Preparation of Propylene Carbonate Acrylate and Poly(propylene carbonate acrylate) Electrolyte Elastomer Gels. ^{13}C NMR Evidence for Li$^+$–Cyclic Carbonate Interaction

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ABSTRACT: The phosgene-free synthesis of fast curing (2-oxo-1,3-dioxolan-4-yl)methyl acrylate (propylene carbonate acrylate, PCA) is presented. Polymerization of PCA in the presence of plasticizing propylene carbonate (PC) results in the formation of reversibly swellable elastomeric gels. The ionic conductivity of poly(PCA) plasticized with 50 wt % PC and containing 1 M lithium triflate is 1.7×10^{-5} S/cm. Evidence for Li$^+$–cyclic carbonate interaction was found in ^{13}C CP-MAS NMR spectroscopic analysis of the model compound poly(vinylene carbonate) containing 1 M lithium triflate.

Introduction

Increasing interest in polymers containing the polar five-membered cyclic carbonate group is due to their potential application as electrolyte supports,[1] as hosts for dyes in nonlinear optics,[2] and as reactive polymers.[3] The parallel search for inexpensive and environmentally safe chemical building blocks is exemplified by the increasing use of CO_2 instead of phosgene in the synthesis of polymers and new materials.[4] The catalytic insertion of CO_2 into the C–O bond of epoxides to form the cyclic carbonate functionality is of particular utility, in that the cyclic carbonate is obtained in high yield and purity under mild conditions,[5] and the generation of stoichiometric chloride salt byproducts is eliminated.

Brosse and co-workers recently described a high-yield multistep synthesis of the highly reactive monomer (2-oxo-1,3-dioxolan-4-yl)methyl acrylate (propylene carbonate acrylate, PCA) involving the use of phosgene and the generation of stoichiometric HCl byproduct.[6a] It was surmised that the multistep sequence was necessary to trap the highly reactive pure PCA monomer at low temperatures to avoid spontaneous polymerization. Although an earlier report by D'Alelio and Huemmer described the phosgene-free multistep synthesis of PCA,[6c] no yield was reported and stoichiometric salt byproducts were also produced. We now report the phosgene-free synthesis of PCA by catalytic insertion of CO_2 into the epoxide moiety of glycidyl acrylate, the preparation of propylene carbonate plasticized poly(PCA) elastomeric electrolyte gels, and ^{13}C NMR evidence for Li$^+$–cyclic carbonate interaction in a model polymer system.

Experimental Section

Preparation of and UV Polymerization of Propylene Carbonate Acrylate. In a modification of the method described by G. Brindöpke (Ger. Patent 3 529 263, 1987; *Chem. Abstr.* **1987**, *107*, 156951z), a two-neck 250 mL round bottom flask fitted with a rubber septum, and containing a magnetic stir bar, was charged with 200 mg (0.76 mmol) of PPh_3, 93 mg (0.56 mmol) of KI, and 400 mg (3.2 mmol, 0.02 mol %) of 4-methoxyphenol. A condensor with an oil bubbler outlet was then fitted, and 22 g (172 mmol) of glycidyl acrylate (Aldrich) was syringed into the vessel. CO_2(g) was continuously bubbled into the magnetically stirred reaction mixture through a needle, with the reaction vessel immersed in a 60 °C oil bath. At various times an aliquot was removed for proton NMR analysis, and the product vs starting material ratios were determined by comparative integration of the stereogenic ring proton(s). After the reaction was deemed complete (20–24 h), the mixture was filtered to remove polymer particles, dissolved in CH_2Cl_2, and washed with Li_2CO_3 saturated ice water. The organic layer was separated, dried over Li_2CO_3, and vacuum filtered using a glass frit. After solvent removal in vacuo, the free-flowing transparent pale green liquid was magnetically stirred for 24 h at 10^{-3}–10^{-4} Torr. The ca. 95% pure monomer thus obtained was stored over 3 Å molecular sieves at −16 °C. Samples stored at 23 °C became syrup-like after 48 h.

UV polymerization (500 W lamp, 0.80 mW/cm^2 at 365 nm, 5 mol % Irgacure 651 (Ciba-Geigy)) of a 250 μm thick film of PCA spin coated onto a NaCl disk was monitored by IR spectroscopy. A tack-free film was obtained in 900 s, with concomitant disappearance of C=C modes. The time scale, lamp power, and film thickness correlate well with the fast polymerization of PCA previously reported in ref 6b. The experiments were conducted in air.

Preparation and Analysis of Poly(PCA)/PC/LiOTf Polymer Electrolyte. Unless otherwise noted, all reagents were predried and handled under strictly dry conditions. Disks prepared for the conductivity measurements were prepared in an inert atmosphere box by casting 1.0 M PCA/PC/lithium triflate solutions into circular PTFE molds of 12.5 mm diameter and 0.5 mm depth. The cast solutions were cured by exposure to direct sunlight for ca. 0.5 h under argon, followed by UV exposure (500 W lamp, 0.80 mW/cm^2 at 365 nm, 5 mol % Irgacure-651 (Ciba-Geigy)) for 900 s under argon. The disks were then carefully lifted intact from the molds, and conductivity measurements were performed. The experimental details for the measurement and the apparatus used are found in ref 7. Differential scanning calorimetry was performed using a Mettler DSC 30 instrument from +50 to −150 °C under a N_2 atmosphere with a 10 °C/min scan rate.

Preparation and Analysis of Poly(VC) 1 M in LiOTf. If an inert atmosphere box, 55 mg (0.34 mmol) of 97% LiOTf (Aldrich) was dissolved in 0.25 mL (0.35 g, 0.40 mmol) of dry (3 Å sieves) freshly distilled VC (Aldrich). AIBN (2 mol %, 13 mg) was added, and the solution was magnetically stirred for ca. $^1/_2$ h. A glass ampule was charged with the homogeneous solution, frozen with N_2(l), and sealed with a torch under vacuum. The ampule was then placed in a 70 °C oil bath for 24 h, after which time the hard glassy polymer was removed

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and ground into a fine powder in an inert atmosphere box. The powder was then loaded into an airtight rotor for the NMR experiment. GPC analysis (Viscotek) of the poly(VC) yielded a chromatogram displaying a bimodal distribution and a molecular weight of ca. 10^6 as compared to a 3×10^6 poly(styrene) standard (Polymer Standard Service). Differential scanning calorimetry (DSC) from 50 to 450 °C (5 °C/min) revealed a broad endotherm commencing at 240 °C and centered at 311 °C. The polymer used for GPC and DSC analysis was twice precipitated from DMF into acetone followed by drying in vacuo.

^{13}C CP-MAS NMR. Experiments were performed on a home-built spectrometer, based on a 7.05 T wide-bore magnet from Oxford Instruments, operating at Larmor frequencies of 299.9997 MHz for ^{1}H and 75.4430 MHz for ^{13}C. MAS was achieved using a 7.5 mm triple resonance probe from Chemagnetics at 4.5 KHz. Data were collected by cross-polarizing from the proton spins to the carbon atoms using the $N = 8$ refocusing SELTICS sequence to suppress the spinning sidebands. Information on SELTICS is found in: Hong, J.; Habison, G. S. *J. Magn. Reson. Ser. A* **1993**, *105*, 128.

Results and Discussion

PCA was prepared in yields exceeding 85% as shown in Scheme 1. The ^{1}H NMR and IR data are consistent with the assigned structure.[8] Due to the highly reactive nature of PCA,[6b] the use of a high inhibitor concentration and a lower temperature was necessary to prevent polymerization during the synthesis. For example, temperatures greater than 60 °C resulted in rapid polymerization, while product yields were unsatisfactory at lower temperatures over a period of 20–24 h. Despite the presence of added inhibitors, the PCA monomer polymerized rapidly when exposed to UV radiation. The experimental parameters used to determine the optimal synthetic conditions are summarized in Table 1.

The preparation of poly(PCA) elastomer electrolyte support was achieved by polymerization of PCA in the presence of 50 wt % propylene carbonate (PC) plasticizer.[1d] The respective glass transition temperatures for 20, 50, and 80% by wt PC samples are ca. 0, −50, and −80 °C. Soaking in water for 12 h to remove the organic solvent yields a gumlike material with good adhesive properties. This material reabsorbs PC or DMSO over a period of 12 h to re-form the tough elastomer gel. These properties are in contrast to those of the hard, brittle, and highly cross-linked homopolymer, which is completely insoluble in polar and nonpolar solvents. Brosse and co-workers have suggested that the observed cross-linking is due to the abstraction of hydrogen atom(s) from the cyclic carbonate moiety, followed by radical recombination.[6a] This process was confirmed in a later study by Kihara and Endo,[9] in which the radical chain transfer of poly(methyl methacrylate) to PC was observed, resulting in a significantly lower molecular weight polymer. The contrasting physical properties of the PCA homopolymer and the PC plasticized poly(PCA) are likely a result of these same processes, thus yielding a swellable elastomer with a lower molecular weight and cross-link density.

Scheme 1

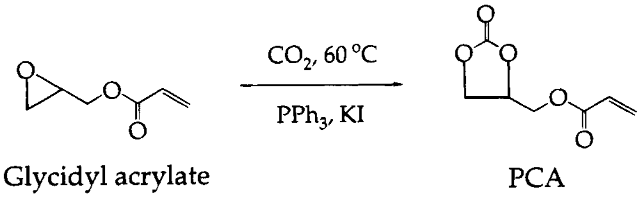

Table 1. Synthesis of PCA (0.02% MEHQ)

temp (°C)	time (h)	% yield (^{1}H NMR)
80	12	polymer
80	24	polymer
60	12	67
60	24	85–90
60[a]	4.5	32
60[a]	10.5	60
60[a]	24	74
40	6.0	10
40	22	40

[a] LiI catalyst.

The ionic conductivity of poly(PCA) 50 wt % in PC and 1.0 M in lithium triflate (LiOTf) (9.5 cyclic carbonate:1 Li$^+$) was examined, as it displayed the best combination of conductivity and film strength. The conductivity value of 1.7×10^{-5} S/cm at 23 °C is consistent with data previously compiled for polymers containing pedant cyclic carbonate groups,[1a-c] and is substantially higher than the ca. 10^{-7} S/cm value (23 °C) for nonplasticized poly(vinylene carbonate) (20 cyclic carbonate:1 Li$^+$).[1c] Although enhanced ion transport due to the plasticizing effect of PC is expected,[1c,d] the combination of a high cross-link density and strong cyclic carbonate–Li$^+$/ester–Li$^+$ interactions within the network could confine the cation within the domains or pockets where diffusion is slowed, resulting in a lower conductivity value than expected.[10]

We investigated the interaction of the cyclic functionality with the lithium cation using ^{13}C CP-MAS NMR. Since both PCA and plasticizer-free poly(PCA) cannot be used to dissolve LiOTf, the study was conducted using the simple model compound poly(vinylene carbonate), the structure of which is shown in Figure 1. CP-MAS NMR spectral analysis of poly(VC) 1.0 M in LiOTf (11 cyclic carbonate:1 Li$^+$) revealed a new carbonyl resonance at 133.4 ppm, as well as uncomplexed carbonyl and C–H backbone resonances at 153.6 and 77.2 ppm, respectively (Figure 2).[11] In contrast, the salt-free poly(VC) spectrum displayed uncomplexed carbonyl and

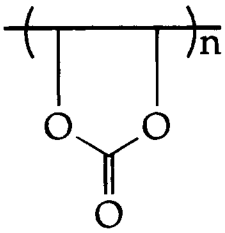

Figure 1. Poly(vinylene carbonate).

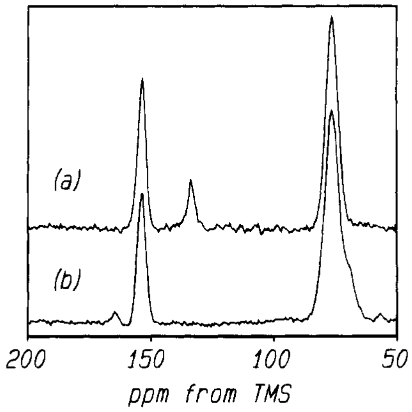

Figure 2. Data from the ^{13}C CP-MAS NMR experiment: (a) poly(VC) 1 M in LiOTf, (b) without LiOTf. In (b) the small peak seen at ca. 160 ppm is due to residual NMF. The peak is ca. 53 ppm may be due to residual monomer.

C−H backbone resonances at 153.6 and 77.2 ppm exclusively. The ca. 3:1 relative ratio of the two carbonyl peaks implies an interaction sphere of more than one carbonyl per Li^+, as well as decreased chain mobility in areas close to Li^+, resulting in more effective cross-polarization. These data strongly suggest that the lithium cation is coordinated to the cyclic carbonate functionality in poly(VC)[11] and may serve as a simple model for the complexation of Li^+ in other cyclic carbonate containing polymer systems.

Conclusions

A high-yield environmentally friendly methodology for the preparation of the highly reactive monomer propylene carbonate acrylate has been elucidated. Polymerization of PCA in the presence of the plasticizing chain transfer agent propylene carbonate yields an elastomer gel with physical properties that are in contrast to those of the homopolymer. We have demonstrated the utility of modern solid state NMR techniques to probe the interaction of Li^+ with the polar cyclic carbonate functionality. Future studies will focus on the cross-polarization of ^7Li spins to the carbonyl carbon, to further probe the molecular level interactions of the two polar species in the solid matrix.

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Registry No. Supplied by Author. (2-Oxo-1,3-dioxolan-4-yl)methyl acrylate (propylene carbonate acrylate, PCA), 7528-90-7.

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(8) ^1H NMR (200 MHz, $CDCl_3$): δ 6.44 (d, 1H, vinyl H(*cis*), J = 15.7 Hz), 6.14 (m, 1H, vinyl H(gem), $J_{cis/gem}$ = 15.7 Hz, $J_{trans/gem}$ = 10.4 Hz), 5.93 (d, 1H, vinyl H(*trans*), J = 10.4 Hz), 4.94 (m, 1H, ring stereocenter), 4.56 (t, 2H, ring CH_2), 4.34 (m, 2H, CH_2). IR: (NaCl) 1794 (carbonate CO), 1734 (ester CO), 1635 and 810 cm^{-1} (C=C).

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