Effect of C_{60} as a Filler on the Morphology of Polymer−Salt Complexes Based on Poly(ethylene oxide) and $LiCF_3SO_3$

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ABSTRACT: The inclusion of C_{60} as a filler in complexes of poly(ethylene oxide) (PEO) and $LiCF_3SO_3$ salt reduces the degree of crystallinity of the material at ambient temperature. The observed effects are manifested as changes in characteristic vibrational modes of the crystalline polymer in FT-Raman spectra over a range of temperatures. The introduction of relatively small amounts of C_{60} also stabilizes ionic substructures present in these systems. Interestingly, no internal modes of the C_{60} molecule are affected by dissolution in PEO or by the presence of varying amounts of $LiCF_3SO_3$ salt in the matrix. From the absence of a shift in the C_{60}:s charge-transfer-sensitive $A_g(2)$ mode, in particular, it appears as though C_{60} essentially acts as an inert filler in these complexes.

Introduction

Investigations of ionically conducting polymer−salt complexes are currently at focus primarily due to a great potential for a range of electrochemical applications including solid thin-film batteries.[1,2] These materials are typically based on various polyethers, such as poly(ethylene oxide) (PEO), into which several inorganic salts are readily dissolved.[3,4] Some major drawbacks of current *polymer electrolytes* stem from the fact that the archetypal host polymer PEO, which has a superior ability to adopt a range of local chain conformations and thus accommodate dissolution of various alkali metal salts,[5] tends to crystallize at ambient temperature.[6] The phase diagram of the PEO−$LiCF_3SO_3$ system shows that pure PEO melts at ~60 °C; a complex of composition $P(EO)_3LiCF_3SO_3$ melts at ~179 °C.[7] Thus, below ~60 °C the electrolyte is a mixture of three phases: a crystalline phase of pure PEO and the stoichiometric compound, both embedded in a minority salt-containing amorphous phase.[8,9]

Since ion transport occurs in amorphous regions of the solutions,[9] this propensity for crystallization at ambient temperature largely precludes use of these PEO-based materials in actual applications. Routes to suppress the formation of crystalline (nonconducting) domains, thus lowering the possible operating temperatures of devices, include the incorporation of various organic solvents (e.g., EC, PC, DMF, DMSO, etc.).[10] These additives act as *plasticizers*, thus enhancing local polymer chain flexibility (i.e., lowering of the systems glass transition temperature, T_g) and, in some cases, also promoting further dissociation of the salt into free charge carriers.[11] Notable problems with this approach are the tendencies of such liquid organic low-molecular-weight additives to promote deterioration of the mechanical properties of the solid electrolyte and to slowly react with lithium electrodes in actual applications.[12,13]

In view of these shortcomings, there is currently an upsurge in interest for the addition of finely divided inorganic fillers to polyether−salt complexes. The overriding goal is to enhance ion transport at relatively low temperatures, while maintaining good mechanical properties.[11,14−17] The enhancement of ionic conductivity has been related to a decrease in the fraction of crystalline PEO present in the complexes. Notably, an apparent enhancement of the lithium ion transference number has recently been interpreted in terms of preferred transport routes involving acidic boundaries of ceramic fillers.[12] Similarly, the addition of polyacrylamide to semicrystalline PEO-based electrolytes has been shown to increase conductivity; yet, in this case the enhancement was associated with interphase phenomena between the organic filler and the polyether matrix.[18] Seminal work by Bruce and co-workers led to the establishment of the crystal structure for the complex formed between PEO and $LiCF_3SO_3$, $P(EO)_3$-$LiCF_3SO_3$.[19] Frech and co-workers have recently extensively studied this system, and various plasticized derivatives thereof, using vibrational spectroscopic methods.[10,20,21] Torell and co-workers have also investigated ionic configurations in HMW PEO complexed with MCF_3SO_3 (M = Na, Li) using Raman scattering techniques.[22]

In the present paper we investigate how an inclusion of small amounts of the symmetric C_{60} molecule affects the degree of crystallinity and ion solvation properties in the PEO−$LiCF_3SO_3$ system. Thus far, at least to our knowledge, C_{60} has only been used as the electrode material in electrochemical applications,[23] due to the relative ease with which for instance Li can be electrochemically intercalated up to stoichiometries of $Li_{12}C_{60}$.[24]

Experimental Section

Composite polymer electrolytes were prepared by dissolving C_{60} in C_7H_8 (toluene) (the former is dissolved when the solution turns purple) and PEO and $LiCF_3SO_3$ in CH_3CN (acetonitrile) under an inert argon atmosphere. The salt had previously been dried under dynamical vacuum at 373 K for 24 h. The solutions were then mixed to desired [O:Li:C_{60}] ratios (i.e., [300:20:1], [100:20:1], and [15:1:0] in the present study) and stirred on a magnetic hot plate (T ~ 350 K) while volatile solvents were allowed to slowly evaporate. After 12 h these mixtures were transferred to a vacuum chamber in which they were further

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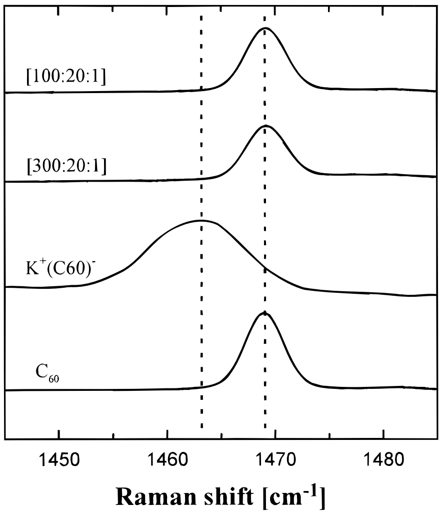

Figure 1. Raman spectra of composite electrolytes of compositions [100:20:1] and [300:20:1], the charged $(C_{60})^-$ molecule and pristine C_{60}, respectively, in the region including the $A_g(2)$ mode of C_{60}. The characteristic charge-transfer-sensitive shift of the $A_g(2)$ mode is indicated by dotted lines. Data for the $K^+(C_{60})^-$ complex are taken from preliminary studies in this laboratory.[28]

dried under dynamic vacuum for a period of 36 h. Finally, the electrolytes were transferred to quartz quvettes and sealed under argon atmosphere.

FT-Raman spectra were recorded using a Bruker IFS 66 with a Raman module FRA 106 and a continuous Nd:YAG laser (1064 nm) in a 180° backscattering geometry at four different temperatures (20, 50, 80, and 100 °C). The spectra are averages of several recordings with a total acquisition time varying from 10 to approximately 50 h. To optimize signal-to-noise ratios with respect to peak separation and acquisition time, a wavenumber resolution of 3 cm^{-1} was used in conjunction with the Happ–Genzel apodization function. The incident laser power was reduced to ca. 30–40 mW, depending on composition, due to the very strong Raman intensity stemming from the $A_g(2)$ mode of C_{60} ("the pentagonal pinch mode") at 1469 cm^{-1}. Given such a low power and a relatively diffuse focus in conjunction with the opaque nature of these samples, we conclude that laser-induced heating effects were negligible in this study. To allow for isothermal conditions, the cuvette containing the sample was placed in an evacuated thermostat with an estimated temperature stability of ±0.2 °C; the sample was allowed to equilibrate at the desired temperature for at least 1 h prior to measurement.

Results and Discussion

The intramolecular $A_g(2)$ mode of C_{60} ("the pentagonal pinch mode") at 1469 cm^{-1} is well-known to shift to lower wavenumbers with decreasing molecular symmetry due to polymerization[25] or charge transfer.[26] This makes it a good probe of possible chemical interactions between C_{60} and the constituents of the PEO–salt complexes. Due to the strongly electronegative nature of the C_{60} molecule,[27] a possible charge transfer could originate in the negatively charged $CF_3SO_3^-$ anion. The Raman spectra shown in Figure 1 reveal no such downshift in wavenumber for the $A_g(2)$ mode—as a point of reference we also include spectra of pristine C_{60} and a $K^+(C_{60})^-$ complex.[28] Hence, it appears as though C_{60} essentially acts as an inert filler in these polymer/salt complexes or that complexes formed are highly symmetric. We further note that no other internal modes of the C_{60} molecules were significantly affected upon dissolution in PEO, nor were any changes observed with varying salt content.

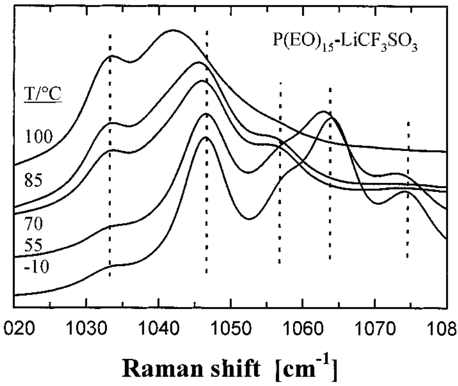

Figure 2. Raman spectra of $P(EO)_{15}LiCF_3SO_3$ as a function of temperature in the region including the characteristic $\nu_s(SO_3)$ mode of the $CF_3SO_3^-$ anion and bands stemming from the crystalline PEO. Dotted lines are drawn as guides to the eye and correspond to bands discussed in the text.

To understand the effects of C_{60} on the vibrational modes of the anion and the polymer host in the PEO–$LiCF_3SO_3$–C_{60} complexes, we begin by analyzing the temperature dependence of ion–ion interactions in a pure polymer/salt complex (ether oxygen to Li^+ to C_{60} ratio [15:1:0]). The symmetric SO_3 stretching mode, $\nu_s(SO_3)$, of the $CF_3SO_3^-$ anion is known to shift in wavenumber when the local chemical environment of the anion is changed.[29,30] The component at ~1032 cm^{-1} has been assigned to "free anions" not interacting directly with lithium cations, while components at ~1042 and ~1052 cm^{-1} have been attributed to contact ion pairs/negatively charged $[Li(CF_3SO_3)_2]^-$ triplets and positively charged $[Li_2CF_3SO_3]^+$ triplets, respectively.[27,30,31]

According to Figure 2, the relative abundance of "free" anions increases with increasing temperature in the range from −10 to 100 °C for the [15:1:0] complex, assuming that the ~1034 cm^{-1} mode has the same origin as the ~1032 cm^{-1} mode from assignments made in ref 27. In common polyether/salt systems, an increase in temperature typically promotes ion aggregation,[32] eventually leading to salt precipitation.[33] In the present semicrystalline system, however, the temperature dependence of the ionic speciation (i.e., a dissociation as inferred from Figure 2) is dominated by the phase behavior of the electrolyte. Notably, the mere existence of "free" anions is contrary to what Frech and co-workers[9] and also Torell and co-workers[22] have reported for similar systems. In this context, we wish to draw attention to recent studies on an analogue oligomer electrolyte where increasing temperature, as well as *decreasing* salt content, led to an increasing relative abundance of associated ionic species.[34] These findings were also correlated to ionic transport properties for the same samples, showing that spectroscopic data regarding the ionic substructure do have a direct bearing on conductivity and diffusion coefficients despite vast differences in time scales probed with the different techniques.[34] The strong 1046 cm^{-1} band apparent in Figure 2 is, however, not covered by the above assignments,[27,30] but it is most probable that this is the $\nu_s(SO_3)$ mode corresponding to the crystalline $P(EO)_3LiCF_3SO_3$ phase; this interpretation agrees with conclusions drawn by Frech and co-workers from infrared spectroscopic studies.[18] At higher temperatures, i.e., over 85 °C, this band shifts to ~1042 cm^{-1}, assigned to contact ion pairs by Frech and co-workers.[30] It is to be noted that the $\nu_s(SO_3)$

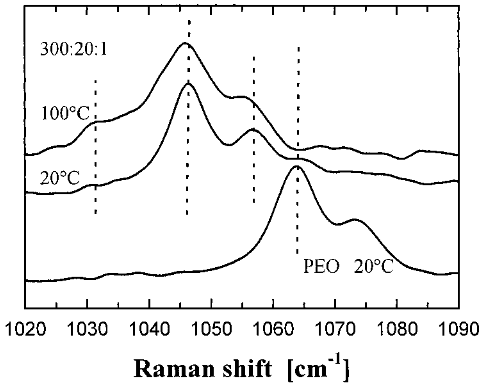

Figure 3. Raman spectra of the composite electrolyte of composition [300:20:1] covering the same region as in Figure 2. The spectrum corresponding to pure (polycrystalline) PEO is also included. Dotted lines indicate spectral bands discussed in the text.

1042 cm^{-1} band also may include contributions from negatively charged triple ion configurations with a similar geometry as for the ion pair.[30,31] A distinct band at ~1056 cm^{-1}, previously reported by Torell and co-workers,[20] gradually shifts to lower wavenumbers with increasing temperature, while bands at ~1064 and ~1074 cm^{-1} which originate in the crystalline PEO,[35] as expected, disappear at temperatures above 60 °C, i.e., when the pure PEO phase has melted.

In Figure 3, the same spectral region for the [300:20:1] compound at 20 and 100 °C together with that of pure PEO at 20 °C is presented. The relative abundance of "free" anions still increases with increasing temperature, but it is worth noting that a component which was located at ~1034 cm^{-1} in the [15:1:0] sample now is found at ~1032 cm^{-1}. The strong ~1046 cm^{-1} band, which was shifted down to ~1042 cm^{-1} at temperatures exceeding 85 °C in the "fullerene free" sample, is unaffected even at 100 °C when C_{60} is present. In view of the strongly electronegative nature of the C_{60} molecule,[27] it is plausible that C_{60} molecules act as cross-linking centers for (basic) PEO segments. If such a process reduces the segmental flexibility of the PEO host matrix, this would stabilize the ionic substructure of the $P(EO)_3LiCF_3SO_3$ stoichiometric phase. Another important observation is that the ~1064 and ~1074 cm^{-1} bands, stemming from coupled skeletal stretching modes (C−O and C−C) and CH_2 stretching modes of the polymer,[29] which were prominent in the [15:1:0] compound, are greatly suppressed in the [300:20:1] compound even far below the melting temperature of the pure PEO phase. It thus appears as though C_{60} breaks up the crystalline structure of this phase. Any coordinations involving the C_{60} molecule and basic polyether segments must be of a highly symmetric nature since we observe no changes in the sensitive intrinsic modes of the fullerene filler; see Figure 1.

Figures 4 and 5 present the "PEO CH_2 region" in which Raman bands at ~845 and ~861 cm^{-1}, respectively, are attributable to the crystalline PEO phase,[29] while the band at ~871 cm^{-1} stems from cation−PEO coordinations.[20,22,36−38] This region also shows that the crystalline PEO phase is suppressed by the inclusion of C_{60}. In particular, this is manifested by a marked relative decrease of the (low temperature) crystalline PEO bands at ~845 and ~861 cm^{-1} as compared to the band at ~871 cm^{-1} (i.e., Figures 4 and 5). Yet another indication of the stabilizing effect of C_{60} on the polymer/salt structures at high temperatures, i.e., at 100 °C, is found through the observation of the ~871 cm^{-1} mode in the [300:20:1] complex over the entire temperature range in Figure 4. We further observe that the band at ~762 cm^{-1}, attributed to the symmetric CF_3 bending mode, $\delta_s(CF_3)$, in $[Li_2CF_3SO_3]^+$ triple ion configurations,[21,30] remains essentially unaffected by increasing temperature when C_{60} is present. This is in contrast to the temperature-dependent shift to lower wavenumbers apparent for the [15:1:0] complex. Thermomechanical and solid-state NMR studies in conjunction with ac-impedance investigations are currently under way in an attempt to determine how the ionic transport mechanisms are influenced by the presence of the structure-breaking C_{60} molecule. The decrease in crystallinity is expected to enhance ionic mobility at relatively lower temperatures. Stabilization of ionic substructures, however, may have an adverse effect on ion transport properties. Still, we note recent reports where the inclusion of acidic ceramic fillers have led to enhancements of the transference number of lithium cations in related composite electrolytes.[12] Moreover, we have recently shown that a greater degree of ionic clustering is associated with a much more efficient ion-transport mechanism in salt-rich PAN−$LiCF_3SO_3$ complexes.[39]

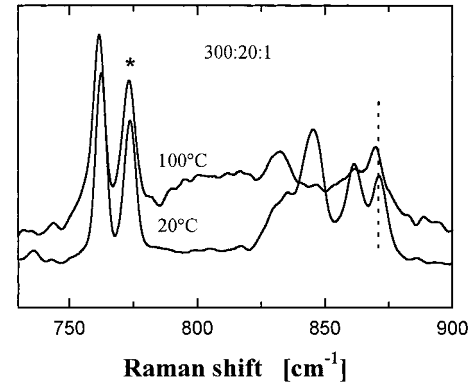

Figure 4. Raman spectra of the region ~720−900 cm^{-1} for the same compound as in Figure 3 at temperatures indicated in the figure. The asterisk indicates a band at ~774 cm^{-1} that originates in the $H_g(4)$ mode of the C_{60} molecule.[40]

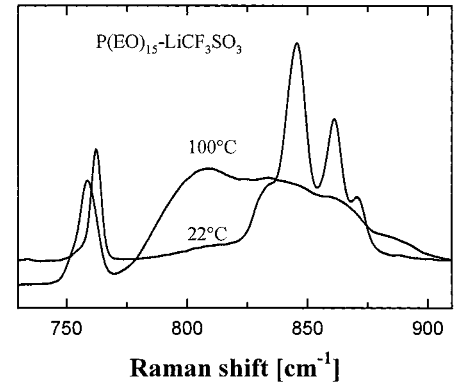

Figure 5. Same spectral region as in Figure 4 for the corresponding "pure" electrolyte. Note the shift in the $\delta_s(CF_3)$ mode at ~760 cm^{-1} to lower wavenumbers with increasing temperature.

Conclusions

FT-Raman studies of a PEO−$LiCF_3SO_3$ salt-in-polymer electrolyte with C_{60} added as a filler have been undertaken as a function of composition and temperature. Several Raman-active modes corresponding to the crystalline nonconducting polymer phase typical of these compounds are absent at ambient temperature—far below the melting point of PEO. This shows that C_{60} works as an effective structure-breaking plasticizer. Moreover, C_{60} seems to stabilize the polymer/salt structures at high temperatures. This is confirmed by the persistence of several characteristic bands at temperatures up to 100 °C. Finally, the absence of a shift in the charge-transfer-sensitive intramolecular $A_g(2)$ mode of C_{60} indicates that C_{60} essentially acts as an inert filler or, alternatively, that any complexes formed between PEO segments and C_{60} molecules are of a highly symmetric nature.

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References and Notes

(1) Scrosati, B. *Chim. Ind. (Milan)* **1997**, *79*, 463.

(2) Ferry, A. In *Recent Research Developments in Macromolecules Research*; Pandalai, S. G., Ed.; Research Signpost, Trivandrum, India, in press.

(3) Bruce, P. G.; Vincent, C. A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3187.

(4) *Polymer Electrolyte Reviews*—1 (a) and *Polymer Electrolyte Reviews*—2 (b); MacCallum, J. R., Vincent, C. A., Eds.; Elsevier: London, 1987 and 1989.

(5) *Solid State Electrochemistry*; Bruce, P. G., Ed.; University Press: Cambridge, 1995; p 122.

(6) Wright, P. V. In ref 4b, p 61.

(7) Robitaille, C. D.; Fauteux, D. *J. Electrochem. Soc.* **1986**, *133*, 315.

(8) Fauteux, D. In ref 4b, p 121

(9) Berthier, C.; Gorecki, W.; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigaud, P. *Solid State Ionics* **1983**, *11*, 91.

(10) Chintapalli, S.; Frech, R. *Macromolecules* **1996**, *29*, 3499.

(11) Bishop, A. G.; MacFarlane, D. R.; McNaughton, D.; Forsyth, M. *J. Phys. Chem.* **1996**, *100*, 2237 and references therein.

(12) Croce, F.; Appetecchi, G. B.; Persi, L.; Scrosati, B. *Nature* **1998**, *394*, 456.

(13) Sukeshini, A. M.; Nishimoto, A.; Watanabe, M. *Solid State Ionics* **1996**, *86*, 385.

(14) Dai, Y.; Greenbaum, S.; Golodnitsky, D.; Ardel, G.; Strauss, E.; Peled, E.; Rosenberg, Yu. *Solid State Ionics* **1998**, *106*, 25.

(15) Quartarone, E.; Mustarelli, P.; Magistris, A. *Solid State Ionics* **1998**, *110*, 1.

(16) Stevens, J. R.; Wieczorek, W. *Can. J. Chem.* **1996**, *74*, 2106.

(17) Wieczorek, W.; Zalewska, D.; Raducha, K.; Florjanczyk, Z.; Stevens, J. R. *J. Phys. Chem. B* **1998**, *102*, 352.

(18) Wieczorek, W.; Zalewska, D.; Raducha, K.; Florjanczyk, Z.; Stevens, J. R.; Ferry, A.; Jacobsson, P. *Macromolecules* **1996**, *29*, 143.

(19) Lightfoot, P.; Metha, M. A.; Bruce, P. G. *Science* **1993**, *262*, 883.

(20) Frech, R.; Huang, W. *Macromolecules* **1995**, *28*, 1246.

(21) Frech, R.; Chintapalli, S.; Bruce, P. G.; Vincent, C. A. *Chem. Commun.* **1997**, 157.

(22) Brodin, A.; Mattsson, B.; Nilsson, K.; Torell, L. M.; Hamara, J. *Solid State Ionics* **1996**, *85*, 111.

(23) Dalchiele, E. A.; Rosolen, J. M.; Decker, F. *Appl. Phys. A* **1996**, *63*, 487.

(24) Chabre, Y.; Jurado, D.; Armand, M.; Romanov, W. R.; Coustel, N.; McCauley Jr., J. P.; Fischer, J. E.; Smith, A. B. *J. Am. Chem. Soc.* **1992**, *114*, 764.

(25) Rao, A. M.; Zhou, P.; Wang, K.-A.; Hager, G. T.; Holden, J. M.; Wang, Y.; Lee, W.-T.; Bi, X.-X.; Eklund, P. C.; Cornett, D. S.; Duncan, M. A.; Amster, I. J. *Science* **1993**, *259*, 955.

(26) *Science of Fullerenes and Carbon Nanotubes*; Dresselhaus, M. S., Dresselhaus, G., Eklund, P. C., Eds.; Academic Press: San Diego, 1995; pp 376−9.

(27) Oshiyama, A.; Saito, S.; Hamada, N.; Miyamoto, Y. *J. Phys. Chem.* **1992**, *53*, 1457.

(28) Edman, L.; Wågberg, T., to be published.

(29) Torell, L. M.; Schantz, S. In ref 4b,p 1.

(30) Huang, W.; Frech, R.; Wheeler, R. A. *J. Phys. Chem.* **1994**, *98*, 100.

(31) Ferry, A. *J. Phys. Chem. B* **1997**, *101*, 150 and references therein.

(32) Torell, L. M.; Jacobsson, P.; Petersen, G. *Polym. Adv. Technol.* **1993**, *4*, 152.

(33) Teeters, D.; Frech, R. *Solid State Ionics* **1986,** *18−19*, 271.

(34) Ferry, A.; Orädd, G.; Jacobsson, P. *J. Chem. Phys.* **1998**, *108*, 7426.

(35) Matsuura, H.; Fukuhara, K. *J. Mol. Struct.* **1985**, *126*, 251.

(36) Kasatani, K.; Sato, H. *Chem. Lett.* **1986**, 991.

(37) Ferry, A.; Doeff, M. M.; De Jonghe, L. C. *J. Electrochem. Soc.* **1998**, *145*, 1586.

(38) Furlani, M.; Ferry, A.; Franke, A.; Jacobsson, P.; Mellander, B.-E. *Solid State Ionics* **1998**, *113−115*, 129.

(39) Ferry, A.; Edman, L.; Forsyth, M.; MacFarlane, D. R.; Sun, J. *J. Appl. Phys.*, in press.

(40) Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J.; Golden, W. G.; Seki, H.; Brown, C. A.; de Vries, M. S. *Chem. Phys. Lett.* **1991**, *179*, 181.

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