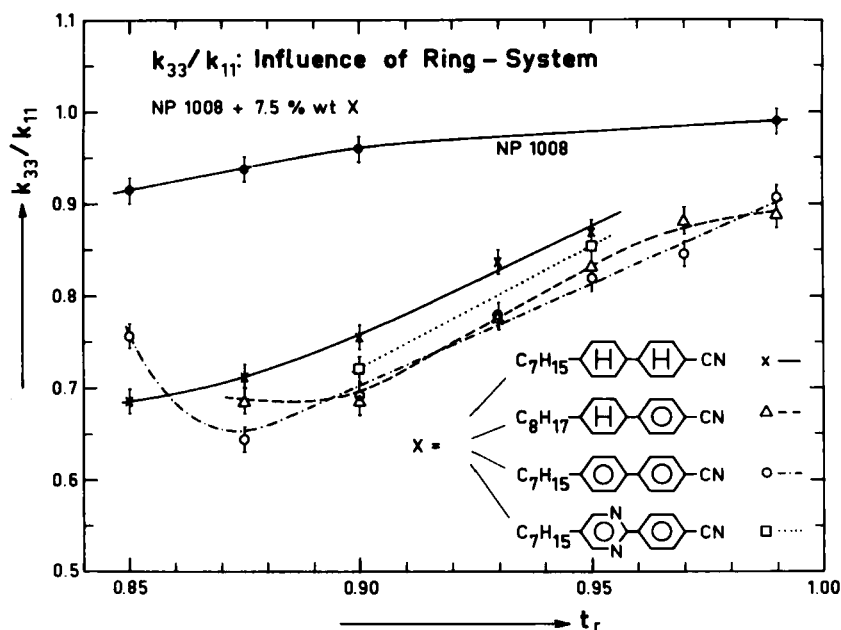

FIGURE 4   Ratio k_{33}/k_{11} versus t_r for NP 1008, and NP 1008 containing 7.5% wt cyano-heptyl(-octyl) component. Parameter X relates to the combination of cyclic systems.

chain length, we have studied four combinations of the cyclic systems: two cyclohexane-rings (CCH 7), a cyclohexane-ring and a benzene-ring (PCH 8), two benzene-rings (CB 7), and a benzene-ring with a pyrimidine-ring. Adding CCH 7 gives the highest k_{33}/k_{11} values of the mixture with NP 1008, adding PCH 8 and CB 7 the lowest values. But in all cases the change in k_{33}/k_{11} for different ring-systems is rather small.

Therefore we conclude that the observed significant lowering in the elastic constant ratio k_{33}/k_{11} of the ternary mixtures compared with that of pure NP 1008 results from an interaction between the CN—group of the terminal polar dopant and the ester mixture. The experimental proof is furnished in Figure 5. We have added alternatively two compounds which differ solely in the terminal CN—group. Only the mixture containing the CN—compound (BCH 5) shows significantly changed k_{33}/k_{11} ratios in comparison with pure NP 1008.

Another two mixtures confirm this result (Figure 6). Not the addition of a very long, four-ring molecule (CBC 56), but the addition of a terminal polar compound (5-[4'-n-butylphenyl]-2-[4"-cyanophenyl]-pyrimidine) gives the considerably reduced k_{33}/k_{11} values. It is interesting to note that all additives to NP 1008 which have been studied so far result in a lowering of the ratio k_{33}/k_{11} of pure NP 1008. From simple geometric considerations, one should expect an increase in k_{33}/k_{11} by adding a long, relatively rigid molecule, such as CBC 56.
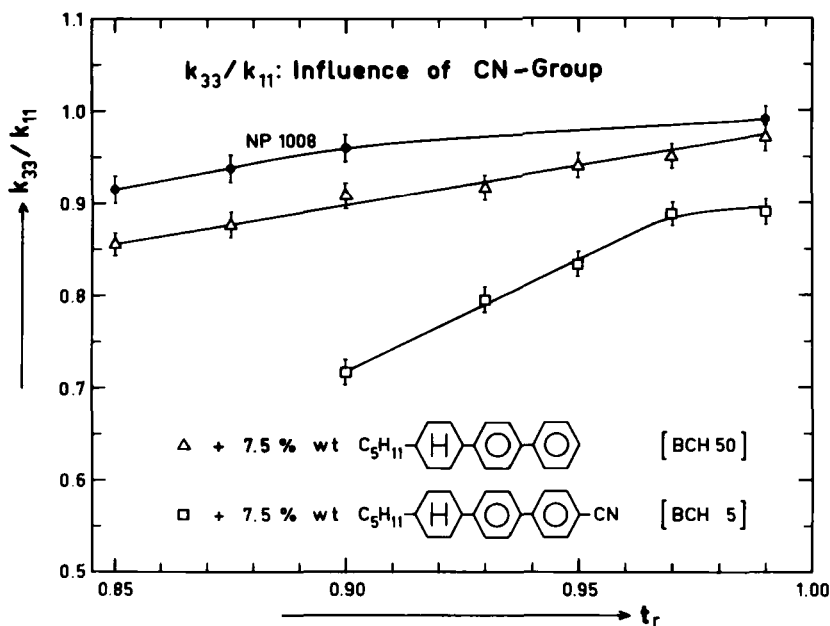

FIGURE 5 Ratio k_{33}/k_{11} versus t_r for NP 1008, NP 1008 containing a terminal non-polar component, and NP 1008 containing a terminal polar component.
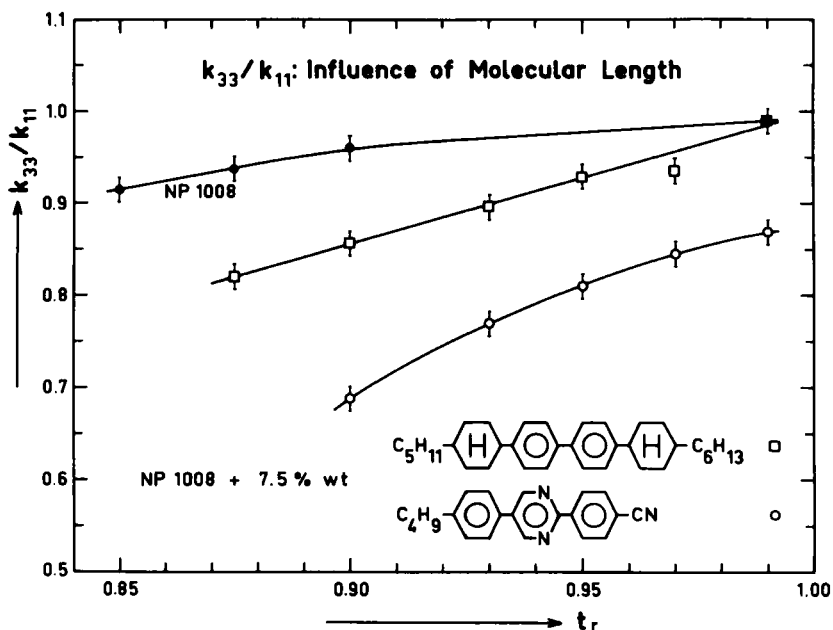
B. S. SCHEUBLE, G. BAUR and G. MEIER

FIGURE 6   Ratio k_{33}/k_{11} versus t_r for NP 1008, NP 1008 containing a four-ring, terminal non-polar component (CBC 56), and a three-ring, terminal polar component.
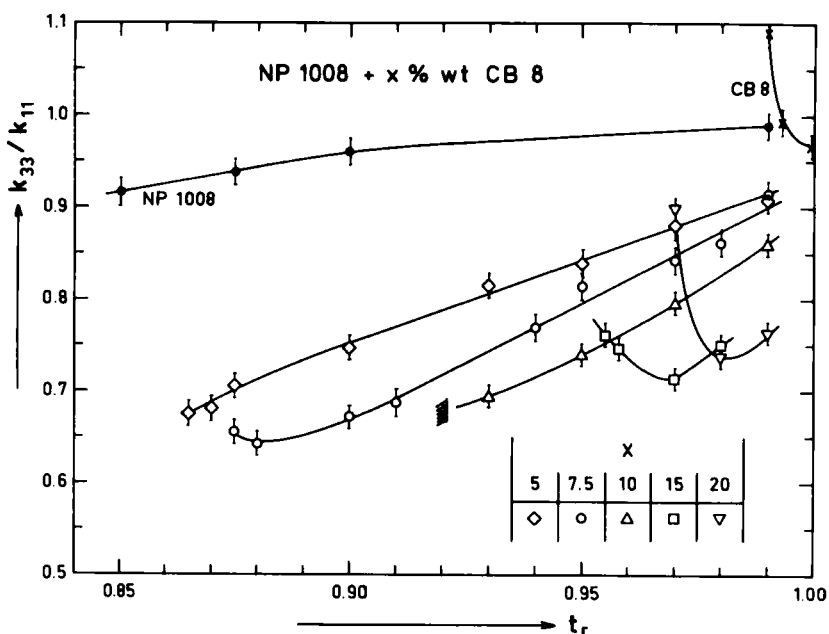

FIGURE 7   Ratio k_{33}/k_{11} versus t_r for NP 1008 and CB 8, and NP 1008 containing X% wt CB 8. Parameter X is 5, 7.5, 10, 15 or 20% wt.

We have observed that significantly reduced k_{33}/k_{11} values of NP 1008 are obtained by adding liquid crystals with a terminal CN—group. The lowest k_{33}/k_{11} ratio is found for terminal polar dopants with an octyl alkyl chain and by doping with a biphenyl or a phenylcyclohexane (Figure 3 and Figure 4). In other words the additives CB 8 and PCH 8 result in the lowest k_{33}/k_{11} values.

As shown in Figure 7 and Figure 8, the k_{33}/k_{11} values are also related to the mixing ratio of NP 1008 and CB 8 or PCH 8. For high reduced temperatures, one observes a decrease of k_{33}/k_{11} with increasing proportions of CB 8 or PCH 8. This has been verified for mixtures containing between five and twenty per cent of one of these two compounds. But the more CB 8 or PCH 8 that is added, the smaller is the nematic phase range. This originates from an induced smectic A phase. The S_A-phase leads to a divergence of k_{33} and therefore to a divergence of k_{33}/k_{11}. The divergence is indicated for 10% CB 8 (Figure 7). For 5% and 7.5% CB 8, one obtains almost no S_A-phase, and a very low k_{33}/k_{11}-ratio of 0.64 for 7.5% CB 8 at $t_r = 0.88$ has been observed. Comparing mixtures which contain the same proportion of CB 8 or PCH 8, the S_A-phase grows at a lower t_r for PCH 8 than for CB 8. Mixtures of NP 1008 plus PCH 8 instead of CB 8 give therefore a larger nematic phase range, but slightly higher values of k_{33}/k_{11}. In the range between five and fifteen per cent
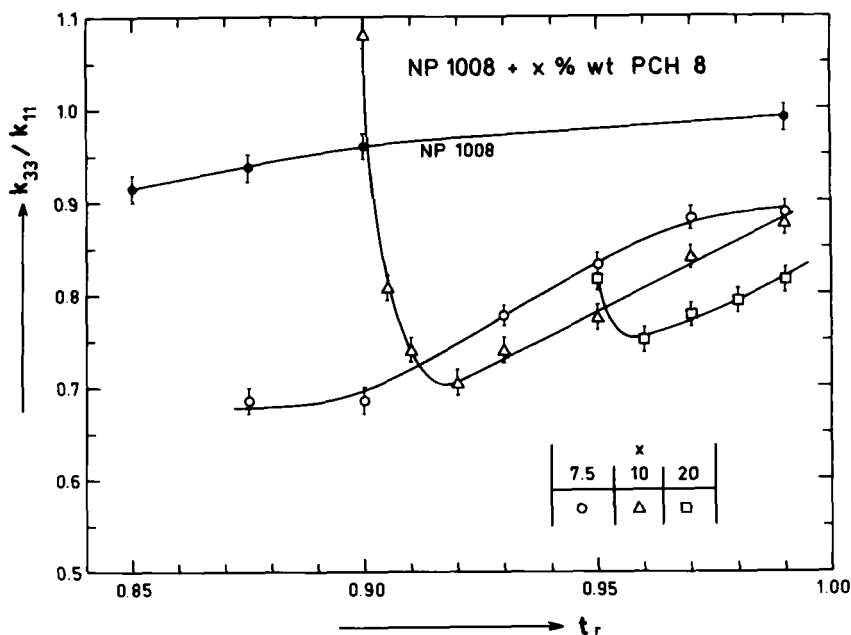

FIGURE 8   Ratio k_{33}/k_{11} versus t_r for NP 1008, and NP 1008 containing X% wt PCH 8. Parameter X is 7.5, 10 or 20% wt.
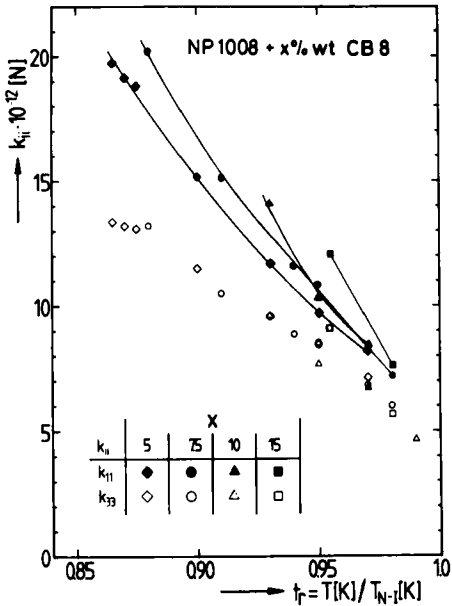
B. S. SCHEUBLE, G. BAUR and G. MEIER

FIGURE 9   Elastic constants k_{11} and k_{33} *versus* t_r for NP 1008 containing X% wt CB 8. Parameter X is 5, 7.5, 10 or 15% wt.

CB 8, the decrease in k_{33}/k_{11} of the mixture with NP 1008 is mainly due to an increase in k_{11}, while k_{33} remains fairly constant for these mixing ratios (Figure 9.)

As is seen from Figure 7 and Figure 8, the limiting factor for obtaining low k_{33}/k_{11} values is the induction of a smectic phase. An induced smectic phase has been observed for certain mixing ratios of terminal polar liquid crystalline compounds and the terminal non-polar ester mixture NP 1008. This is in agreement with the result of Engelen *et al.*[19] We have tried to suppress the smectic phase by adding another terminal non-polar component: a dialkyl-phenylcyclohexane (PCH 32) with a very low viscosity. Figure 10 shows that the nematic phase range is enlarged and the divergence of k_{33}/k_{11} is shifted to a lower reduced temperature. The k_{33}/k_{11} ratios of this four component mixture are slightly higher compared with the corresponding NP 1008/PCH 8 mixture.
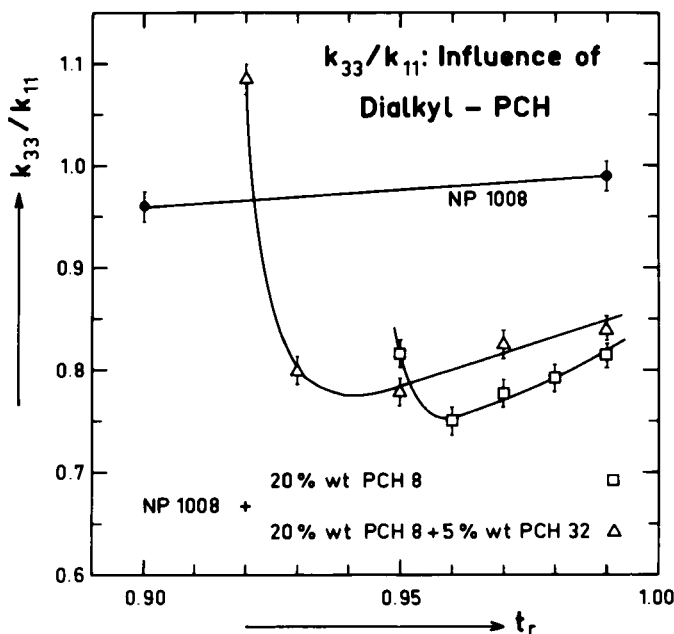
Acknowledgments

FIGURE 10   Ratio k_{33}/k_{11} versus t_r for NP 1008, NP 1008 containing 20% wt PCH 8, and additionally 5% wt PCH 32.

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