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STRUCTURE, MORPHOLOGY, THERMAL AND CONDUCTIVITY PROPERTIES OF GEL ELECTROLYTE SYSTEM BASED ON POLYVINYL CHLORIDE AND LiClO4

The dynamics of atoms and molecules in gel electrolyte based on polyvinyl chloride and a solution of $LiClO_4$ in propylene carbonate was studied by the method of quasielastic scattering of slow neutrons. The coefficients of self-diffusion of atoms and molecules are determined and a possible variant of the mechanism of charge transport in this system is proposed.

Keywords: solid polymer electrolytes, polyvinyl chloride, X-ray scattering, calorimetric scattering, quasi-elastic neutron scattering.

Introduction

Solid Polymer Electrolytes (SPE) have received wide attention for applications as materials for various electrochemical devices such as light-weight, rechargeable Li batteries, displays, Smart windows and sensors [1, 2]. However, to achieve the performance level of conventional liquid electrolyte-based Li batteries SPEs must exhibit high conductivity at room temperature. Two broad classes of polymer electrolyte materials satisfy this requirement. The first group consists of solvent-free, conventional SPEs containing Li salt. The second group consists of electrolytes, which contain, in addition to the polymer host and Li salt, a significant proportion of liquid solvents, termed plasticizers (gel SPEs). At present, gel SPEs have conductivity levels of 10^{-3} S/cm and are widely used for SPE-based rechargeable batteries among the polyvinyl chloride (PVC) based ones [2 - 5]. However, in spite of the fact that large use is currently made of gel SPEs in practical high-density, advanced batteries, their fundamental behavior at molecular level and their structure/morphology peculiarities have not been completely clarified. Here, we present the data of X-ray scattering, calorimetric and quasi-elastic neutron scattering investigation of the polymer gel electrolytes based on PVC.

Gels have unique functional properties and are widely used in industry, particularly in medicine, for the production of photosensitive materials and power supplies. The specific properties of gels lie in the structural features of polymers – the ability to form highly porous compounds with different pore sizes in which liquid, in particular, can be placed. The dynamics of atoms and molecules of the liquid in such pores to a greater extent forms macroscopic characteristics of the gels. The energy of the motions of atoms and molecules in the condensed matter is small and is located in the thermal region. It is convenient to study this energy range by neutron spectroscopy, in frequency, using quasi-elastic slow neutron scattering (QENS).

Experiment

Glass transition temperatures of PVC-PC and PVCPC-$LiClO_4$, gels as well as their components PVC, PC and PC-$LiClO_4$ solutions were studied by the DSC technique (DuPont 1090 unit) with heating rate of 16 K/min. Polymer gel electrolytes based on 20 % PVC and containing 80 % of propylene carbonate (PC)-$LiClO_4$ solution (0.18 g $LiClO_4$ – for 1.5 ml PC) as the liquid phase were prepared using tetrahydrofuran (THF) as a common solvent of the compounds involved.

Structure and morphological properties of the above-mentioned systems were studied by wide-angle X-ray scattering (WAXS) using DRON-2.0 apparatus and small-angle X-ray scattering (SAXS) using the Kratky-type camera.

Conductivity data of the gel electrolytes were obtained using impedance test.

The self-diffusion processes of pure PC and PC-$LiClO_4$ solution in the free state and in the pore of PVC gels were studied by quasi-elastic neutron scattering technique (QENS).

QENS measurements were performed using a multidetector time-of-flight spectrometer NURMEN which is realized on atomic reactor of Institute for Nuclear Research, National Academy of Sciences of Ukraine.

The QENS spectra for different scattering angles were obtained for 17 h for each sample at a temperature of 295 K. The procedure for extracting information on the dependence of the energy broadening of the quasistable peak (ΔE) on the square of the transmitted momentum (k^2) from the QENS spectra is the following.

The quasi-elastic peak for each value of k^2 is approximated by the Lorentz curve and the values of the maximum intensity of the peak and peak width at half of its height are determined. From a definite value of ΔH, the width of the spectral line corresponding to the time resolution of the experimental setup is subtracted. The value of H_0 is determined from the experiments on the scattering of slow neutrons by vanadium.

The difference $\Delta H(k^2) = H(k^2) - H_0(k^2)$, measured in units of time, obtained for each k^2 value, is converted into energy units (MeV): $\Delta H(k^2) \to \Delta E(k^2)$. Further calculation of the characteristics of the dynamics of atoms and molecules in the samples was carried out according to the scheme given below.

The dependence $\Delta E(k^2)$ has the form

$$\Delta E\left(k^2\right) = \frac{h}{\pi \tau_0}[1 - \frac{\sin(kl)}{kl} exp\left(-2W\right)] + \frac{h}{\pi}D_l k^2, \quad (1)$$

where h – Planck's constant; τ_0 – the lifetime of atoms (molecules) in the vibrational state; $exp(-2W)$ – Debye - Waller factor; l – the length of the atomic jump

$$l^2 = 6D_f \cdot \tau_0, \quad (2)$$

where D_f, D_t – the diffusion coefficients and the diffusion of the Lagrangian particle, respectively.

The Debye - Waller factor takes into account the contribution of the vibrations of atoms (molecules) and is related to the maximum intensity of neutron scattering and the square of the transmitted momentum by the following relation:

$$I_0\left(k^2\right) \sim exp\left(-2W\right) \sim exp\left(-x^2 k^2\right). \quad (3)$$

The constant x^2 is proportional to the mean-square deviation of atoms or molecules from the equilibrium position because of thermal oscillations:

$$x^2 = \frac{1}{1 + ... + (n-1)} \sum_{i=l}^{n-1} \sum_{j=1}^{n} \frac{\ln I_0(k_j^2) - \ln I_0(k_i^2)}{k_i^2 - k_j^2}, \quad (4)$$

where n – the number of detectors used in the experiment. Knowing x^2, we determine the Debye - Waller factor. Then for large values of k^2 ($k^2 \to \infty$) we obtain

$$\Delta E\left(k^2\right) = \frac{h}{\pi \tau_0} + \frac{h}{\pi}D_l k^2. \quad (5)$$

The accuracy of this approximation is $\geqslant 95$ %. Differentiating (5) with respect to k^2, we find the value of the diffusion coefficient of the Lagrange particle

$$D_l = \frac{\pi}{h} \cdot \frac{\partial(\Delta E)}{\partial(k^2)}. \quad (6)$$

Determining D_l from (5), we determine the value τ_0.

For small values of k^2 ($k^2 \to 0$), using formula (1) we obtain

$$\Delta E\left(k^2\right) = \frac{h}{6\pi \tau_0} + \frac{hk^2 D_l}{\pi} \quad (7)$$

and taking into account (2),

$$\Delta E\left(k^2\right) = \frac{hk^2}{\pi}(D_f + D_l) = \frac{hk^2}{\pi}D, \quad (8)$$

where D – total diffusion coefficient.

Differentiating (8) with respect to k^2, we find the value of D

$$D = \frac{\pi}{h} \cdot \frac{\partial(\Delta E)}{\partial(k^2)}. \quad (9)$$

The accuracy of approximation (7) is $\geqslant 90$ %.

Results

Thermograms of PVC film cast from the THF solutions and annealed at 273 K for 8 h in vacuum show glass transition temperature, Tg, of 333 K. One can point out that this value corresponds to far lower temperature compared to Tg, of the starting powdered PVC sample (358 K). Thus, the sample studied contains some amount of THF.

This finding is an evidence in favor of the well-known notion of complex forming of low molecular esters/ethers with electron - accepting groups of PVC [6].

Fig. 1 shows the DSC curves of PC and the PC-LiClO$_4$, PVC-PC and PVC-PC-LiClO$_4$ samples. As one can see, pure PC is characterized by a glass transition jump of heat capacity at 164 K. In the case of the system PVC-PC one can observe an increase of glass transition temperature to 167 K that is certainly related to glass transition of PC confined in micropores of PVC matrix. It is interesting that after incorporating PC into the micropores of PVC, the glass transition is increased by 3 K. The addition of salt to the PVC-PC system results in raising T_g of both the pure PC and PVC-PC gel by 10 K to 174 and to 177 K, respectively.

The WAXS curve of PVC film prepared from THF solution and dried and annealed after this at 373 K in vacuum displays slight crystalline reflexes

that are in accordance with the literature data of PVC [7]. They are diffused enough because of the small size of the crystallites, of about 1 nm, as it is characteristic of PVC [8].
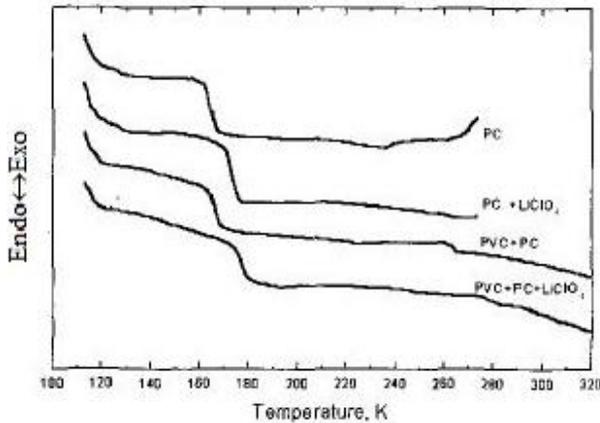

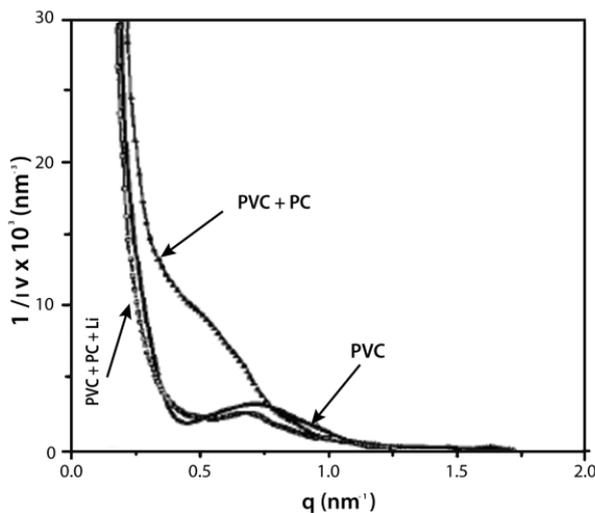Fig. 1. DSC curves of the gel electrolytes based on PVC.

Fig. 2. Small-angle scattering curves of the sample studied.

The SAXS data of pure PVC and PVC-PC and PVC-PC-LiClO$_4$ systems are presented in Fig. 2. In the case of pure PVC one can observe the well pronounced interference maximum that corresponds to a Bragg distance of about 8.7 nm. The curve of the PVC sample obtained by casting from PVC-PC-THF solution shows the slightly pronounced SAXS maximum that corresponds to periodicity values of about 12.0 nm. The SAXS curve of the PVC-PC-LiClO$_4$, system is characterized by the Bragg distance value of about 9.3 nm. This indicates that the gels involved consist of microdomains of a different composition. Those are most likely to be the polymer- and solvent-rich ones and results from both liquid-solid and liquid-liquid phase separation processes, as it usually occurs in the PVC-solvent systems [8]. Thus, the gel system studied is of heterogeneous structure.

Fig. 3 represents three-dimensional correlation functions that are calculated from the SAXS curves

presented in Fig. 2 using FFSAXS-program [9]. The curves of the pure PVC and the PVC-PC gel display diffused maximum at 9.0 and 12.0 nm, respectively. The correlation curve of the PVC-PC LiClO$_4$ system, contrary to the corresponding SAXS curves, displays two phenomena. These are, a presence of the maximum that is characteristic of the pure PVC matrix situated at somewhat lesser radial distance of 6.0 nm, and the maximum of PC riches regions that is characteristic for PVC-PC gel at 12.0 nm.
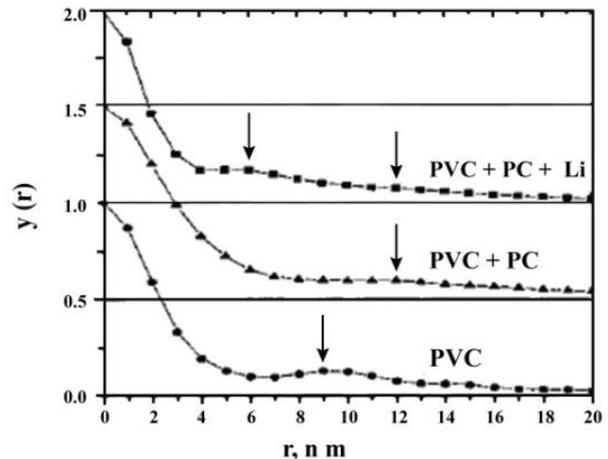

Fig. 3. Three-dimensional correlation curves of pure PVC, PVC-PC and PVC-PC-LiClO$_4$ systems.

Table 1 represents both the electron density values of the samples investigated, calculated from general formulations for the initial components of the samples investigated and the values of the mean square of the electron density difference calculated from SAXS data curves presented in Fig. 2. One can see that the significant increase of PVC-PC gel heterogeneous structure contrast occurs after introducing LiClO$_4$.

Table 1. **Electron density and mean square of electron density values of the samples investigated**

Sample	ρ_{el}, el^6/nm^3	$\Delta\rho_{el}^{2r}$, el^6/nm^3
PVC	431,5	66,2
PC	383,7	
LiClO$_4$	621,8	
PC-LiClO$_4$	407,5	
PVC-PC		96
PVC-PC-LiClO$_4$		169,8

Using the data of the impedance test in the Li-MnO$_2$ system it was shown that the conductivity of the PVC-PC-LiClO$_4$ gel electrolyte is $5 \cdot 10^{-4}$ S/cm at room temperatures. This value is in excess of the conductivity for liquid ($\sim 3 \cdot 10^{-4}$ S/cm) [10, 11] and solid ($\sim 10^{-5}$ S/cm) [12, 13] electrolytes. Single-particle and collective dynamics of solvent molecules (PC and PC-LiClO$_4$) in free state and in the pores of polymer gels based on PVC in the ranges of observation times 10^{-10} - 10^{-12} s were determined by quasi-elastic neutron scattering technique. In the

QENS experiments a monochromised neutron beam with energy $E_0 = 12.97$ MeV was used. The neutron spectra were recorded over a range of scattering angles $\Theta = 9.5 - 101.3^0$.

Typical QENS spectra are presented in Fig. 4.

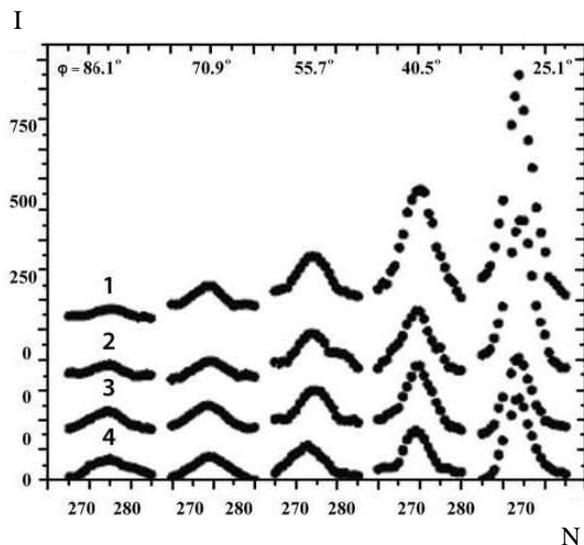Using QENS data, the information on microscopic dynamics of liquid molecules may be extracted from

the energy broadening of quasielastic neutron peaks measured at different values of the wave vector transfer $k = (4\pi/\lambda) \sin(\Theta/2)$, where h is the neutron wavelength. The energy broadening ΔE was measured at the middle of quasielastic neutron peak height. The plots of ΔE vs k^2 for the system studied are given in Fig. 5.
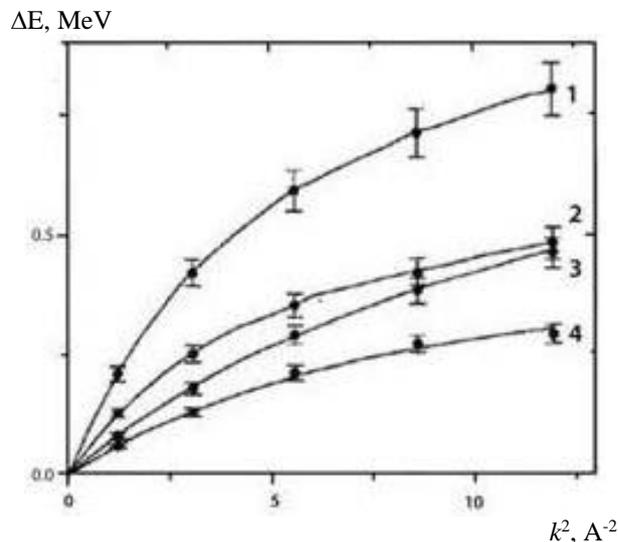
I

N

Fig. 4. QENS spectra of the sample studied. 1 - PC; 2 - PC-LiClO$_4$; 3 - PVC-PC; 4 - PVC-PC-LiClO$_4$. I - counts per channel; N - number of analyzer channel. Energy values, energy of incident neutron beam $E_0 = 12.97$ MeV. E - energy of scattered neutron beam: 2 MeV for channel number N = 260, 0 MeV for N = 275, and 0.5 MeV for N = 280.

ΔE, MeV

k^2, A^{-2}

Fig. 5. The plots of ΔE vs k^2 of the sample studied. 1 - PC, 2 - PC-LiClO$_4$, 3 - PVC-PC, 4 - PVC-PC-LiClO$_4$.

Further QENS data were interpreted by an approach which accounts for the hierarchy of time scales of molecular motions: slow collective motions of liquid molecules contained in Lagrange's clusters and rapid single-particle motions (Frenkel's jump diffusion) [14]. Using QENS data at large and small values of the wave vector transfer the total self diffusion coefficients D and its collective D_l, and single-particle D_f, parts were determined. D, D_l and D_f as well as characteristic time τ_0 data are represented in Table 2.

Table 2. **Diffusion of atoms and molecules in the samples investigation**

Sample	D 10^{-5} cm^2/s	D_f 10^{-5} cm^2/s	D_l 10^{-5} cm^2/s	τ_0 10^{-12} s
PVC-PC	0,86	0,53	0,33	3,40
PVC-PC-LiClO$_4$	0,52	0,41	0,11	4,90
PC	0,32	0,20	0,12	5,76
PC-LiClO$_4$	0,24	0,20	0,04	5,08

It follows that the total self-diffusion coefficient of liquid molecules decreases with increasing PVC content in the gel systems and with increasing of salt

concentration. The analysis of the diffusion data shows that the charge carrier motions in the PVC-PC-LiClO$_4$ systems can be described by the mechanism of continual diffusion of the PC-LiClO$_4$ in the content of Lagrange's clusters and the jump diffusion of single molecules.

Conclusions

X-ray scattering, calorimetric, and quasi-elastic neutron scattering investigations of the polymer gel electrolytes systems consists from polyvinyl chloride, propylene carbonate and LiClO$_4$. It was established that after incorporating PC into the micropores of PVC gels the glass transition of PC increased by 3 K. This is, evidently, a reflection of an effect of confining liquid PC in the pores of PVC microphase-separated morphology. Addition of salt to the PVC-PC system results in raising T_g, of both the pure PC and PVC-PC gel by 10 K. The SAXS data of pure PVC, PVC-PC and PVC-PC-LiClO$_4$ indicate that the gels based on PVC consist of microdomains of a different composition. Single-particle and collective dynamics of solvent molecules in free state and in the pores of polymer gels based on PVC were studied by quasi-elastic neutron scattering technique.

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СТРУКТУРА, МОРФОЛОГІЯ, ТЕРМІЧНІ ТА ЕЛЕКТРОПРОВІДНІ ВЛАСТИВОСТІ ГЕЛЕВОЇ ЕЛЕКТРОЛІТНОЇ СИСТЕМИ НА ОСНОВІ ПОЛІВІНІЛХЛОРИДУ ТА LiClO₄

Досліджено динаміку атомів і молекул у гелевому електроліті на основі полівінілхлориду та розчину $LiClO_4$ у пропіленкарбонаті методом квазіпружного розсіювання повільних нейтронів. Визначено коефіцієнти самодифузії атомів і молекул та запропоновано можливий варіант механізму переносу заряду в цій системі.

Ключові слова: тверді полімерні електроліти, полівінілхлорид (ПВХ), рентгенівське розсіювання, калориметричне розсіювання, квазіупружне розсіювання нейтронів.

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СТРУКТУРА, МОРФОЛОГИЯ, ТЕРМИЧЕСКИЕ И ЭЛЕКТРОПРОВОДНЫЕ СВОЙСТВА ГЕЛЕВОЙ ЭЛЕКТРОЛИТНОЙ СИСТЕМЫ НА ОСНОВЕ ПОЛИВИНИЛХЛОРИДА И LiClO₄

Исследована динамика атомов и молекул в гелевом электролите на основе поливинилхлорида и раствора $LiClO_4$ в пропиленкарбонате методом квазиупругого рассеяния медленных нейтронов. Определены коэффициенты самодиффузии атомов и молекул, предложен возможный вариант механизма переноса заряда в этой системе.

Ключевые слова: твердые полимерные электролиты, поливинилхлорид (ПВХ), рентгеновское рассеяние, калориметрическое рассеяние, квазиупругое рассеяние нейтронов.