Effect of pressure on the molecular motion of a poly(γ-benzyl L-glutamate) lyotropic liquid crystal as studied by ^{1}H nuclear magnetic resonance

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The proton spin–spin relaxation time T_2 of poly(γ-benzyl L-glutamate) (PBLG) in methylene chloride (CH_2Cl_2) solution and volume changes were measured under pressures up to 500 kg cm^{-2} as a function of PBLG concentration, the main aim being to obtain new information about the molecular motion and side-chain conformation of the PBLG liquid crystal. The results obtained suggest that conformational changes of the PBLG side chains and intermolecular distance are important factors in understanding the pressure effect on molecular motion and magnetic orientation of the PBLG liquid crystal.

(Keywords: molecular motion; poly(γ-benzyl L-glutamate); nuclear magnetic resonance)

INTRODUCTION

Poly(γ-benzyl L-glutamate) (PBLG), which has long side chains, forms liquid crystals in concentrated solutions in solvents such as methylene chloride (CH_2Cl_2) which is under consideration here[1-7]. PBLG is recognized as being a cylindrical rod supported by an inner core with considerable rigidity sheathed in a soft outer core of flexible chains. The molecular motion of CH_2Cl_2 in such a system is considerably restricted in the liquid crystal, and consequently its n.m.r. signal is split into a doublet by dipolar interaction between the protons[8-16]. This splitting provides useful information about the PBLG nematic liquid crystal. Also, quadrupole splittings observed in the ^{2}D n.m.r. of magnetically oriented nematic solutions of PBLG with selectively deuterated side chains provide direct information about the order parameters of the C–D bond directions in the side chain[17-19]. Especially, such n.m.r. experiments provide some general insights into the dynamic structural organization of the side chain on the periphery of the α-helix. Nevertheless, we still encounter some unknowns for the molecular motion, the side-chain conformation, etc.

Recently, we have undertaken a preliminary investigation of the ^{1}H n.m.r. and volume change of a PBLG lyotropic liquid crystal under high pressure[20]. From these experiments we have gained useful information about the dynamic structural organization of the PBLG side chain on the periphery of the α-helix in the liquid crystal state. So far, most n.m.r. studies on the PBLG liquid crystal have used temperature as the only experimental variable, while the pressure was left constant, usually at 1 atm. However, the use of pressure[21-26] is very effective in overcoming the limited interpretation of the results obtained for the liquid crystal at atmospheric pressure, and further is expected to provide another dimension in the investigation of PBLG liquid crystals because volume changes under pressure have a major effect on molecular motion in the system. In the present work, which is aimed at obtaining new information about the molecular motion and magnetic orientation of the PBLG liquid crystal, in addition to the previous preliminary work, n.m.r. relaxation and volume change experiments of this system were performed under pressures up to 500 kg cm^{-2}.

EXPERIMENTAL

PBLG was prepared from the *N*-carboxy anhydride of γ-benzyl L-glutamate. Its average molecular weight was 3.3×10^4 as determined by intrinsic viscosity[27]. The solvent CH_2Cl_2 was purified by ordinary distillation. The concentration of the polymer was varied up to 25 wt% (PBLG/CH_2Cl_2).

The high-pressure apparatus used in this experiment is described in detail elsewhere[28,29].

^{1}H pulsed n.m.r. measurements were carried out with a Bruker PC-20 spectrometer operating at 20 MHz at 39°C. The sample cell was not subjected to spinning and the orientation of the liquid crystalline solution was achieved in the magnetic field of the n.m.r. magnet. The

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n.m.r. experiment was started after the cholesteric liquid crystalline solution was completely changed to nematic liquid crystalline solution after 3 h. The pulse sequence used for the measurement of the proton spin–spin relaxation time T_2 was the Carr–Purcell–Meiboom–Gill (CPMG) method[30]. Data for the decay process for the PBLG liquid crystal solution were analysed as the sum of some single-exponential components, e.g. CH_2Cl_2 and PBLG components. The decomposition of the signal was made using the non-linear least-squares method by microcomputer (NEC PC9801, Nippon Denki Co. Ltd).

The n.m.r. capillary cell was also used for the volume change experiment. The cell was placed in a constant-temperature water bath at 25°C. The volume change was measured by means of a cathetometer.

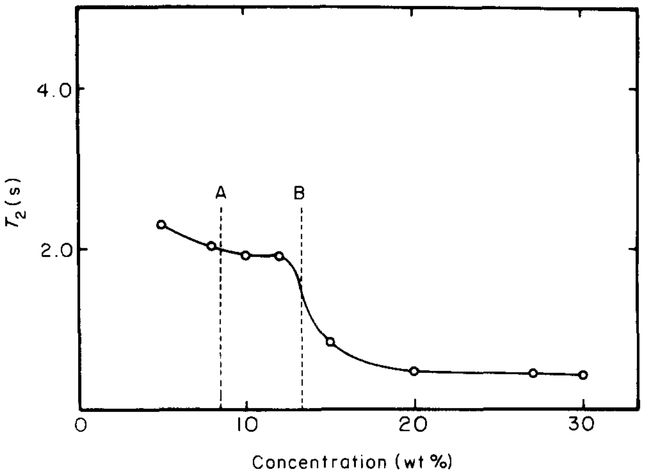

Figure 2 Plot of T_2 for the long T_2 component as a function of PBLG concentration at atmospheric pressure

RESULTS AND DISCUSSION

Figure 1 shows the PBLG concentration dependence of the echo envelope from $PBLG/CH_2Cl_2$ solutions. It is apparent that at high PBLG concentration these signals are mainly composed of two components: a long T_2 component corresponding to CH_2Cl_2 and a short T_2 component due to the PBLG side chain. If we look carefully at the T_2 signal at higher PBLG concentrations, a third T_2 component corresponding to the PBLG main chain can be distinguished from the other components. In order to demonstrate clearly that the three observed T_2 components correspond to the CH_2Cl_2 solvent, PBLG side chain and PBLG main chain, we measured the echo envelope from 15% PBLG/deuterated methylene chloride (CD_2Cl_2) solution and also from 15% $PBLG/CH_2Cl_2$ solution. In the $PBLG/CD_2Cl_2$ solution, the long T_2 component that appears in the $PBLG/CH_2Cl_2$ solution disappeared. This means that the long T_2 component in the $PBLG/CH_2Cl_2$ solution is due to the CH_2Cl_2 solvent. The two remaining components have a moderately short T_2 and an extremely short T_2 component, the latter being due to the PBLG main chain for which molecular motion is considerably restricted by the formation of the α-helix. This means that at high PBLG concentration the T_2 value of the PBLG can be obtained within a small error limit from the T_2 signal in $PBLG/CH_2Cl_2$ solution.

Figure 2 shows the plot of the T_2 value for the long T_2 component as a function of PBLG concentration (X_{PBLG}), where the T_2 value at $X_{PBLG}=0$ represents the CH_2Cl_2 component. The $PBLG/CH_2Cl_2$ solution shows three regimes[31–34] on varying the PBLG concentration: the isotropic solution regime (I), the biphasic regime (II) with the isotropic solution in equilibrium with the liquid crystalline solutions, and the liquid crystalline solution regime (III). The $PBLG/CH_2Cl_2$ solution becomes liquid crystalline spontaneously when the PBLG concentration exceeds a certain limiting value in the solution. The liquid crystalline phase is preceded by a biphasic regime which exists over a narrow range of PBLG concentrations. The point A (the highest concentration below which only the isotropic phase exists) and the point B (the lowest concentration above which only the liquid crystal solution exists) were determined from observation of the dipole splitting of the ^1H signals obtained from the CH_2Cl_2 solution in $PBLG/CH_2Cl_2$. A biphasic regime exists between the points A and B. As seen from this figure, there is a marked change in the relaxation time at the transition from isotropic solution to liquid crystalline solution. Therefore, the liquid crystalline phase can be readily recognized from the observation of T_2 data. This means that the molecular motion of CH_2Cl_2 is abruptly restricted in going from isotropic solution and biphasic regime to liquid crystalline solution. Such a marked change appears in the relative flow viscosity, optical rotatory dispersion, circular dichroism, dielectric relaxation, electric dichroism and X-ray diffraction on passing from isotropic solution to liquid crystalline solution.

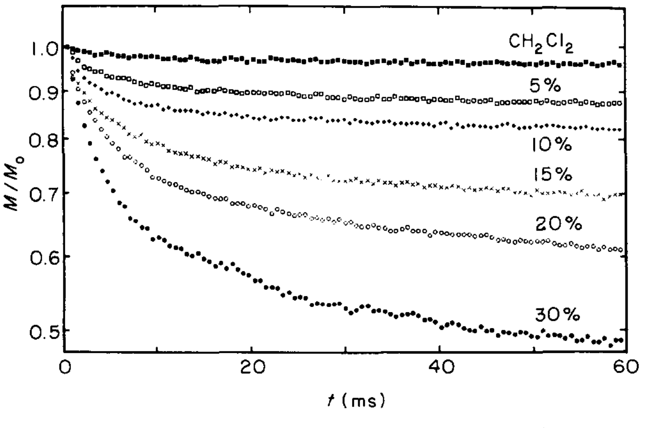

Figure 1 T_2 signal from $PBLG/CH_2Cl_2$ solution as a function of PBLG concentration at atmospheric pressure

Figure 3 shows the pressure dependence of T_2 for pure liquid CH_2Cl_2 up to 400 kg cm^{-2}. The value of T_2 decreases slowly with increasing pressure. This means that the decrease of the value of T_2 is most probably due to a decrease of molecular motion. Such an experimental finding is physically quite reasonable because the molecules are so closely packed in the dense liquid.

Figure 4 shows the pressure dependence of T_2 for CH_2Cl_2 in $PBLG/CH_2Cl_2$ isotropic solution and liquid crystalline solution. In the isotropic solution, 5% $PBLG/CH_2Cl_2$ solution, the value of T_2 for CH_2Cl_2 decreases very slowly up to about 150 kg cm^{-2}, while above 150 kg cm^{-2} it decreases rapidly. This trend is different from that found for the pure liquid CH_2Cl_2 and also the value of T_2 is shorter than that of the pure liquid CH_2Cl_2. This most probably means that the molecular

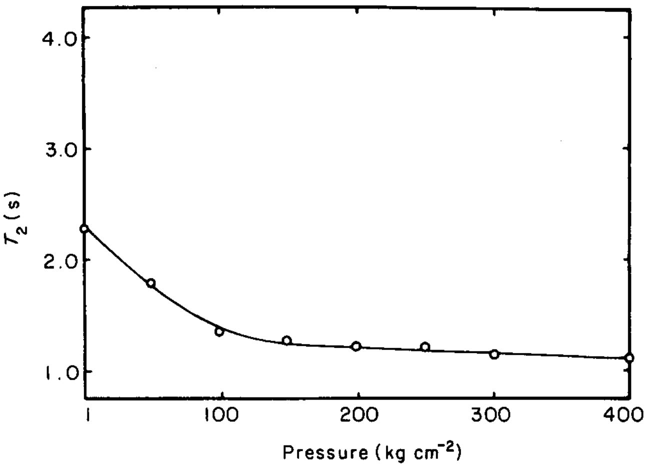

Figure 3 Pressure dependence of T_2 for pure liquid CH_2Cl_2

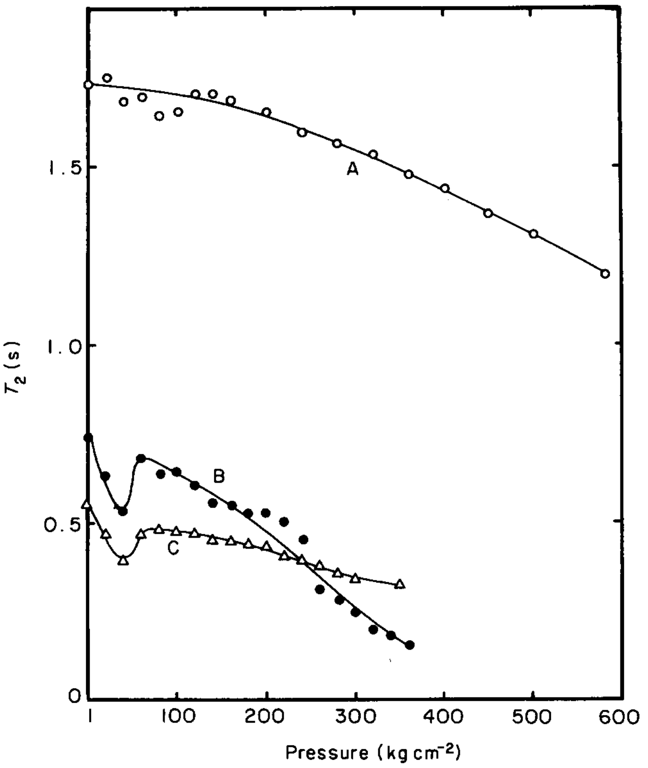

Figure 4 Pressure dependence of T_2 for CH_2Cl_2 in 5% PBLG/CH_2Cl_2 solution (curve A), 15% PBLG/CH_2Cl_2 solution (curve B) and 20% PBLG/CH_2Cl_2 solution (curve C)

motion of CH_2Cl_2 is restricted by the PBLG polymers. On the other hand, in liquid crystalline solutions, 15 and 20% PBLG/CH_2Cl_2 solutions, the value of T_2 for CH_2Cl_2 decreases with increasing pressure up to 60 kg cm^{-2}, increases above 60 kg cm^{-2} and again decreases slowly above ~80 kg cm^{-2}. Thus, the T_2 curve has a minimum and a maximum. This behaviour is considerably different from that for pure liquid CH_2Cl_2 and isotropic solution. The whole trends of T_2 for 15 and 20 wt% solutions are very similar to each other. The T_2 value for the former is much longer than that for the latter. This means that the molecular motion of CH_2Cl_2 in the latter is more restricted than that in the former. This suggests that a marked change of the side-chain conformation influences the molecular motion of the CH_2Cl_2 molecules because at higher PBLG concentration the interactions between the long 'extended'[17,18,35] bulky side chains become stronger compared with that at lower PBLG concentration and so such interactions are much more complicated. This suggestion may be supported from the observation of T_2 for PBLG side chains and the pressure dependence of the volume change for the liquid crystalline solution, as will be seen below.

Figure 5 (curve A) shows the pressure dependence of T_2 for the PBLG side chain in a 20% PBLG/CH_2Cl_2 solution. It is seen from this figure that the T_2 curve has a minimum at about 60 kg cm^{-2} and a maximum at about 80 kg cm^{-2}. This suggests that the slow decrease of T_2 up to 60 kg cm^{-2} arises from the decrease of the intermolecular distance between the α-helical PBLGs; that the increase of T_2 from 60 to 80 kg cm^{-2} is due to disturbance to molecular motion or orientation through changes of the PBLG side chains from 'extended' to 'compact' conformation, as reported previously[20], by the further decrease of the intermolecular distance; and that the decrease of T_2 above 80 kg cm^{-2} is due to the restriction of molecular motion by the decrease of the intermolecular distance between the α-helical PBLGs with the 'compact' conformation. These observed trends are very similar to those for CH_2Cl_2 in the same solution. This means that the behaviour of the molecular motion of CH_2Cl_2 molecules is closely related with that of the side chains. If we look at curves B and C in *Figure 4* and *Figure 5* (curve A) in detail, we find that the value of the pressure at the T_2 minimum for the PBLG side chain is higher (about 60 kg cm^{-2}) by about 20 kg cm^{-2} than that for the T_2 minimum of CH_2Cl_2. This difference may suggest the following: It is apparent that the T_2 behaviour of the CH_2Cl_2 solvent is directly affected by the change in molecular motion of the PBLG side chain or the conformational change. The appearance of the T_2 minimum in the CH_2Cl_2 solvent at pressures lower by 20 kg cm^{-2} compared with the case of the PBLG side chain shows that the conformational change begins at pressures lower than 80 kg cm^{-2}, but there is no increase in molecular motion. For convenience, the pressure dependence of the separation ($\Delta\nu$) between the dipole splittings of the proton pair on each CH_2Cl_2 is reproduced from the data presented in the previous paper[20] as shown in *Figure 5* (curve B), compared with

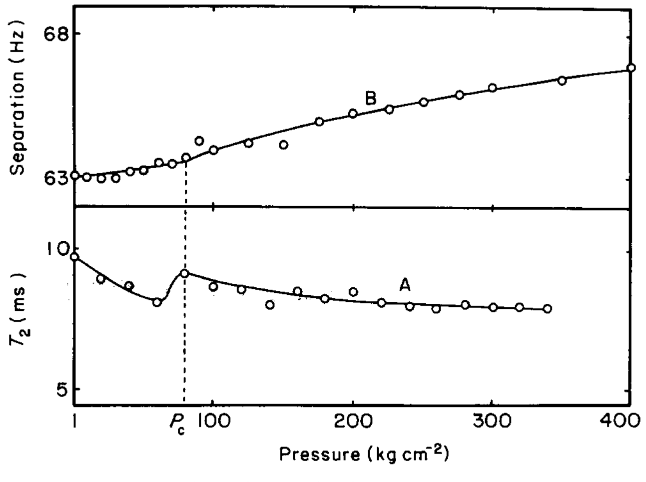

Figure 5 Pressure dependences of T_2 for the PBLG side chain (curve A) and dipolar splitting $\Delta\nu$ (curve B) of CH_2Cl_2 in 20% PBLG/CH_2Cl_2 liquid crystalline solution

the T_2 data. The separation is a function of the order parameter of the liquid crystal. It is observed that $\Delta\nu$ increases slowly and linearly with increasing pressure up to about $80\,kg\,cm^{-2}$, and increases rapidly above $80\,kg\,cm^{-2}$. This $\Delta\nu$ behaviour at about $80\,kg\,cm^{-2}$ is closely related to the above-mentioned T_2 behaviour at the same pressure. To explain such behaviour, it was proposed previously[20] that the slow change of $\Delta\nu$ up to $80\,kg\,cm^{-2}$ arises from a balance between the disturbance of the orientation of CH_2Cl_2 due to the change of the PBLG side chains from 'extended' to 'compact' conformation, and increasing pressure; while above $80\,kg\,cm^{-2}$ the abrupt change of $\Delta\nu$ comes from the decrease of the intermolecular distance between the α-helical PBLGs. This interpretation does not conflict with the behaviour observed for T_2.

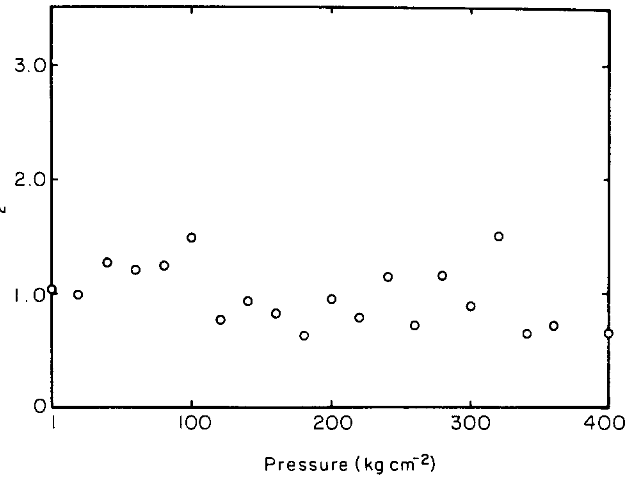

Figure 6 Pressure dependences of T_2 for CH_2Cl_2 in 10% PBLG/CH_2Cl_2 biphasic regime

Figure 6 shows the pressure dependence of T_2 for CH_2Cl_2 in the biphasic regime. The plot of T_2 against pressure shows some scatter. Following this experiment, we discovered a lot of liquid crystalline spherulites of large size which had grown during the n.m.r. measurement under high pressure. From this observation we suggest that some scatter of the T_2 data arises from the unstable state of the biphasic regime in which the fluidity of CH_2Cl_2 and PBLG molecules occurs due to the growth of the liquid crystalline spherulites.

The volume ratio V/V_0 (V_0 is the volume at atmospheric pressure, and V the volume at any given pressure) of pure liquid CH_2Cl_2 and the PBLG/CH_2Cl_2 solutions is shown as a function of pressure in *Figure 7*. Also, the pressure dependences of the slope of V/V_0 ($d(V/V_0)/dp$) against pressure p are observed in these figures. It is apparent that the volume ratio of pure liquid CH_2Cl_2 decreases monotonically with increase in pressure; $d(V/V_0)/dp$ is almost independent of pressure, while the volume ratio of PBLG/CH_2Cl_2 solutions varies abruptly up to about $80–100\,kg\,cm^{-2}$ and decreases monotonically above about $80–100\,kg\,cm^{-2}$. If we look at the plot of $d(V/V_0)/dp$ against pressure, such behaviour can be clearly recognized. The value of the slope up to about $80–100\,kg\,cm^{-2}$ increases with increase in the PBLG concentration. From this we suggest that marked changes in the liquid crystalline solution may come from changes of the side-chain conformation from 'extended' to 'compact' in addition to the decrease of the intermolecular distance between the α-helical PBLGs. This may support the above-mentioned interpretations for T_2 and $\Delta\nu$.

Finally, we conclude that the conformational changes of the PBLG side chains and the intermolecular distance are important factors in understanding the pressure effect.

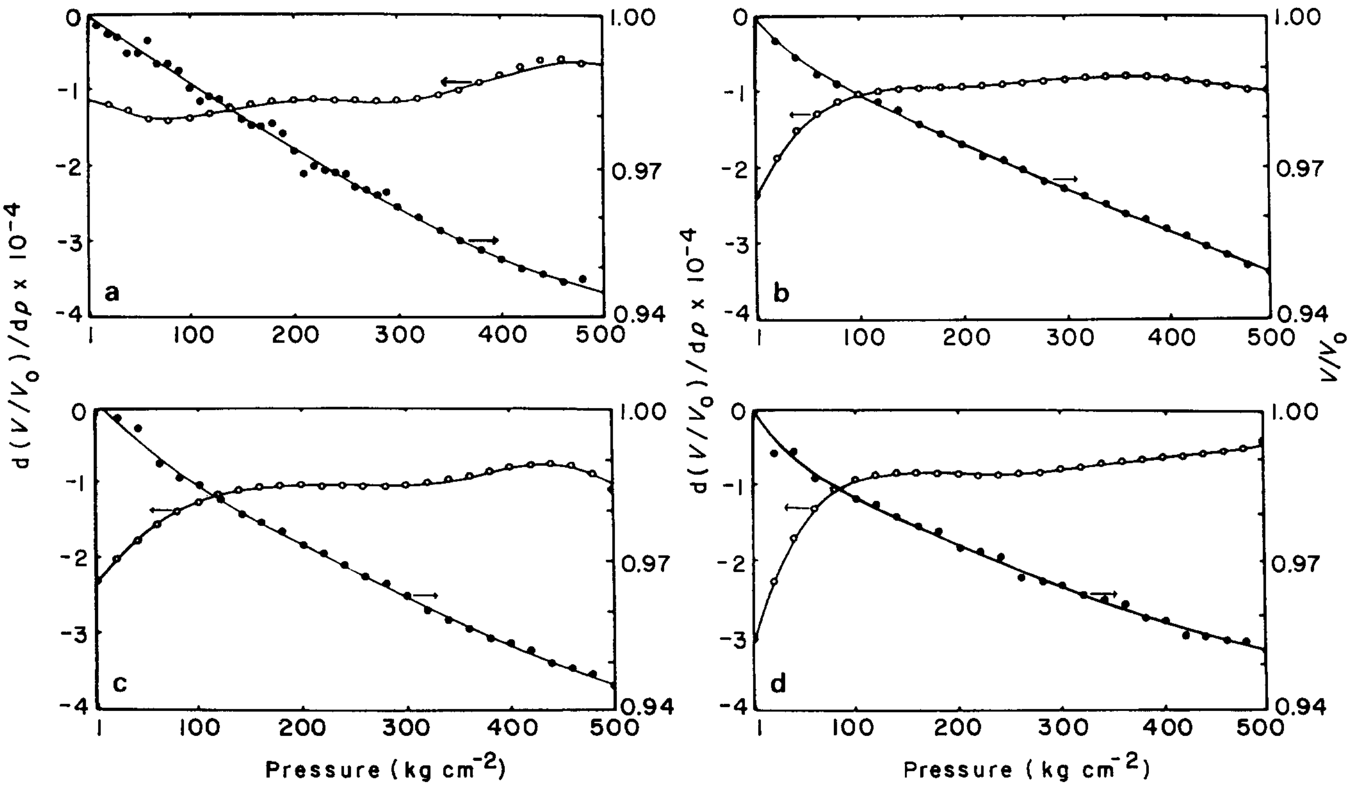

Figure 7 Pressure dependence of V/V_0 and $d(V/V_0)/dp$ for (a) pure liquid CH_2Cl_2, (b) CH_2Cl_2 in 5% PBLG/CH_2Cl_2 isotropic solution, (c) 10% PBLG/CH_2Cl_2 solution and (d) 15% PBLG/CH_2Cl_2 liquid crystalline solution

The present work shows that high-pressure n.m.r. offers more useful perspectives in interpreting interactions between the PBLG side chains and solvent in PBLG/CH_2Cl_2 solution and would suggest the potential applicability of such an approach to further investigations.

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