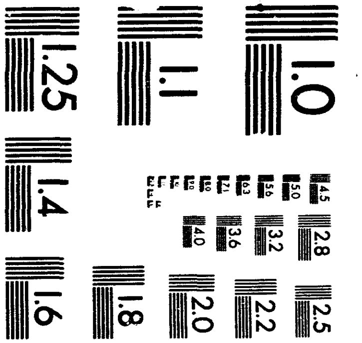
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ENHANCED ION DISSOCIATION OF $LiCF_3SO_3$ BY NEW CARBONATE PLASTICIZERS: RAMAN AND IR STUDIES

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ABSTRACT

The extent of ion dissociation of $LiCF_3SO_3$ in propylene carbonate [PC] and new, modified carbonates [MC-3, MC-5] prepared in our laboratory has been determined by Raman spectroscopy. In the modified carbonates, the polyether groups $-CH_2(OCH_2CH_2)_nOCH_3$ (n=3 for MC-3 and n=5 for MC-5) replace the 4-CH_3 substituent of PC. The spectra clearly show that both MC-3 and MC-5 promote ion dissociation of the Li triflate salt relative to PC. Furthermore, MC-5 solutions contain more free ions than MC-3 solutions, and are less affected by concentration changes. Infrared spectra demonstrate that Li^+ cations associate less with the carbonyl of the modified carbonates than with the carbonyl of PC. These results suggest that the enhanced ion dissociation of Li triflate in MC-3 and MC-5 arises from complexation of the Li^+ to the oxygens of the polyether sidechains, and that MC-5 with its six ether oxygens forms the more stable complex.

INTRODUCTION

Solid polymer electrolytes containing a Li^+ salt dissolved into a polyethylene oxide (PEO) host are promising materials for batteries (1,2). A drawback of these materials has been their relatively low conductivities at ambient temperatures. Ion conduction in polymer electrolytes depends both upon the number of ionic charge carriers and the local relaxation processes of the polymer chains, and only occurs in the amorphous regions of the material. PEO films are semi-crystalline at room temperature. Increasing the salt concentration in the polymer in an attempt to increase the number of charge carriers also leads to increased "stiffness" through interchain crosslinking and larger crystalline regions. In addition, ionic salts only completely dissociate into ions in their polymer hosts at very dilute concentrations. Usually the system contains many neutral ion pairs or larger aggregates. Thus the number of actual charge carriers can be quite small, even with high salt concentrations.

One strategy for improving the conductivities of polymer electrolytes has been to an add an organic compound with a high dielectric constant such as propylene carbonate (PC), Figure 1, as a plasticizer. PC increases the conductivity of PEO/$LiCF_3SO_3$ films by an order of magnitude (3), unfortunately, it is also volatile and evaporates from the samples.

New carbonate plasticizers that contain the polyether groups $-CH_2(OCH_2CH_2)_nOCH_3$ in place of the 4-CH_3 substituent of propylene carbonate (Figure 1) have recently been synthesized in our laboratory (3). These retain the high dielectric constant of the cyclic carbonate, while the polyether substituent decreases the volatility of the material and improves its compatibility with PEO. The plasticizers are called modified carbonates, MC-n, where n is the number of ethylene oxide units in the sidechain. MC-3 improves the conductivity of PEO/$LiCF_3SO_3$ films by a factor of 20 relative to PC used in the same systems as a plasticizer, and by more than two orders of magnitude over PEO/$LiCF_3SO_3$ films with no added plasticizer (3).

In order to determine possible causes for this dramatic improvement in conductivity, specifically, whether the modified carbonates promote the ion dissociation of the salt, we have investigated solutions of $LiCF_3SO_3$ in MC-3, MC-5 and PC by Raman and infrared spectroscopy. In a number of recent papers, Torell and coworkers have identified a band in the Raman spectra of triflate anions ($CF_3SO_3^-$) that is sensitive to the aggregation state of the anion (4-9). This band allows one to distinguish quantitatively between the amounts of free anions, cation-anion pairs, and larger aggregates. From the infrared spectra, the relative extent of Li^+ complexation to the carbonyl oxygens of the modified carbonates and PC can be determined (10,11).

EXPERIMENTAL

The modified carbonates were synthesized as described in Ref. 3. Propylene carbonate and anhydrous $LiCF_3SO_3$ were purchased from the Aldrich Chemical Company. Samples were prepared by first dissolving $LiCF_3SO_3$ in acetonitrile. After PC, MC-3, or MC-5 was added to the solution, the acetonitrile was evaporated off in a vacuum oven set at 30°C and 0.5 torr. This procedure was followed because the modified carbonates are viscous: the kinetic viscosities of PC, MC-3, and MC-5 were measured as 2.1, 22.7, and 35.8 cSt, respectively, using Cannon-Fenske Routine Viscometers.

Raman spectra were obtained on an instrument constructed at Brookhaven National Laboratory. This spectrometer consists of a Princeton Instruments liquid nitrogen cooled CCD (coupled charge device) detector mounted on a 0.64m JY HR640 spectrograph with a 1200g/mm grating. The samples were placed in standard 1x1 cm emission cuvettes and excited by the 514 nm line of an Ar ion laser set at approximately 100 mW of power.

The Raman scattering from the sample was collected 90° from the incident laser beam. The Raman spectra shown in Figures 2-5 are single scans of raw data, uncorrected except for subtraction of the CCD dark current. The raised baseline on the high frequency side of the spectra arises from a luminescent impurity in the triflate salt (12).

The FTIR spectra were taken in transmission mode on a Mattson Cygnus 100 spectrometer.

RESULTS

Raman Spectra

Figure 2 shows the ν_1 symmetric stretching mode of the SO_3 group of the $CF_3SO_3^-$ anion, for $LiCF_3SO_3$ dissolved in CH_3CN. This mode has been identified in a number of recent papers by Torell and coworkers (4-9) as a sensitive probe of the aggregation state of $CF_3SO_3^-$ anions. Three peaks are apparent in the band profile in Figure 2. They represent free $CF_3SO_3^-$ anions at 1033 cm^{-1}, Li^+-$CF_3SO_3^-$ ion pairs at 1042 cm^{-1}, and larger, less-well-specified aggregates at >1050 cm^{-1} (6-8). The justification for these assignments are given in Refs. 6 and 8. Briefly, the peak at 1033 cm^{-1}, assigned to the free triflate anion, was the only component detected in dilute aqueous solutions. Its frequency is also unaffected by the cation of the triflate salt. The middle peak, assigned to cation-anion ion pairs, grows in at the expense of the 1033 cm^{-1} peak as salt concentrations are increased. In addition, its frequency does depend upon the cation; 1043 cm^{-1} for Li^+ and 1039 cm^{-1} for Na^+. At even higher concentrations, the high frequency component appears. The Torell group has performed band profile analyses with three Lorentzian components to obtain quantitative values for the amounts of free ions, ion pairs, and larger aggregates in a given solution. For the purposes of this paper, however, the relative heights of the three peaks give an adequate qualitative measure of each species.

Figure 3 shows the SO_3 symmetric stretching mode for two solutions of $LiCF_3SO_3$ in PC. The less concentrated sample, with a Li:PC mole ratio of 1:6, has a detectable, though small, free ion peak. Its spectrum is dominated by the ion-pairing and larger aggregate components. As the salt concentration is increased to a mole ratio of 1:3, the free ion peak essentially disappears, the ion-pair peak is quite diminished, and the predominant species becomes the larger cation-anion aggregates.

In contrast to the $LiCF_3SO_3$/PC solutions, the Raman spectra of $LiCF_3SO_3$ dissolved in the modified carbonates MC-3 (Figure 4) and MC-5 (Figure 5) indicate that these systems contain substantial amounts of free ions. For MC-3, the free ion peak dominates in the less concentrated 1:6 Li:MC-3 solution. At a mole ratio of 1:3 there are roughly equal amounts of free $CF_3SO_3^-$ anions and Li^+-$CF_3SO_3^-$ ion-pairs. Neither MC-3 solution contains the larger aggregates. The dissociation of $LiCF_3SO_3$ into separated ions is even more pronounced in MC-5. The $LiCF_3SO_3$/MC-5 solution with a Li:MC-5 mole ratio of 1:3 has the same proportion of free triflate anions as the more dilute 1:6 Li:MC-3 sample. Indeed, an MC-5 solution with a Li:MC-5 mole ratio of 1:1 has a bigger free ion peak than the most dilute PC sample (1:6 Li:PC, Figure 3). The major species in the 1:1 spectrum are Li^+-$CF_3SO_3^-$ ion-pairs. It is difficult to say without a Lorentzian analysis whether any of the larger cation-anion aggregates are present, even at this very high salt concentration.

Infrared Spectra

FTIR spectra detailing the carbonyl stretching band at ~1800 cm^{-1} of PC and MC-3 are shown in Figures 6 and 7, respectively. The bands for pure PC and pure MC-3 are superimposible, demonstrating that the carbonyl groups of PC and MC-3 are indistinguishable. Nonetheless, the PC carbonyl shows a greater sensitivity to Li^+ than does the MC-3 carbonyl. As increasing amounts of $LiCF_3SO_3$ are added to PC (Figure 6), its carbonyl band broadens and shifts to lower frequencies in a manner consistent with previously reported FTIR spectra on $LiClO_4$ dissolved in PC (10,11). When the same molar amounts of $LiCF_3SO_3$ are added to MC-3 (Figure 7), the Li^+-induced broadening and shifting of the carbonyl band are significantly smaller.

The perturbation to the carbonyl band in the presence of Li salts arises from complexation of Li^+ cations to the carbonyl oxygens; the more extensive the complexation, the larger the spectral perturbation. Thus our FTIR results clearly demonstrate that Li^+ cations associate less tightly with the carbonyl of MC-3 than with the carbonyl of the PC, and that this effect is not caused by inherent differences between the carbonyls.

DISCUSSION

Our Raman spectra clearly demonstrate that, as solvents, the modified carbonates MC-3 and MC-5 enhance ion dissociation of $LiCF_3SO_3$ relative to PC. However, this effect is not limited to a Li^+ salt in solution: near edge X-ray absorption studies have established that MC-3 also enhances ion dissociation of a K^+ salt in PEO films (3). These results strongly suggest that the increased ion conductivity observed in PEO-$LiCF_3SO_3$ films containing MC-3 as a plasticizer can be largely attributed to increased ion dissociation of the salt. PEO films containing MC-5 as a plasticizer have not yet been tested. Since MC-5 dissociates $LiCF_3SO_3$ more completely than MC-3, and at higher salt concentrations, it should lead to greater improvements in the ion conductivity of polymer films than MC-3. Reduced ion pairing has been directly related to increased conductivity in other polyelectrolyte systems (13).

Why do the modified carbonates MC-3 and MC-5 significantly increase dissociation of alkali metal salts into ions relative to PC? The modified carbonates contain a polyether sidechain at the C4 position of the carbonate ring, whereas this substituent is a methyl group in PC (Figure 1). It is reasonable to assume that the ether oxygens play a significant role in the ion dissociation of the salt; that they drive the dissociation by complexing with alkali metal cations more strongly than the carbonyl oxygen of a carbonate ring.

Fish and Smid (10) recently reported infrared and ^{13}C NMR studies on $LiClO_4$ dissolved in PC and in mixtures of PC and a polyethylene glycol derivative [TEGDME = tetraethylene glycol dimethyl ether]. They found that Li^+ cations complexed with the PC carbonyl only when the TEGDME was absent. In solutions containing both PC and TEGDME, Li^+ bound preferentially to the ether oxygens of the TEGDME. The authors concluded that the carbonyl oxygen of PC is a relatively poor cation chelating agent. Our FTIR spectra on Li triflate in PC and MC-3 show that Li^+ cations associate substantially less with the MC-3 carbonyl than with the PC carbonyl, even though the two carbonyls are essentially equivalent and the MC-3 solutions contain considerably more "free" ions. MC-3 contains ether oxygens whereas PC does not. Thus our FTIR results together with the Fish and Smid data suggest that the polyether substituents of the modified carbonates bind Li^+ more strongly than the carbonyl oxygens. (MC's have an advantage over mixtures of PC plus short chain PEO or PEG derivatives as plasticizers for polymer electrolytes because the covalently bound polyether substituent of MC greatly reduces its volatility.)

Why is MC-5 more effective at dissociating $LiCF_3SO_3$ than MC-3? The answer may lie in the relative stabilities and/or geometries of the polyether:Li^+ complexes formed by the MC-3 and MC-5 sidechains. By adding chelating agents to oxymethylene-linked PEO/$NaCF_3SO_3$ systems, Chen et al. (13) demonstrated that reduced ion-pairing, as detected by Raman spectroscopy, led to increased conductivity. The effectiveness of a given chelator correlated with the stability of its Na^+ complexes and its ability to isolate the cation from the anion. A perusal of the Li^+ structures in the Cambridge Structural Database (14) shows that Li^+ forms complexes with four to seven ligands. It is four-coordinate with monodentate ligands such as acetonitrile and diethylether. The higher coordination numbers occur with polydentate compounds such as crowns and cryptands when sterically possible. The sidechains of the modified carbonates MC-3 and MC-5 contain four and six ether oxygens, respectively, each separated by $-CH_2CH_2-$ groups. The six ether oxygens of MC-5 most likely form a more stable complex with Li^+ and more effectively shield the cation from the anion than the four ether oxygens of MC-3.

CONCLUSION

The modified carbonates are promising materials for polymer electrolytes because of their favorable properties as plasticizers and because they promote the ion dissociation of the salt.

ACKNOWLEDGMENTS

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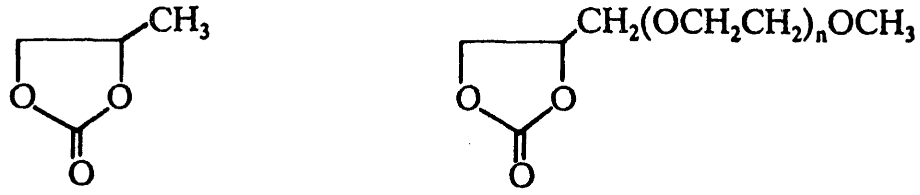

propylene carbonate (PC)

modified carbonate (MC)
n=3 MC-3
n=5 MC-5

Figure 1. Structural formulae of propylene carbonate (PC) and the modified carbonates MC-3 and MC-5.

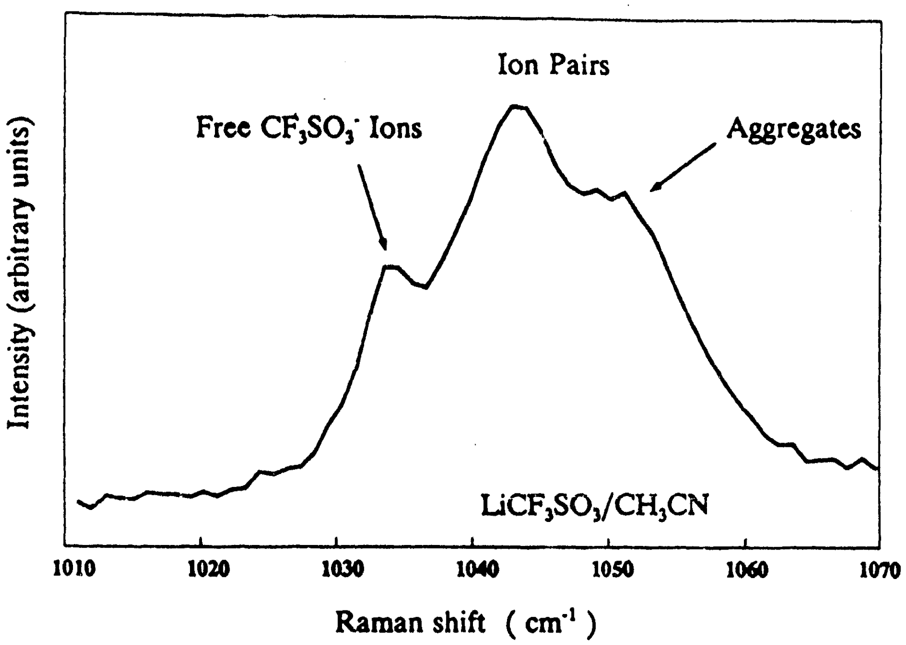

Figure 2. The SO_3 symmetric stretching mode for $LiCF_3SO_3$ in CH_3CN (1M solution).

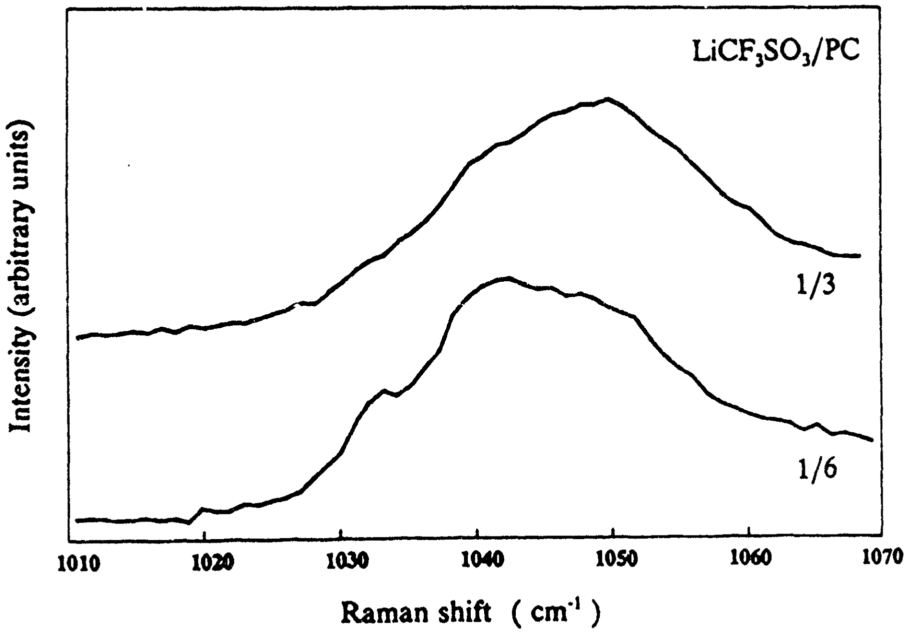

Figure 3. The SO_3 symmetric stretching mode for $LiCF_3SO_3$ in PC at Li:PC mole ratios of 1:6 and 1:3.

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