Synthesis, Characterization and Properties of Polycarbonate Containing Carboxyl Side Groups

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Summary: Diphenolic Acid, DPA [bis(4-hydroxyphenyl)pentanoic acid]can be made from cellulose-rich waste. The t-butyl ester was converted to homo- and copolycar- bonates (with bis-phenol-A, BPA). Deblocking the ester yielded polycarbonates with pendent carboxyl groups that exhibit all the properties of polyelectrolytes and retain solubility in aqueous base without degradation for long periods.

Keywords: copolymerization, functionalization of polymers, polycarbonates, renewable resources, water-soluble polymers

Introduction

Recent progress made in the field of green chemistry is the development of diphenolic acid. It is synthesized by the condensation of phenol and levulinic acid, a compound prepared from the recycling of cellulose-rich wasters such as wood, paper, sewage sludge, paper mill sludge and food processing waste.[1] Because the diphenolic acid has a structure similar to bisphenol A (BPA) and a price only one third of the cost of the latter, it is interesting and of potential commercial value to develop polycarbonate derivatives and functional polycarbonates based on the use of diphenolic acid.

In previous work, high molecular weight polycarbonate derivatives have been synthesized by the condensation of diphenolate esters and phosgene.[2,3,4] In the current research, a new kind of polycarbonate derivative containing unprotected carboxyl side groups has been synthesized.

The reaction route is shown in Scheme 1.

It has been found that the free carboxyl group on diphenolic acid caused cross-linking and branching when directly polymerized with phosgene. Therefore, to obtain well-defined linear polycarbonates, the carboxyl group was first protected by esterification with *tert*-butanol.[5] After the formation of the corresponding homo-polycarbonate the *t*-butyl group can be quantitatively cleaved with trifluoroacetic acid at room temperature or by heating above 200 °C.

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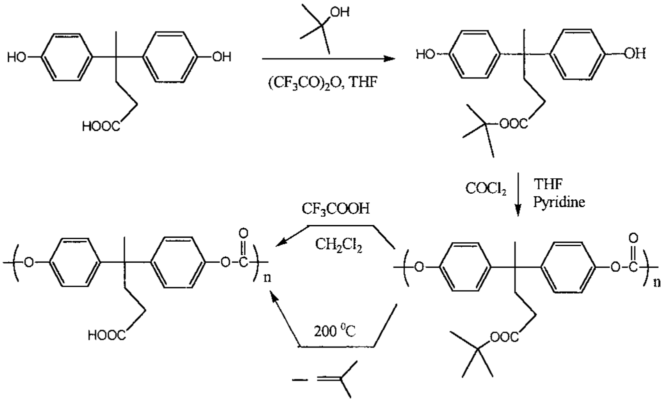
The obtained polycarbonate acid can be dissolved in dilute, aqueous NaOH solution and exhibits properties typical of a polyelectrolyte.[6]



Scheme 1. Synthesis of Polycarbonate Carboxylic Acid.

Carboxyl groups in a polymer may act as cross-linking agents through hydrogen bonding, which influences the physical properties of the polymer. By using small amounts of Zn^{2+} or Al^{3+} ions the carboxyl groups can be cross-linked more strongly by generation of ionic bonds.[7] It has also been found that the presence of carboxyl groups influence the thermo-stability of the polymer. The glass transition temperatures of polymers with different extents of cross-linking have been investigated in this work (vide infra).

Experimental Part

General Methods

Fourier-Transform Infrared (FTIR) spectra were recorded on a Perkin Elmer Paragon 1000 spectrophotometer. Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian Unity 500 spectrometer. Viscosity measurements were carried out in aqueous solution with a Cannon-Ubbelohde viscometer. All solutions were filtered through Gelman Acrodisc CR PTFE syringe filters with a pore size of 0.8 µm. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were carried out on Perkin Elmer Series 7 instruments at a heating rate of 10 °C/min under nitrogen. TGA measurements were carried out at a heating rate of 20 °C/min under nitrogen. Gel Permeation Chromatography (GPC) was performed using a Waters 2410 liquid chromatograph equipped with a refractive index detector. A universal calibration was made with narrowly dispersed polystyrene standards.

Solvents and Reagents

THF was distilled from sodium metal. Methylene chloride was distilled from calcium hydride. Diphenolic acid and Bisphenol-A were purchased from Aldrich and used without further purification. Pyridine was distilled from calcium hydride and stored over 4A molecular sieves. *Tert*-butanol was distilled from calcium hydride before use.

Synthesis

1. *tert*-butyl 2,2-bis(4-hydroxyphenyl)valerate

In a 500-ml, 3 neck round bottom flask diphenolic acid (30.1g, 0.1 mol) was dissolved in 100 ml of THF. An ice bath was used to cool the solution to which trifluoroacetic anhydride (50 ml) was added dropwise through an addition funnel over a period of 10 minutes. After The ice bath was then removed and the reaction mixture was stirred at room temperature for 3 hours. Under cooling in an ice bath 80 ml of tert-butanol was added through an addition funnel to the reaction mixture over 5 minutes. The ice bath was then removed and the reaction mixture was stirred overnight at room temperature. A 10% aqueous potassium carbonate solution was used to neutralize the reaction mixture. The oil-like product was extracted with methylene chloride in a separatory funnel. The methylene chloride was removed on a rotary evaporator and the residue was poured into a large excess of hexane. The precipitated product was filtered and dried. The crude product was dissolved in aqueous KOH solution. Dry ice was added and the product gradually precipitated. The solid was filtered and washed with pure water. To remove unreacted diphenolic acid completely, this procedure should be repeated twice. Finally, the obtained white solid was dried at 60 °C for 12 hours. The pure product should be white crystals (m.p. 131-132 °C, 20.4g, yield: 58.9%).

^{1}HNMR(acetone-d_6) ppm 8.18(s, 1H, **OH**), 7.06(d, 4H, aromatic ring), 6.78(d, 4H, aromatic ring), 2.34(t, 2H, CH_2-**CH_2**-COO), 2.03(t, 2H, **CH_2**-CH_2-COO), 1.57(s, 3H, C-**CH_3**), 1.42(s, 9H, O-C(**CH_3**)$_3$). ^{13}C NMR (acetone-d_6) 177.44 (C=O), [155.45, 140.46, 128.38, 114.96] (aromatic carbon atoms), 79.52 (O-**C**-(CH_3)$_3$), 44.40 (O-C-(**CH_3**)$_3$), 33.85(O=C-**CH_2**-CH_2), 27.63 (O=C-CH_2-**CH_2**), 13.47(C-**CH_3**). FTIR (KBr) 3413 cm^{-1}(-OH), 2972 cm^{-1}, 1732 cm^{-1} (COO-) 1612 cm^{-1}, 1511 cm^{-1}, 1368 cm^{-1}, 1225 cm^{-1}(C-O), 1190 cm^{-1}, 1153 cm^{-1}, 1012 cm^{-1}, 834 cm^{-1}(ϕ-H).

2.Poly[oxycarbonyloxy-1,4-phenylene-4-tert-butyloxycarbonyl-1-methyl-propylidene-1,4-phenylene]

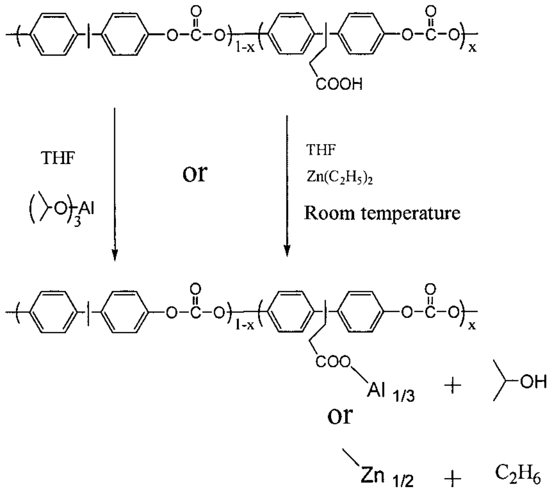
A 3-neck 250 ml round bottom flask was equipped with a stir bar, a gas inlet and outlet tubes. The gas inlet tube was connected to a phosgene tank with a flow meter and regulator. The outlet tube was connected to a trap containing ammonium hydroxide. A water bath was placed under the reaction flask. *tert*-Butyl diphenolate (15g, 0.04 mol), pyridine (20 ml) and THF (80 ml) were added to the flask. Phosgene was slowly introduced to the reaction mixture at a flow rate of 200 ml/min. The reaction mixture was kept at 20°C. The phosgene flow was stopped after 45 minutes. The reaction mixture was washed with 10% aqueous HCl solution and a large amount of methanol, sequentially. The precipitate was collected by filtration. The polymer was dissolved in THF and precipitated in methanol. The purified polymer was dried in vacuum overnight at 60 °C (14.7 g, yield: 91%). ^{1}HNMR($CDCl_3$) ppm 7.12(m, 8H, aromatic), 2.33(t, 2H, CH_2**CH_2**COO), 1.95(t, 2H, **CH_2**CH_2COO), 1.55(s, 3H, C**CH_3**), 1.34(s, 9H, O-C(**CH_3**)$_3$). FTIR (KBr) 2974 cm^{-1}, 1774 cm^{-1} O-COO-), 1725 cm^{-1} (COO-), 1504m^{-1}, 1391m^{-1}, 1229m^{-1}(C-O), 1195cm^{-1}, 1163cm^{-1}, 1011cm^{-1}, 834 cm^{-1}(ϕ-H). A similar procedure was used to synthesize polycarbonate containing both *tert*-butyl diphenolate and bisphenol-A units.

3. Poly[oxycarbonyloxy-1,4-phenylene-(4-carboxy-1-methyl-propylidene)-1,4-phenylene]

The above-mentioned polymer (3.0 g) was dissolved in 40 ml of methylene chloride, and 5 ml of trifluoroacetic acid was added. The reaction mixture was kept at room temperature for 3 hours. Finally, methylene chloride was evaporated under vacuum at room temperature. The residual liquid was treated with a large amount of water. The precipitated polymer was washed with distilled water several times and then dried in vacuum at 50 °C for 5 hours (2.5g, yield: 98%). ^{1}HNMR(DMSO-d_6) pm 7.27(m, 8H, aromatic), 2.38(t, 2H, CH_2**CH_2**COO), 1.96(t, 2H, **CH_2**CH_2COO), 1.57(s, 3H, C**CH_3**). FTIR (KBr) 2971 cm^{-1}, 1773 cm^{-1} O-COO-), 1709 cm^{-1} (COOH), 1504m^{-1}, 1229m^{-1}(C-O), 1195cm^{-1}, 1163cm^{-1}, 1014cm^{-1}, 831 cm^{-1}(ϕ-H).

4. The introduction of metal ions into the polymer matrix

Zn^{2+} and Al^{3+} ions can be quantitatively introduced into the polycarbonate containing free carboxyl groups as shown in Scheme 2. Polymer acid, 0.5 g, was dissolved in 20 ml of completely dried THF. Solid aluminum isopropoxide was added to the solution, followed by heating to reflux for 20 minutes. An insoluble and transparent gel was obtained. The solvent was removed in vacuum at 50 °C for 10 hours. The preparation of the Zn^{2+}-containing polymer was carried out at room temperature. When adding a 1.0 M hexane solution of diethylzinc, a similar gel was obtained and dried under vacuum under the same condition as for aluminum ions.



Scheme 2. Introduction of metal ions into the polymer matrix.

Results and Discussion

1. Polymer Characterization

The ^{1}HNMR and FTIR spectra of *tert*-butyl diphenolate polycarbonate and free diphenolic acid polycarbonate are shown in Figure1 and Figure 2, respectively. The spectra are in accord with the expected structure of the two polymers. A series of copolymers with the following structure have been synthesized and their molecular weights were measured by GPC. The data are collected in Table 1.

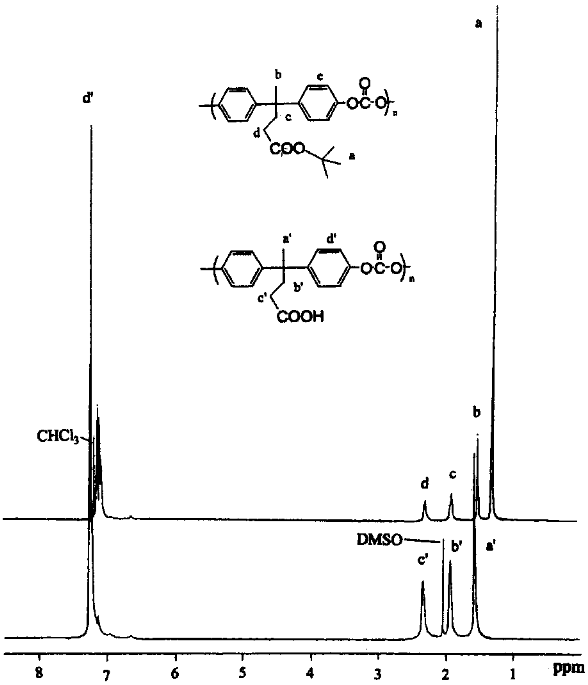


Fig. 1. ^{1}H NMR spectra of tert-butyl diphenolate polycarbonate (top) and diphenolic acid polycarbonate (bottom).

Table 1. Molecular weight of co-polycarbonate esters.

X	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	PDI
0.05	3.4	2.1	1.62
0.10	2.8	1.3	2.15
0.20	1.5	0.8	1.87
0.50	1.9	1.1	1.73
0.75	2.0	1.2	1.67
1.00	2.3	1.5	1.53

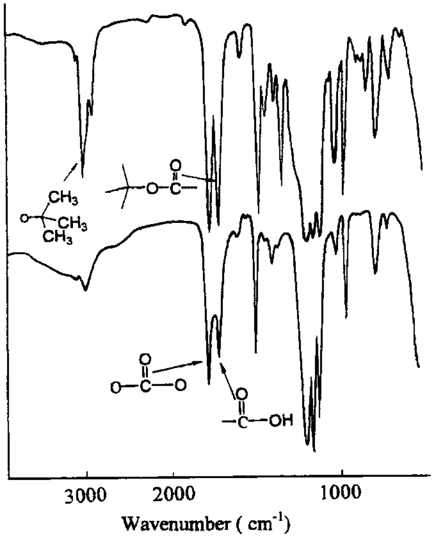
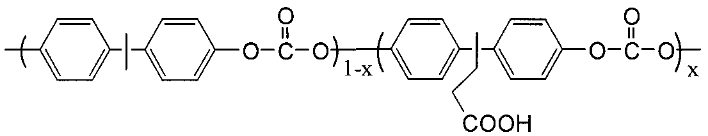


Fig. 2. FTIR spectra of tert-butyl diphenolate polycarbonate and diphenolic acid polycarbonate.

The glass transition temperatures of polycarbonate ester and polycarbonate acid have also been investigated by DSC. The results are shown in Figure 3. For the polyester the lowest T_g can be found at a composition of x = 0.5. The introduction of the *tert*-butyl side group led to a decrease of T_g as compared with the BPA-based homopolycarbonate. After the *tert*-butyl side group was cleaved with trifluoroacetic acid in methylene chloride the obtained polymer has the following structure:



The dependence of T_g on polymer composition can be seen in Figure 3. T_g first decreases from 148 °C (x = 0) to 131 °C (x = 0.10) and then increases from 131 °C to 147 °C with increasing content of carboxyl groups. The minimum value is observed at x = 0.10. Clearly the influence of hydrogen bonding can be seen to retard local chain motion compared to the ester-containing polymer.

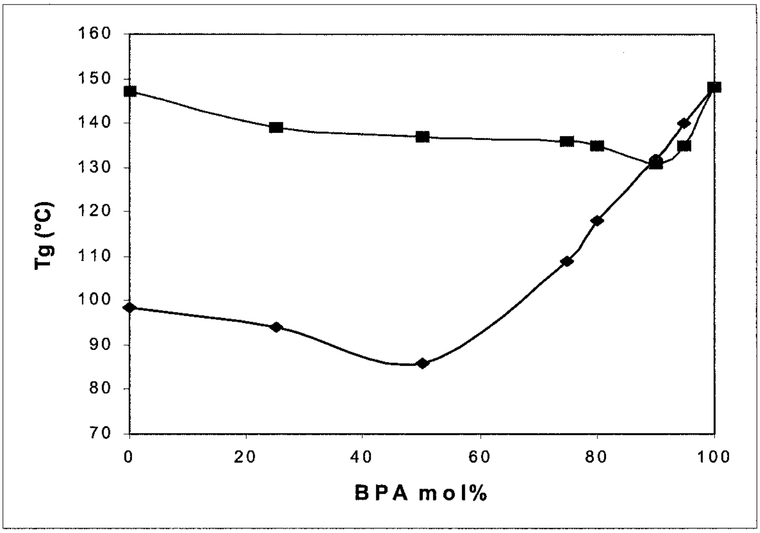


Fig. 3. The T_g of polycarbonate ester (bottom) and polycarbonate acid (top) of different compositions.

The viscosity of the polycarbonate containing free carboxylate groups (X = 0.75 and 1.0) in aqueous base solution has also been investigated. The results are shown in Figure 4. It is clear that the two polymers show typical behavior of polyelectrolytes because viscosity increases markedly as concentration decreases as a result of coil expansion.

2. The Thermal Transformation of *tert*-butyl diphenolate Polycarbonate

Figure 5 shows the TGA data of both *tert*-butyl diphenolate polycarbonate(solid line) and free diphenolic acid polycarbonate (broken line). The latter was prepared by chemical de-protection as mentioned above. It is clear that the former loses about 15% of its weight at around 200 °C, which means that the *tert*-butyl ester can be transformed into the free acid accompanied by the generation of one molecule of isobutene. In the temperature range after liberation of the protecting group, the two curves are very similar, which indicates that they correspond to the same material (free diphenolic acid polycarbonate).

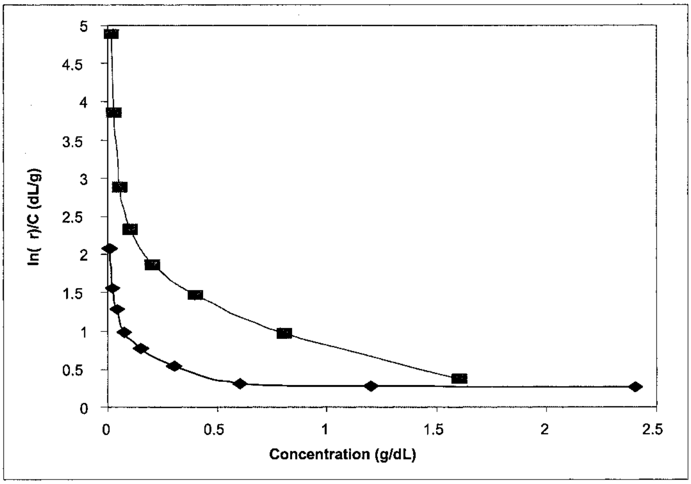
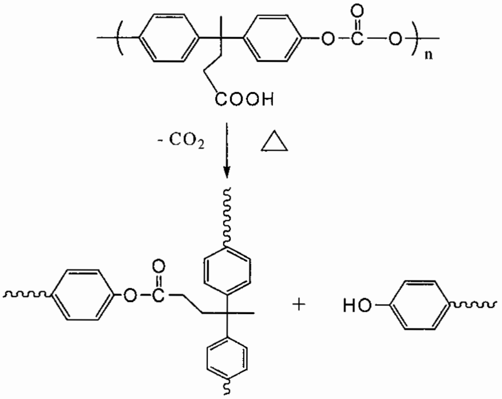


Fig. 4. The concentration-dependent viscosity of polyacids in aqueous solution at 20 °C: x = 1.0, pH = 9 (top); x = 0.75, pH = 10 (bottom).

3. The Formation of Hyperbranched Polymer[5]

As seen in Figure 5, when heating the free acid polycarbonate in the region from 250 °C to 300 °C, there is a weight loss of 12%. To know what happened in this region, IR spectra have been recorded when the sample was heated at 260 °C for different times (see Figure 6). Two significant changes appeared in the IR spectra as the heating time increased. The peak at 3380 cm^{-1} appeared as a result of the generation of hydroxyl groups during the heating process. The peak at 1773 cm^{-1} and 1704 cm^{-1} in the spectrum of the sample before heating should be ascribed to the carbonate bonds and carboxyl groups. Both of them gradually disappeared and a new peak at 1753 cm^{-1} appeared. The above results provide evidence for the formation of hyperbranched polymer through the transesterification reaction of carboxyl groups and carbonate bonds accompanied by the elimination of one molecule of carbon dioxide. This elimination corresponds to the weight loss of 12% observed in Figure 5. In the meantime, new ester bonds and phenol groups are produced in a reaction that might be described as shown below in Scheme 3.



Scheme 3. Transesterification of polycarbonate acid to hyperbranched polyester.

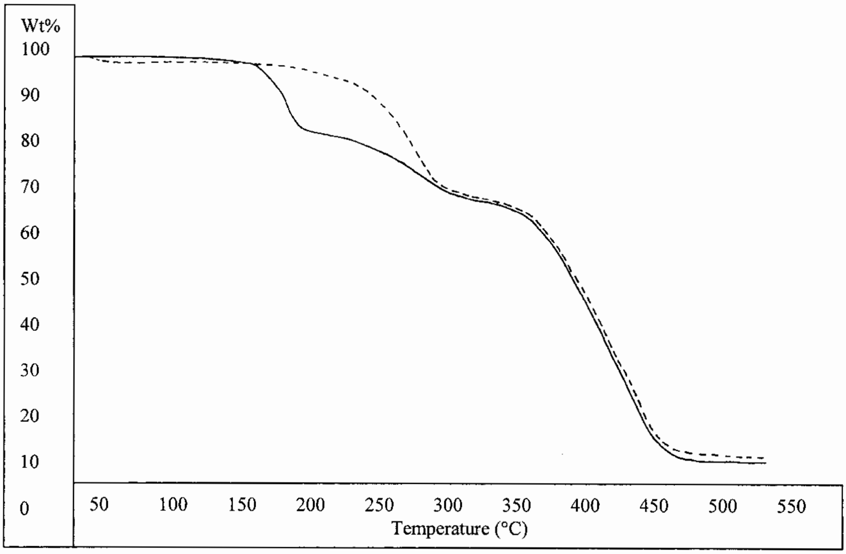


Fig. 5. TGA trace of tert-butyl diphenolate polycarbonate (solid line) and free diphenolic acid polycarbonate (broken line).

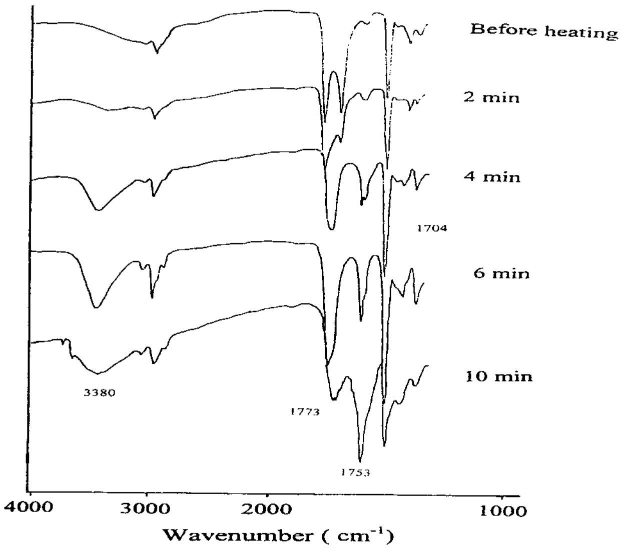


Fig. 6. IR spectra of free acid polycarbonate after heating at 260°C for different times.

4. Properties of Metal Ion Cross-linked Polycarbonate

Polycarbonate acid can react with diethyl zinc very quickly to produce a gel. The DSC measurement of these gels showed that the T_g of the materials increased as the wt-% of Zn increased (see Fig. 7). However, as the Zn wt-% reaches as high as 5 % the glass transition can no longer be observed from DSC measurements. A similar phenomenon has also been observed from the DSC results of Al cross-linked polycarbonate acid (see Fig. 8). Although Zn-complexed polymer showed relatively lower T_g values as compared with Al-complexed polymer the glass transition also disappeared as the Zn wt % reached 5 %. It has also been found that in the case of polymers with a low content of Zn (for example 1% or 2%) the formed gel can be made soluble again by heating at around 60 °C. However, the obtained solution can not be reversibly converted into a gel by cooling. This phenomenon has not been found in the Al cross-linked system and is currently being studied further.

5. The Titration of Polycarbonate Acid

The polycarbonate acid can be dissolved in dilute aqueous NaOH solution. The formed carboxlate groups will act as weak bases. In fact, every carboxlate group on the polymer has a different ionization constant, depending on its local environment. Therefore when this polycarboxylate is neutralized with HCl the titration curve should be quite different from that of a low molecular weight base. Fig. 9 shows the titration curve of sodium polycarbonate carboxylate with aqueous HCl solution. For the sake of comparision a curve of the same NaOH titrated with the same HCl solution is also included. As more HCl is added to the basic polymer solution the pH value gradually decreases from pH = 12 to pH = 3 without any sharp transition. Once the pH reaches 8 the polymer preciptates rapidly from the solution as the polycarbonate acid. This titration behavior is typical of a polyacid, which is quite different from low molecular weight analogs.

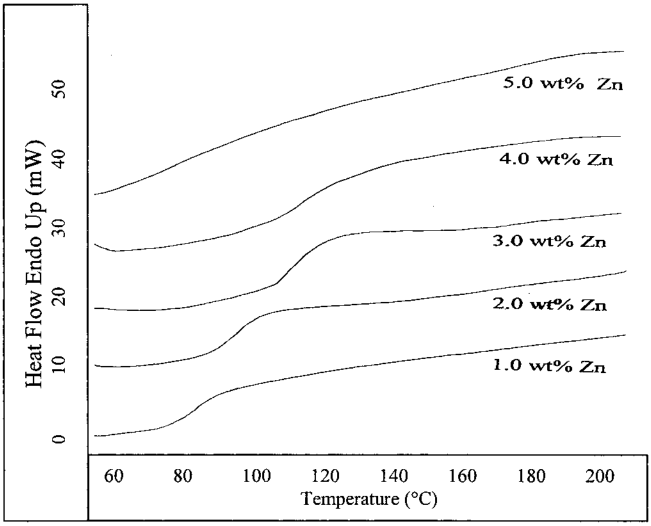


Fig. 7. DSC results for polycarbonate containing different amount of Zn^{2+}.

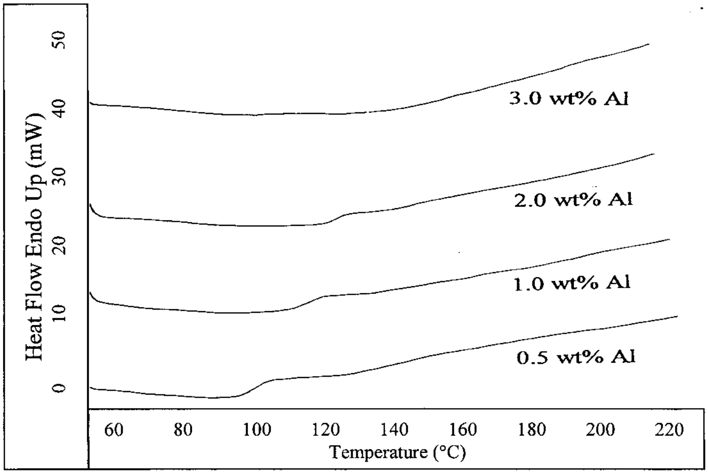


Fig. 8. DSC results for Polycarbonate containing different amount of Al^{3+}.

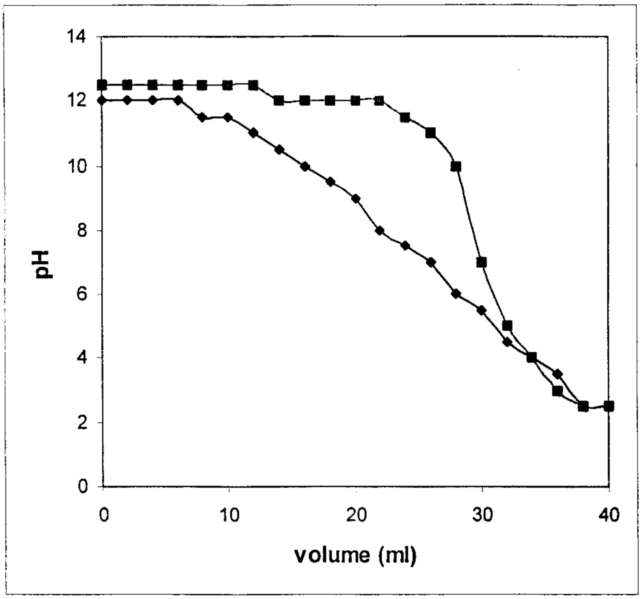


Fig. 9. Titration curve of NaOH by HCl without (top) and with 0.5g of polycarbonate acid (bottom). The concentration of NaOH and HCl is 0.01M. The volume of NaOH solution is 30 ml.

6. Stability of Polycarbonate Acid in Aqueous Basic Solution

Usually NaOH or KOH can catalyze the hydrolytic degradation of polycarbonate in a medium rich in water.[8] The carbonate bond is sensitive to inorganic or organic bases. It is interesting and important to investigate the stability of the polycarbonate acid because the polymer is soluble in aqueous base solution. Figures 10 to 12 contain data collected to measure the change in viscosity of the polymer solution as a function of time at particular concentrations and temperatures. The results show that the polycarbonate carboxylate is stable for some time in basic conditions at relatively lower temperatures. In strongly basic conditions and higher temperatures the polymer will degrade. It is proposed that the negative charge of the carboxylated backbone repels OH^- ion and prevents it from attacking the backbone carbonate bonds. This rationalization of why the polycarbonate acid is not as unstable as might be expected is under further investigation.

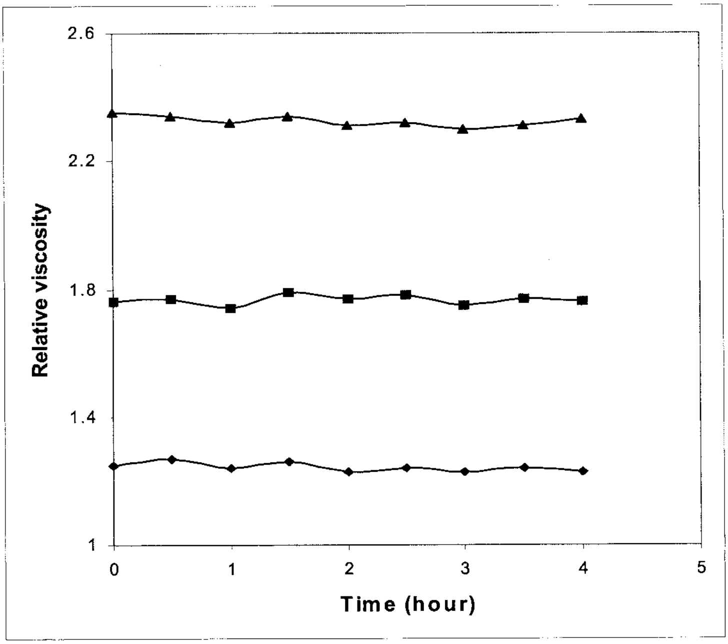


Fig. 10. Stability of homopolycarbonate acid at pH = 8 and different temperatures from top to bottom (2.0 g/dl, 75 °C; 1.0 g/dl, 50 °C; 0.5 g/d, 20 °C).

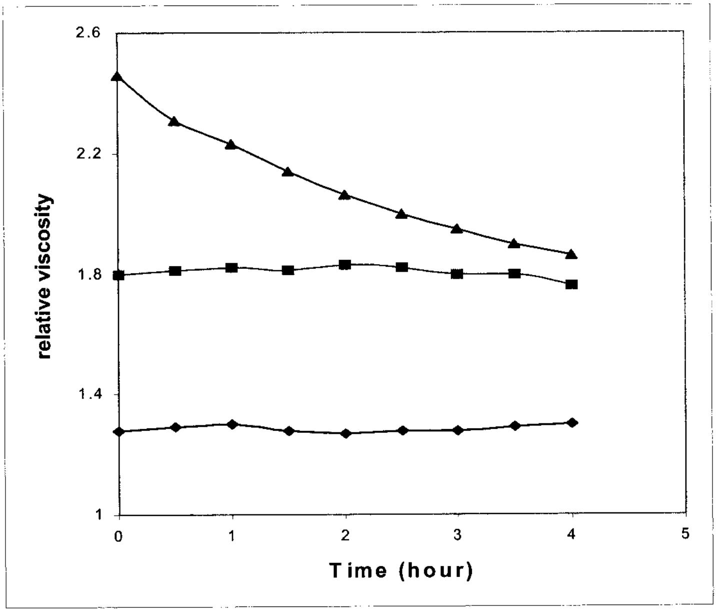


Fig. 11. Stability of homopolycarbonate acid at pH = 10 and different temperatures from top to bottom (2.0 g/dl, 75 °C; 1.0 g/dl, 50 °C; 0.5 g/d, 20 °C).

Conclusion:

Polycarbonate derivatives containing diphenolic acid as a repeat unit have been synthesized in three steps --- esterification of diphenolic acid with *tert*-butanol, condensation with phosgene, and cleavage of the tert-butyl group with trifluoroacetic acid or by thermolysis. Heating the polycarbonate acid at higher temperature leads to the formation of hyperbranched polymer. The structures and properties of obtained polymers have been characterized and investigated. The free diphenolic acid polycarbonate showed polymeric electrolyte behavior and good stability in aqueous base solution. The free carboxyl groups on the polycarbonate acid derivative can be cross-linked by using metal ions such as Al^{3+} and Zn^{2+}. The cross-linked polymer showed increasing T_g values with increasing amounts of metal ion.

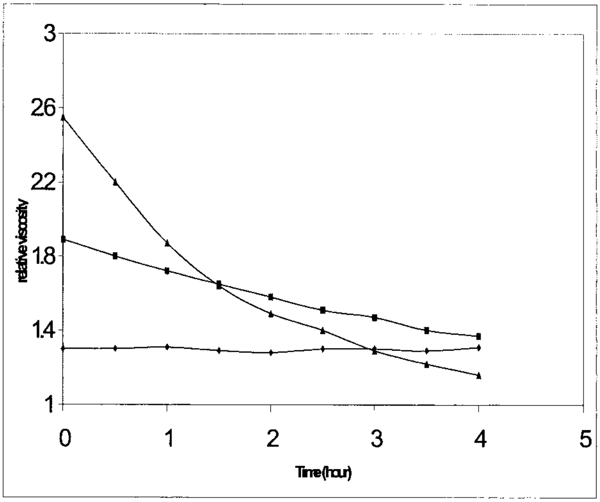


Fig. 12. Stability of homopolycarbonate acid at pH = 12 and different temperatures from top to bottom (2.0 g/dl, 75 °C; 1.0 g/dl, 50 °C; 0.5 g/dl, 20 °C).

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