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Binary Mixtures of Rod-like Molecules with *p*-Methoxybenzylidene-*p*′-*n*-Butylaniline†

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Abstract—We have studied the effect of various rod-like molecules on the nematic-isotropic transition temperature, T_c of *p*-methoxybenzylidene-*p*′-butylaniline (MBBA). Specifically, we have former binary systems of MBBA with the even alkanols, $C_2 - C_{18}$ and the polypeptide, poly-γ-benzyl-*l*-glutamate (PBLG). The results are briefly: (*a*) all the alkanols contribute to a lowering of T_c. Evidence is presented that the longer rods (if rigid) tend to depress T_c less; (*b*) in the two-phase system of PBLG and MBBA, the large agglomerated regions of PBLG and MBBA appear to have a transition temperature slightly higher than the pure nematic region.

Introduction

Although liquid crystals behave mechanically as liquids, they preserve some of the crystalline order of the solid. In the pioneering work of Dave and Dewar,(1,2) the general conditions under which binary mixtures of liquid crystals and solutes will behave as a liquid crystal were investigated. It was found that, the more nearly the solute molecules resembled those of the solvent molecules in size, shape and polarity, the less the liquid-nematic transition temperature, T_c was depressed.

Now, if the solute molecules are long and thin, we expect them to be oriented by the nematic so that their long axis tends to lie parallel to the long axis of the liquid crystal molecules.(3,4) This will be

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particularly true of a mixture such as *p*-methoxybenzylidene-*p*-*n*-butylaniline⁽⁵⁾ and the alkanols (see Fig. 1) where each CH_2 group of the alkanols can interact attractively with the *n*-butyl tail of MBBA. On a molar basis, this interaction is about 0.6 kcal/CH_2 group $\sim 4k_BT$[6]. Consequently we do not expect a distribution of such solute molecules to disturb the parallel arrangement of nematic molecules nor appreciably lower the transition temperature of a nematic. This we found not to be the case when we added dodecanol (C_{12}) to MBBA. For this mixture, we found that the transition temperature fell linearly with increasing concentration of dodecanol so that about 6% by weight was sufficient to lower the transition temperature of MBBA ~ 20 °C. Intuitively, the effect of a very long, rigid rod floating in the nematic phase, on the nematic-isotropic transition temperature, would be an increase in T_c; i.e. nematic molecules would not only interact with nearest neighbours but via the rod would be rigidly attached to molecules several molecular units away. Thus, we began a study of the effect of molecular length of solute on the transition temperature of MBBA. We used only the even alkanols from C_2—C_{18} as solutes in order to preclude a possible steric effect—i.e. an odd-even effect, arising from the staggered conformation of these molecules.

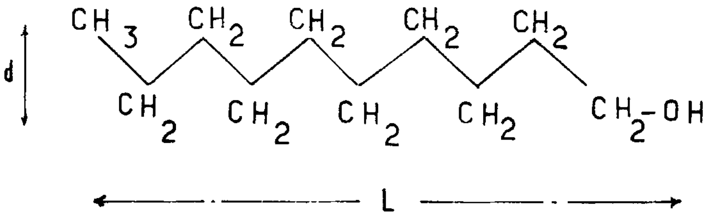

Figure 1. Conformation of the even numbered alkanols, $CH_3—(CH_2)_{n-1}—OH$

Experiment

Solutions of MBBA and the alkanols were stirred magnetically for several minutes in a closed crucible. All the alkanols went in to solution easily from C_2 to C_{14}. For C_{16} and C_{18}, it was necessary to heat the MBBA slightly while simultaneously stirring. For very slight concentrations (< 1% by weight) of hexadecanol and octodecanol this seemed to produce a stable solution when subsequently cooled to room temperature.

Drops of the solution were transferred rapidly from the crucibles and sandwiched between glass cover slides which were separated by 50 μ spacers. A thermocouple was attached to the sample and then placed in an enclosed brass oven. The temperature of the oven was controlled by means of a thermostatted, circulating oil bath.

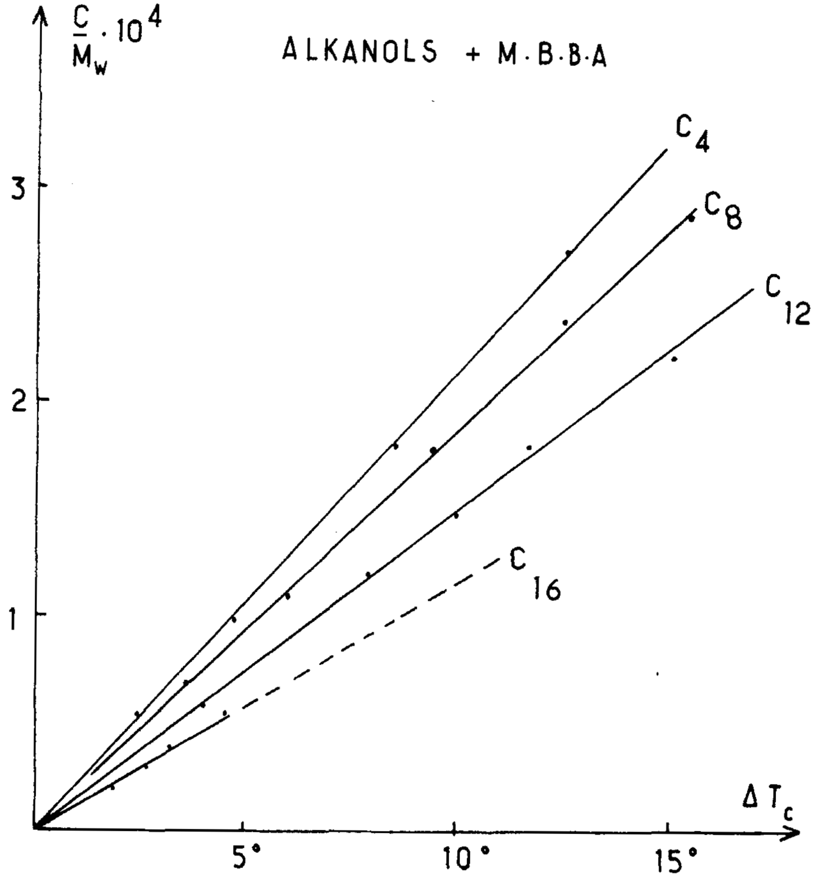

Figure 2. The decrease in the nematic–isotropic transition temperature versus percent by weight alkanol/molecular weight in solution.

Results

Figure 2 shows the decrease in T_c with molecular concentration of solute. The curves were found to be linear in concentration for the first 15–20 °C depression of T_c. For T_c's of the order of 25 °C, slight deviations from this linear relation were noticed (ΔT_0 being somewhat smaller than one would expect). This may be due simply to inadequate temperature control of the samples near room temperature (~22 °C). These curves were measured several times for each solute and we found generally that (*a*) the starting purity of MBBA did not appreciably affect the resulting slope and (*b*) orienting the samples by rubbing the glass plates had the effect of introducing scatter in the data points, but the slope of the best fit straight line fell within the range of values one obtained from data obtained under cleaner conditions.

In Fig. 3, we plot the slopes of Fig. 2 reduced by n, the number of carbon atoms in the alkanol chain as a function of n. Starting from the very short alkanol, C_2, we see that increasing the number of carbons (or lengthening the alkanol chain) makes it less effective in

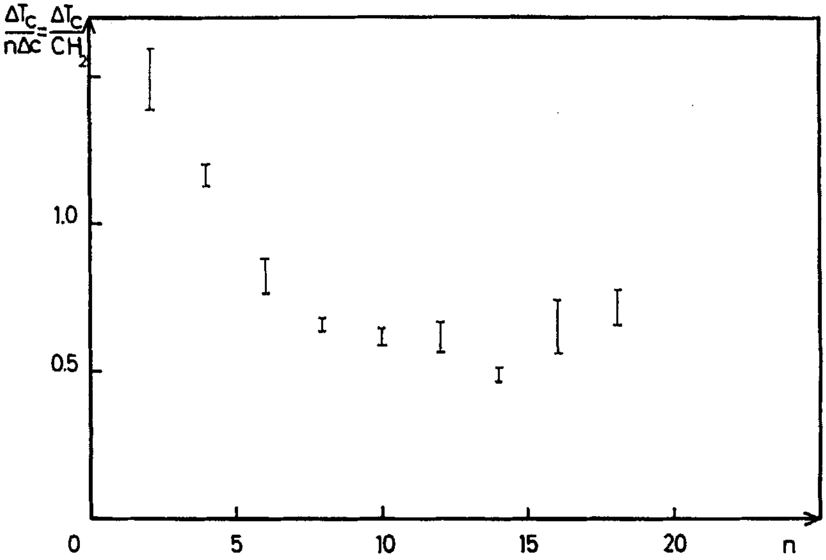

Figure 3. The slope of curves in Fig. 2 divided by n versus n, i.e., $\Delta T_c/CH_2$ group.

destroying the mesophase. This is the trend until C_{14}. For C_{16} and C_{18}, the trend appears to reverse. This is, perhaps, because in dilute solution in MBBA, C_{16} and C_{18} are not rigid.

Extrapolating the curve of Fig. 3 between C_2 and C_{14} until $\Delta T_c = 0$, we find this would correspond to a molecular length of 50–70 Å.

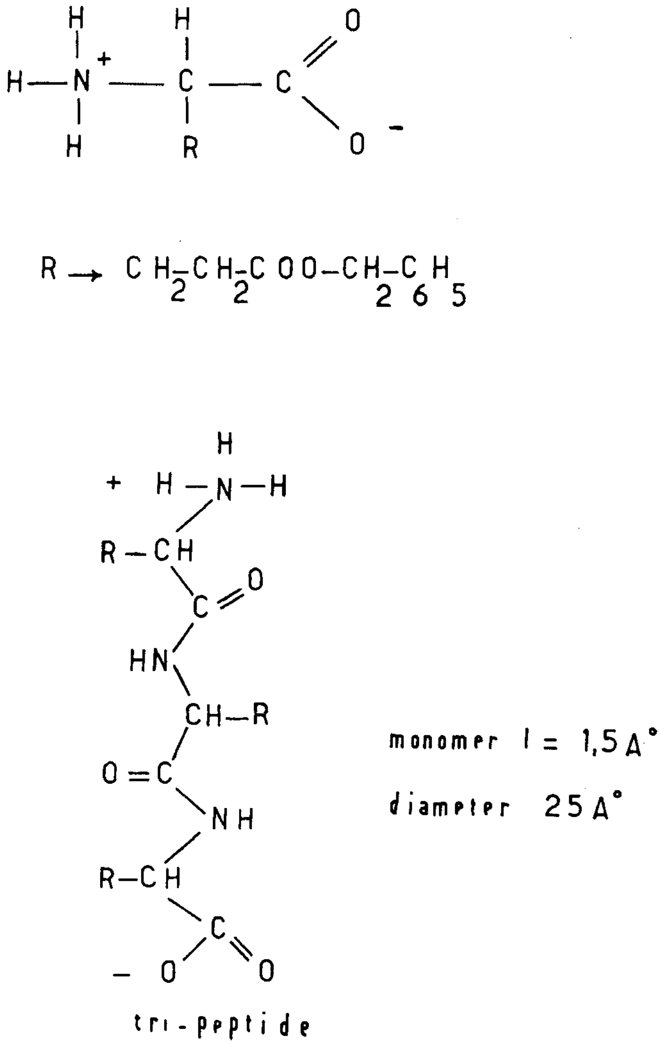

Figure 4. Conformation of PBLG.

We would also like to report briefly the results of measurements on the T_c of MBBA upon the addition of a very long rigid rod.

For a very long rigid rod, we added poly-γ-benzyl-l-glutamate (PBLG) to MBBA, (length ~ 1000 Å). The polypeptide, shown in Fig. 4 was first dissolved in a solution of dimethyl formamide (to obtain the α-helix conformation) and left for several days on a magnetic stirrer. The polypeptide in solution was then added to MBBA and the solvent was pumped off. Typical concentrations in MBBA were $\sim 0.03\%$ by weight of PBLG. Placing a drop of this sample between rubbed glass plates (shown in Fig. 5) we were able to see large regions of nematic oriented by the glass plates (black between crossed polaroids) and smaller regions oriented by PBLG. There appeared to be a rather large attractive force between the coloured polypeptide regions so that within several minutes the smaller aggregates formed quite large aggregates. The nematic–isotropic transition for this system is shown in Fig. 6(a) and 6(b). The agglomerated mixture of PBLG and MBBA do indeed have a T_c slightly higher than the pure nematic (~ 0.4–$0.6\,^\circ$C).

Figure 5. PBLG + MBBA aggregates (light areas) floating in oriented nematic (black between crossed polaroids). The small aggregates diffuse through the nematic to form large aggregates (magnification 1000 ×).

Remarks

1. We have assumed that the long chain alkanols behave in solution as rigid rods. Although this is known to be true if the alkanols are solid, this may not be the case in the liquid state.(7) Specially in dilute solutions where no interaction between chains occur. Experimental evidence indicates also that a large dielectric constant of the solvent favours the flexibility of the chain molecule. It would be

interesting to know (e.g. by means of a Raman Spectra) if this flexibility of these long chain molecules depends on the ordering ability of the solvent as we have assumed for molecules with a length of the order of MBBA.

2. Mixtures of MBBA and tetradecanol very frequently gave the homeotropic texture. In this case, the OH group of the alkanol, attracted to the acid impurities adhering to the microscope slides, tends to orient a surface layer of MBBA. This orienting effect was most noticeable for C_{14} which is about the length of MBBA. This ordering of the C_{14} alkanol by the glass surface may explain why the transition temperature for C_{14} is somewhat smaller than one would expect (Fig. 3).

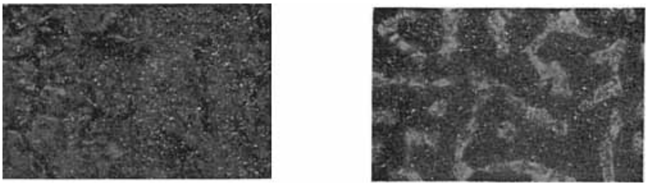
(a) (b)

Figure 6. (a) Large aggregates (magnification 100 ×) embedded in non-oriented MBBA when both phases are nematic; (b) dark region is isotropic MBBA pure; light region, MBBA + PBLG aggregates. T_c for MBBA in this region 0.4–0.6 °C higher.

Conclusion

Since there are so many possible interactions which can exist between solute and solvent molecules we have tried to study a system which limits the number of possible variables. Specifically, we have taken the homologous series of alkanols (CH_3—$(CH_2)_{2k-1}$—OH) where k varied from 1 to 9.

We have studied the depression in the nematic–isotropic transition temperature of MBBA as a function of $n = 2k$. We have observed that the longer molecules give a $\Delta T_c/CH_2$ smaller than the shorter molecules. Some evidence is presented that rigid rods like PBLG (~ 1000 Å) increase the T_c of the nematic phase.

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