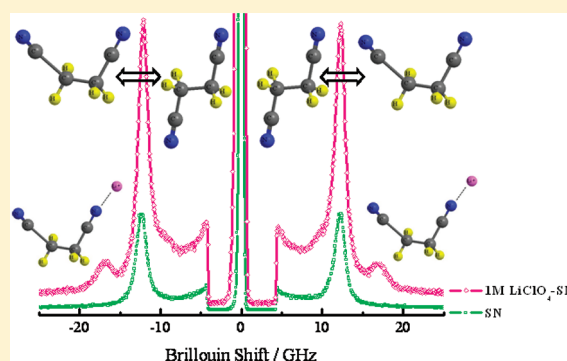


Brillouin Scattering Investigation of Solvation Dynamics in Succinonitrile-Lithium Salt Plastic Crystalline Electrolytes

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Supporting Information

ABSTRACT: Temperature dependent Brillouin scattering studies have been performed to ascertain the influence of solvent dynamics on ion-transport in succinonitrile-lithium salt plastic crystalline electrolytes. Though very rarely employed, we observe that Brillouin spectroscopy is an invaluable tool for investigation of solvent dynamics. Analysis of various acoustic (long wavelength) phonon modes observed in the Brillouin scattering spectra reveal the influence of trans–gauche isomerism and as well as ion-association effects on ion transport. Although pristine SN and dilute SN-LiClO₄ samples show only the bulk longitudinal-acoustic (LA) mode, concentrated SN-LiClO₄ (~0.3–1 M) electrolytes display both the bulk LA mode as well as salt induced Brillouin modes at ambient temperature. The appearance of more than one Brillouin mode is attributed to the scattering of light from regions with different compressibilities (“compactness”). Correspondingly, these modes show a large decrease in the full width at half-maximum (abbreviated as ν_f) as the temperature decreases. Anomalous temperature dependent behavior of ν_f with addition of salt could be attributed to the presence of disorder or strong coupling with a neighbor. The shape of the spectrum was evaluated using a Lorentzian and Fano line shape function depending on the nature and behavior of the Brillouin modes.



1. INTRODUCTION

Plastic crystalline soft matter electrolytes^{1–6} have been the subject of intense investigations over this decade due to their potential electrochemical applications.^{7,8} The phenomenon of plasticity in a material originates from orientational disorder above a particular temperature, characteristic to the material. A plastic crystalline state⁶ has been observed in wide range of inorganic and organic materials.^{1,3,9} The organic materials are particularly interesting as the transition has often been observed in the ambient temperature range. In the realm of ionics, plasticity has been demonstrated to enhance ionic conductivity. Succinonitrile^{2–4,10–13} (SN; N≡C–CH₂–CH₂–C≡N) a nonionic polar (dielectric constant, $\epsilon = 55$) organic plastic crystal comprise an excellent solvent for dissolving wide range of salts. SN possesses a wax-like appearance in the temperature range ~–35 to +60 °C. In the plastic phase SN adopts different conformations typically marked by a mixture of trans (~20%)¹⁴ and gauche isomers. It has been proposed that the trans conformer is an impurity phase which enhances lattice defects thus enhancing ionic conductivity. The orientational disorder originates from trans–gauche isomerism involving rotation of CN moieties about the central C–C bond. The SN crystal structure in the plastic phase depending on salt concentration crystallizes into bcc or orthorhombic crystal system¹⁰ for $T > T_{np}$

(T_{np} : normal crystal to plastic transition temperature), whereas for $T < T_{np}$ in the normal crystalline phase, the structure is monoclinic. Additionally all rotator motions are frozen for $T < T_{np}$. SN-based electrolytes show high conductivity in the plastic phase regime, and this has been attributed to the solvent dynamics, i.e., trans–gauche isomerism.

The mechanism of ionic conductivity in plastic crystalline electrolytes is generally strongly coupled to the solvent dynamics and ion association effect. Although solvent conformational rearrangement “dynamics” is proposed to enhance ionic conductivity, ion association leads to a decrease in ionic conductivity. Recently, we have demonstrated the effect of solvent dynamics on ion-transport via dielectric relaxation spectroscopy¹⁵ where various relaxation processes influencing ion transport mechanism were found to be dependent on temperature and salt concentration. We discuss here the influence of solvent dynamics on ion transport using Brillouin scattering. Brillouin scattering^{16–22} is a very sensitive technique for probing surface and bulk acoustic phonons as well as microstructure. We envisage that using this tool, comprehensive of ion transport at the mesoscopic scale will

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be better achieved. The earliest light scattering study on succinonitrile was reported by Sherwood et al.²³ by means of a low-resolution interferometer spectrometer. The measurements revealed valuable information on the dependence of structural relaxation of plastic crystals on various parameters such as temperature. In the past decade Masui et al.²² have reported a comprehensive study on light scattering of pure single crystal succinonitrile in the plastic and liquid phases over a wide frequency range (microscopic to macroscopic regime). They have observed the presence of a quasi-elastic component (also known as reorientational mode) throughout the measurement. The width of this mode decreased by approximately three times in the plastic phase compared to that of the liquid phase. This indicates a higher degree of reorientational motion in the liquid phase compared to the plastic phase. Along with this they observed that there is no change in the trans–gauche population between the phases. The two orders of increase in conductivity across plastic to liquid transition temperature as reported by Das et al.¹⁰ can be purely attributed to change in the degree of reorientation between the two phases. Our focus here is to investigate solvent dynamics across the transition between plastic to crystalline phases in pure SN and Li-salt:SN plastic crystalline electrolytes.

In this article, we present the temperature dependence of the bulk acoustic phonons in pristine SN and SN-LiClO₄ electrolytes from 300 to 200 K. The influences of salt concentration and temperature on solvent dynamics and ion-association effect have been investigated. The Brillouin data were further analyzed using Lorentzian and Fano resonance function for identification of behavior of various Brillouin modes. We attempt here to understand the ion transport mechanism in SN-LiClO₄ based on the concept of molecular liquids as opposed to concentrated solid state defect chemistry.

2. EXPERIMENTAL MATERIALS AND METHODS

Prior to the electrolyte preparation succinonitrile (SN, Aldrich) was sublimated twice to remove impurities, and lithium perchlorate (LiClO₄, lithium battery grade, Chemetall GmBH) was preheated at 110 °C under vacuum to rule out effects arising out of physisorbed water. The plastic crystalline electrolyte was prepared by adding the requisite amount of LiClO₄ ($x = 0.005$ – 1 M or 0 – 7 mol % where M is molarity and x is the concentration of LiClO₄ salt in plastic electrolytes) in molten SN and stirred at 60 °C under dry N₂ atmosphere until a homogeneous mixture was obtained. Homogeneous transparent samples were obtained for all concentrations of LiClO₄. The solidified melt was stored in glass vials under vacuum at 25 °C until further use.

Brillouin spectra of the samples were recorded in the back-scattering geometry using the p-polarized 532 nm line of single mode solid-state diode pumped frequency doubled Nd:YAG laser (model COMPASS 315M-150, Coherent Inc., U.S.A.) as the excitation source. The scattered light was analyzed using a 3 + 3 pass tandem Fabry–Perot interferometer (JRS Scientific Inc., Switzerland), which has a finesse ~ 100 and is equipped with a photo avalanche diode (Perkin-Elmer, Canada) as the detector. The spectra were collected at a free spectral range of 30 GHz, equivalent to an etalon spacing of 5 mm. Temperature-dependent measurements were carried out using a closed cycle helium cryostat (CTI Cryogenics, U.S.A.). The sample temperature was measured with an accuracy of ± 1 K. The line-shape parameters like peak frequency, full width at half-maximum (ν_f), and

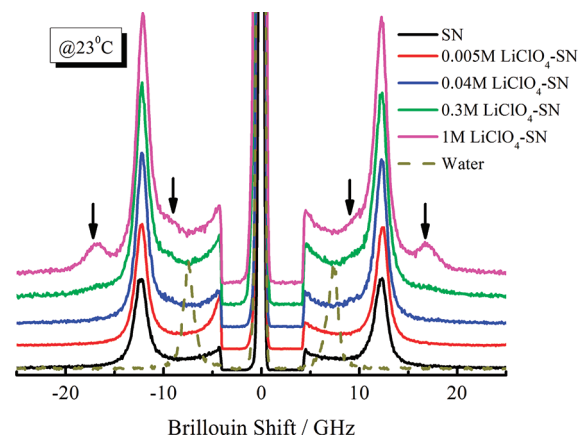


Figure 1. Room temperature (23 °C) Brillouin spectra of x -M LiClO₄–SN ($x = 0$ – 1 M) and water.

intensity were extracted by a nonlinear least-squares fitting of the data with a Lorentzian and when necessary with a Fano resonance function,²⁴ along with an appropriate background.

3. RESULTS AND DISCUSSIONS

Brillouin spectra of pristine SN and plastic crystalline electrolytes were obtained at various temperatures, covering the wide temperature range from plastic to normal crystalline phase. Figure 1 shows room temperature (at 296 K) Brillouin spectra of pure SN and x M LiClO₄–SN ($x = 0$ – 1) recorded using free spectral range of 30 GHz. The spectra display one well resolved Brillouin peak at ~ 12.2 GHz for all the samples. This mode is associated with the bulk longitudinal acoustic (LA) mode of pristine SN in the plastic phase, very similar to the observation by Masui et al.²² The disparity in the Brillouin shift could be related to the differences in the experimental geometry employed in the present work and that by Masui et al. Additionally, differences in the LA mode could also be attributed to the sample nature (crystalline or amorphous) and selected wave vector in the experiment. In the liquid to plastic transition, Masui et al. suggest that the trans–gauche population shows no change across the transition temperature. Instead there is a large change in the reorientation fluctuations. This is observed from the fwhm of the quasi-elastic mode which was three times higher in the liquid phase compared to the plastic phase. In order to observe the quasi-elastic mode in the plastic phase, one has to perform a high resolution Brillouin experiment. Since our interest in this manuscript was to look at the acoustic modes, we have not carried out high resolution experiments, and moreover the specular reflections from the sample increased the Rayleigh components. Using the present data as shown in the Supporting Information (Figure S1), we can observe the presence of the quasi-elastic mode in the plastic phase which disappears in the crystalline phase. This qualitatively suggests that there is a further decrease in the reorientation fluctuations in the crystalline phase. Masui et al.'s paper showed a very weak TA mode which we do not observe in the present work. Further, we could not get any idea regarding the intensity of the LA mode as this was not shown in their paper. All of these difference could also be attributed to the fact that Masui et al. used single crystal and polarized light for Brillouin experiments, whereas we have performed these experiments on an amorphous plastic crystal (SN) and unpolarized Brillouin experiments.

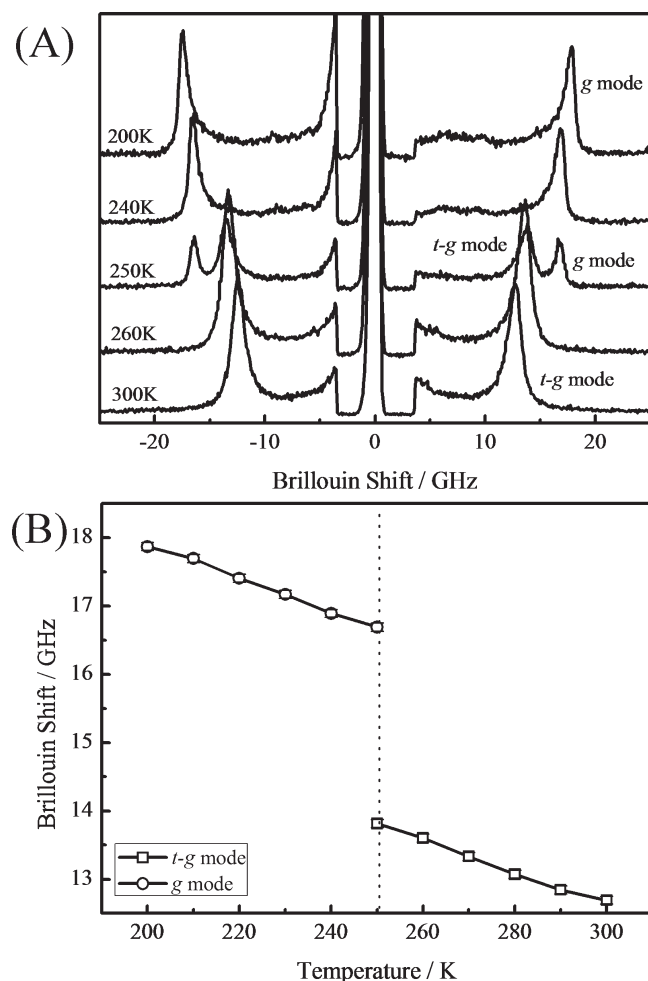


Figure 2. (A) Brillouin spectra of pristine succinonitrile at various temperatures and (B) temperature dependence of Brillouin peak positions for pure succinonitrile. The open square symbol with error bar in (B) represents the Brillouin shift for the t-g mode, and open circles with error bar symbolize g mode.

The present LA mode is attributed to the intrinsic trans–gauche isomerism of the solvent molecule. There is no appreciable change in the Brillouin peak position of this acoustic mode with addition of salt (see Figure 1). However, two additional modes appear with increase of salt concentration at around 9.4 and 17 GHz (shown by arrow in Figure 1), along with the main acoustic mode of succinonitrile, which becomes more eminent in the case of a predominantly high concentration of salt (1 M LiClO₄–SN).

Figure 2A shows Brillouin spectra for pristine SN at various temperatures spanning from the plastic to normal crystal transition point. The acoustic mode at 12.2 GHz signifies the presence of only one type of crystal structure in pristine succinonitrile at 300 K and is designated as the t-g mode. This mode shows a linear dependence of the mode frequency as a function of the temperature as shown in Figure 2B and is attributed to trans–gauche isomerism of SN molecules. An abrupt shift of the Brillouin peak to higher frequency with decreasing temperature indicates a transition from the liquid-like plastic phase (bcc, t-g mode) to a more solid-like monoclinic phase. The trans isomer has a significantly larger molecular envelope than the gauche isomer.²⁵ Hence the hardening of the acoustic mode arises due to

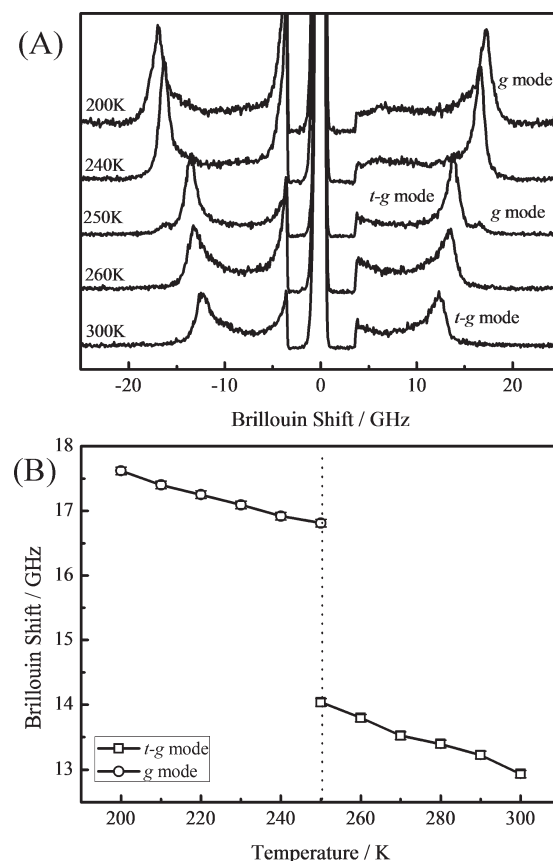


Figure 3. Temperature dependence of (A) Brillouin spectra and (B) Brillouin peak positions of 0.04 M LiClO₄–SN. The open square symbol with error bar in (B) represents the Brillouin shift for the t-g mode, and open circles with error bar symbolize the g mode.

the more compact gauche isomer. Below 250 K the single peak at around 17 GHz confirms the presence of the more solid-like and completely different crystal system (monoclinic) with predominantly all gauche conformation and is hereafter designated as g-mode. At 250 K, the coexistence of two Brillouin peaks (t-g and g modes) is ascribed to scattering of light from regions of different compressibility. This indicates the presence of two different types of crystal structures (bcc and monoclinic) at that temperature. In such a case, the lower-frequency peak could be assigned to the disordered (amorphous) phase, whereas the higher-frequency component could be a signature of the crystalline phase.

In Brillouin scattering, sampling is performed over a large number of molecules. Therefore, the t-g mode of SN at 300 K is associated with trans–gauche isomerism with a bcc crystal structure. Near normal to plastic crystalline transition temperature ($T_{np} \approx 250$ K), the higher frequency Brillouin mode (g mode) points toward the presence of more solid-like lattice structure with all gauche conformation while the presence of the low frequency mode (t-g mode) indicates persistence of mixed trans–gauche conformation phase. For $T < T_{np}$, the t-g mode disappears completely and high frequency g mode exists with monoclinic crystal structure. In general, the trans phase induces higher degree of disorder in the sample leading to faster dynamics. We speculate that with increase in temperature, i.e., with availability of more thermal energy, higher number of SN molecules will transform from the gauche to trans conformation. The availability of excess thermal energy and higher disorder

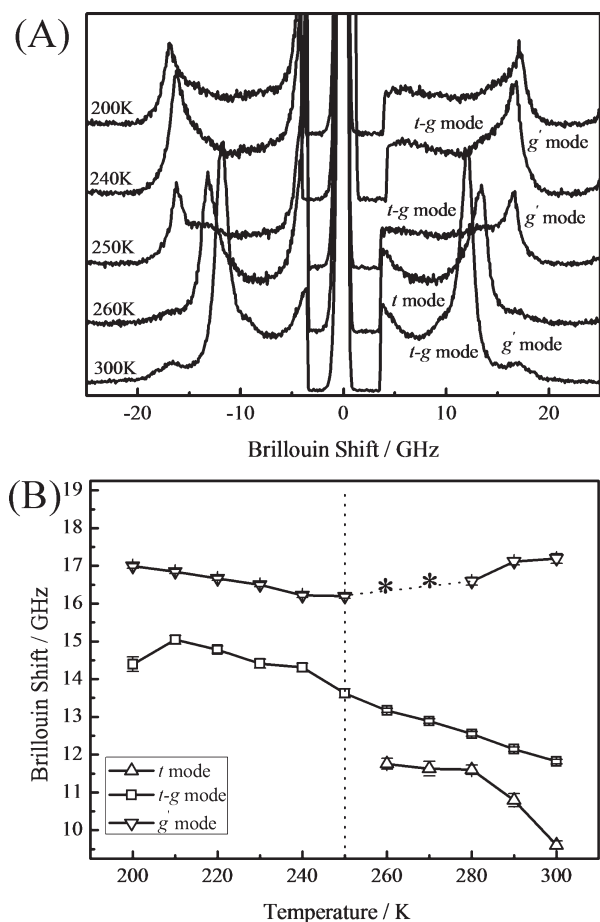


Figure 4. (A) Brillouin spectra of 1 M LiClO₄-SN at various temperatures. (B) Temperature dependence of Brillouin peak positions for 1 M LiClO₄-SN. The open up-pointing triangle with error bar in (B) represents Brillouin shift for *t*-mode, and the open square and open down-pointing triangles with error bar symbolize *t*-g and *g'* modes, respectively. The asterisk (*) stands for the value obtained from visualization due to poor fitting of the high frequency *g'* mode at relevant temperatures.

makes it easier for molecules in gauche conformation to transfer to trans phase. Decreasing temperature will result in an opposite effect transferring in more number of SN molecules in gauche phase. This accounts for the shift in frequency to higher values with lowering temperature as shown in Figure 2. A careful inspection of Figure 2A shows that below T_{np} all of the Brillouin peaks (*g* modes) are comparatively asymmetric in the low frequency side compared to the spectrum at 300 K. This asymmetric line shape can be accounted for by Fano resonance and which is attributed to the electron–phonon coupling phenomenon.²⁶ The spectra were fitted well with single Fano line shapes with exponential background $\{I = A[(q + \{2(\omega - \omega_c)/w\})^2]/(1 + \{2(\omega - \omega_c)/w\}^2) + A_1 \exp(\omega/B)\}$ where I = intensity, ω_c = resonance frequency, ω = frequency, w = line width, q = asymmetry parameter or Fano parameter, A_1 and B = constant; rather than Lorentzian function. Relatively low values of the Fano parameter ($q \approx 4.6$ at 200 K) suggest the presence of electron–phonon coupling at low temperature.

In general, pure SN freezes to a more compact predominantly all gauche conformation below T_{np} where the backbone electrons lose mobility and, hence, a reduction in conductivity.^{2,3,6,10} Thus

electrons couple with the lattice phonons. This would lead to stronger electron phonon coupling and, hence, a lower q value at low temperature in the case of pristine SN. Electrolytes with low salt concentration, i.e., 0.04 M LiClO₄-SN also show a behavior similar to pristine SN, but peaks were observed to be more asymmetric at higher temperatures (300 K, $q \approx 4$) than at lower temperature (200 K, $q \approx 7.6$) as shown in Figure 3A. This suggests stronger electron–phonon coupling at 300 K. For a 0.04 M LiClO₄-SN sample, the majority of Li⁺ ions are free and mobile. These ions show a lower degree of association.¹⁰ This introduces partial ordering in SN, leading to lower electron mobility. Due to this backbone electrons are more localized, and hence, there is an increase in electron–phonon coupling reflected by a decrease in the value of the asymmetry parameter (at 300 K, $q \approx 4$). On the other hand at low temperature (below 250 K), the solvent becomes more rigid, reducing Li⁺ ions mobility. To counter this part of Li⁺ ions get encapsulated in rigid SN network. The presence of Li⁺ ions influences the electrons, leading to lower electron–phonon coupling. This is manifested via a higher estimated value of the asymmetry (Fano) parameter (at 200 K, $q \approx 7.6$). This accounts for the asymmetric nature of Brillouin spectra as a function of temperature for the 0.04 M LiClO₄-SN samples.

In higher salt concentration regimes ($x = 0.3$ –1 M), the appearance of additional peaks at 300 K suggests the presence of a higher degree of disorder due to structural changes resulting from the presence of salt (Figure 4A). Apparently the Brillouin profile consists of three modes at 300 K for 1 M LiClO₄-SN such as (a) a central mode at 12.2 GHz (labeled as *t*-g mode), (b) a high frequency mode at 17 GHz (*g'* mode), and (c) a low frequency mode at 9.4 GHz (*t* mode). For $T > T_{np}$ triple Lorentzian functions with an appropriate background were used to fit the data, whereas for $T < T_{np}$ a double Lorentzian was used. The high frequency Brillouin mode (*g'* mode at 17 GHz) suggests rigidity inside the system. This rigidity is interpreted as a result of the interaction of the lithium ion present in the system with the electronegative cyano group of SN leading to formation of SN–Li⁺ adducts. Similar observations have been reported earlier based on in situ single crystal X-ray diffraction study and infrared spectroscopy.¹⁰ This type of interaction induces stiffness in certain portions of lattice which results in a broad Brillouin peak (*g'* mode) in high frequency regime. The stiffness resulting out of SN–Li⁺ adducts can be equated to rigid and compact crystal lattice which typically is a zone comprising of aggregation of gauche conformations. The appearance of the small hump in the low frequency regime (*t* mode at 9 GHz) could be due to the change in gauche to trans isomer ratio based on the new thermodynamics in the bulk SN phase.

Near the transition temperature (T_{np}) the intensity of the *t*-g mode diminishes significantly and the low frequency *t* mode completely disappears, whereas the high frequency *g'* mode becomes very prominent. This observation implies a decrease in all trans/mixed trans–gauche and an increase in all gauche conformations. However, the peak becomes very broad and asymmetric at $T < 250$ K. The broadening is attributed to the presence of SN in the trans conformation rather to Fano resonance effect. The 1 M LiClO₄-SN contains a high concentration of Li⁺ ions. The mobility of ions is extensively influenced by both the ion–solvent interaction as well as the association effect. Interaction of the ion with solvent will lower the electron–phonon coupling strength at 300 K, thus increasing the q value. Due to freezing of charge carriers below the transition

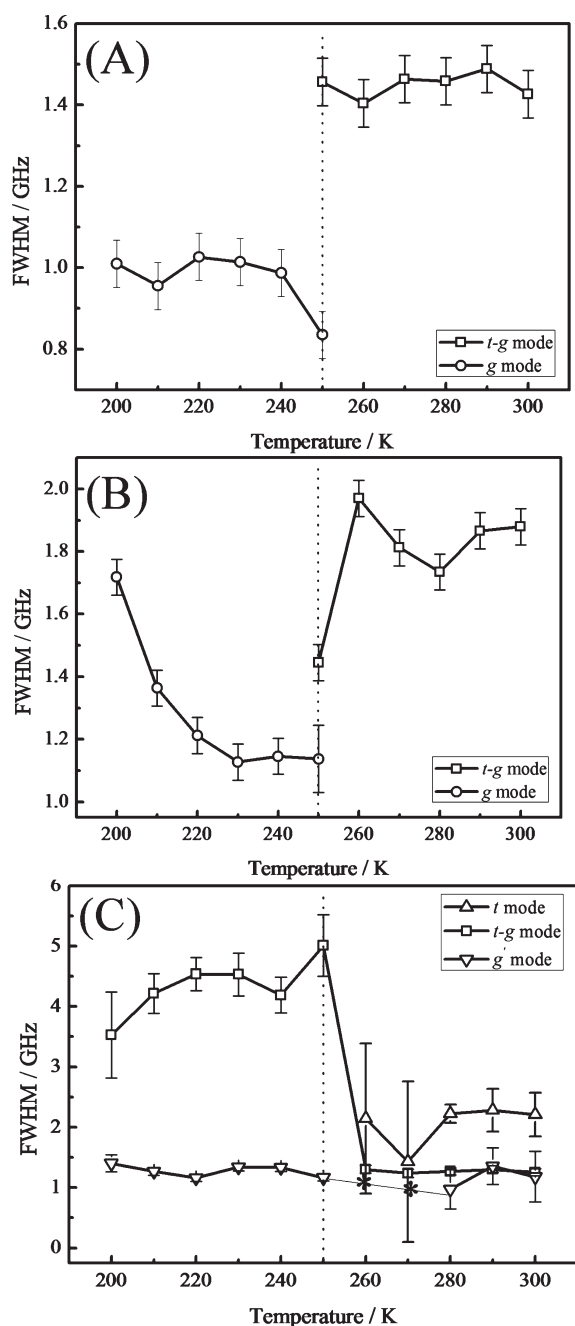


Figure 5. Temperature dependence of the ν_f of (A) pure succinonitrile, (B) 0.04 M LiClO_4 -SN, and (C) 1 M LiClO_4 -SN plastic crystalline electrolytes. The open up-triangle with error bar represents Brillouin shift for t mode, open square and open down-triangles with error bar symbolize t -g and g' modes, respectively. The asterisk (*) represents the value obtained from visualization due to poor fitting of the high frequency g' mode at relevant temperature.

temperature, we have more delocalized electrons and hence less electron-phonon coupling. Therefore, the q value is expected to be very high due to less coupling. However, using the Fano resonance function, we obtained very low values of asymmetry parameter q (~ 3). This observation rules out the influence of Fano resonance on the line shape in the case of 1 M LiClO_4 -SN electrolytes; instead these are well fitted with double a Lorentzian function. Therefore, in high salt concentration electrolytes, in

addition to highly compressed lattice zones with all gauche conformation (g' mode) there also exist disordered mixed trans-gauche conformation (t -g mode) zones which gives rise to reasonably broad asymmetry bands in the low frequency side. Here the asymmetry clearly indicates the presence of structural disorder in terms of trans isomer still below the transition temperature. Figure 4B depicts the temperature variation of the Brillouin shift for 1 M LiClO_4 -SN where the peak position does not show any significant amount of change with a decrease in temperature due to the presence of highly disordered trans phase in the structure below the transition temperature.

Figure 5 shows the temperature variation of the full width at half-maximum (ν_f) of pristine succinonitrile and plastic crystalline electrolytes. For all samples ν_f displays a significant change in magnitude in the proximity of T_{np} (250 K). The ν_f in t -g mode is higher than that in the g mode for pure SN, and the value decreases at 250 K as shown in Figure 5A. The decrease in ν_f is attributed to the transition of SN from a rotator (mixed trans-gauche) plastic crystalline to a rigid (predominantly gauche) normal crystalline phase. Shrinking of ν_f from room temperature to the transition temperature is a consequence of an increase in the lifetime (slow relaxation) due to a more compact structure. No further narrowing is observed for $T < 250$ K. The decrease in magnitude of ν_f with temperature for 0.04 M LiClO_4 -SN (Figure 5B) is expected to be due to the freezing of charge carriers into the lattice. However, the sharp increase in ν_f at much lower temperature ($T \approx 230$ K) is related to a decrease in the lifetime (fast relaxation). We envisage this relaxation process to be due to the coordination of Li^+ with SN. At temperature such as 230 K the system is very rigid similar to conventional crystalline solids. The SN- Li^+ is assumed to vibrate at frequencies similar to lattice vibrational frequencies ($\sim 10^{13}$) as in solid. Hence, the increase in ν_f is at ~ 230 K. It is interesting to observe the (Figure 5C) variation of ν_f with temperature for 1 M LiClO_4 -SN. Here, for $T < T_{np}$ full width at half-maximum for 1 M LiClO_4 -SN is considerably broader compared to that for the 0.04 M LiClO_4 -SN sample. This unusual increase in the ν_f below the transition temperature signifies very fast relaxation and attributed to presence of higher degree of disorder already present in the solid crystalline phase of 1 M LiClO_4 -SN samples. The trans phase induces higher degree of disorder in the sample leading to faster dynamics. The large value of ν_f is again a direct evidence of fraction of SN molecules existing in trans conformation below the transition temperature.

CONCLUSIONS

Various acoustic modes observed in Brillouin scattering demonstrate that there is a large influence of ion transport mechanism in succinonitrile-Li salt electrolytes with long wavelength phonon modes. An increase in the number of Brillouin modes in moving from pristine SN to LiClO_4 -SN electrolytes suggests the important role of ion-solvation and solvent-salt interaction on ion-transport. On the basis of the results discussed here, Brillouin spectroscopy is an invaluable tool for investigating solvent dynamics. The present study again confirms and supplements our line of approach of employing solution-chemistry based concepts over conventional solid state (defect) chemistry in comprehension of ion-transport in organic plastic crystalline solids. We envisage that such fundamental studies will further facilitate in designing electrolytes for electrochemical applications such as rechargeable lithium-ion batteries.

■ ASSOCIATED CONTENT

S Supporting Information. Addition figure showing the masking of Rayleigh and Brillouin peaks observed in the experiment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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