

Poly(vinyl-t-butyl carbonate) synthesis and thermolysis to poly(vinyl alcohol)

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SUMMARY

The use of the t-BOC protecting group for the preparation of an organic soluble derivative of poly(vinyl alcohol) is reported. Poly(vinyl-t-butyl carbonate) can be obtained by free-radical polymerization of the monomer using peroxide or azo initiators at 90-120°C. The t-BOC polymer is thermolyzed cleanly to poly(vinyl alcohol) with evolution of carbon dioxide and 2-methyl-propene when heated to 210-220°C. The t-BOC polymer may be useful for imaging processes involving acid-catalyzed thermolysis.

INTRODUCTION

Our previous work with the t-butoxycarbonyl group (t-BOC) has shown that it could be used effectively as a protecting group for alcohols and phenols [1-3] in addition to its more classical use for the protection of amino groups [4,5]. Of particular relevance to this study is the previously demonstrated use of t-BOC groups to modify the solubility of polar polymers such as novolac [1], poly(p-hydroxystyrene) [2], or its x-methylstyrene [3] analog. Thus the t-BOC protected phenolic polymers are soluble in a wide variety of organic solvents while their phenolic precursors dissolve readily in aqueous base or in lower alcohols. Poly(vinyl alcohol) is a widely used material which owes much of its usefulness to its water solubility. This study reports on the preparation of a relatively non-polar organic soluble precursor of poly(vinyl alcohol), PVA, which can be readily modified into water-soluble PVA through simple thermolysis or acidolysis reactions.

Vinyl(t-butyl carbonate) is a monomer which has been known for some time [6]. It was first reported by Schaeffgen in 1968 and was polymerized using tributyl boron to yield a polymer which was poorly characterized. In our hands, this polymerization procedure led to materials containing significant impurities and was of little practical value. More recently Boileau et al. [7] reported the preparation of vinyl (t-butyl carbonate) in 38% yield from vinyl chloroformate and t-butanol, but not its polymerization. We now report that vinyl(t-butyl carbonate) can be prepared in significantly higher yield under classical conditions while less satisfactory results are obtained under phase-transfer catalysis.

RESULTS AND DISCUSSION

Polymerization of vinyl-t-butyl carbonate can be readily achieved using certain free-radical initiators as shown in Table 1. Essentially no high polymer formation is observed with AIBN while significantly

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TABLE 1. Polymerization of vinyl t-butyl carbonate

Init. ^a	Init. Conc. (mole %)	Solvent ^b	T(°C) ^c	Time h	Yield (%)	GPC ^d		
						Mn	Mw	Mw/Mn
t-BuPO	1.0	none	120	0.2	100 ^e	--	--	--
t-BuPO	0.6	Toluene	120	40	39	9,900	14,100	1.42
BPO	0.93	none	100	0.2	61	15,200	50,700	3.34
BPO	0.48	Benzene	90	48	37	33,900	44,800	1.32
BPO	0.23	none	88	48	--	--	--	--
ACHN	0.45	none	100	24	100 ^e	--	--	--
ACHN	0.45	Toluene	120	20	41	14,300	19,900	1.39

a) Initiator: t-BuPO= di-t-butyl peroxide; BPO =benzoyl peroxide; ACHN = azobiscyclohexacarbonitrile

b) Where a solvent is shown, a 50% monomer solution was used

c) Refers to bath temperatures

d) GPC in THF using polystyrene calibration standards.

e) Material is an insoluble gel.

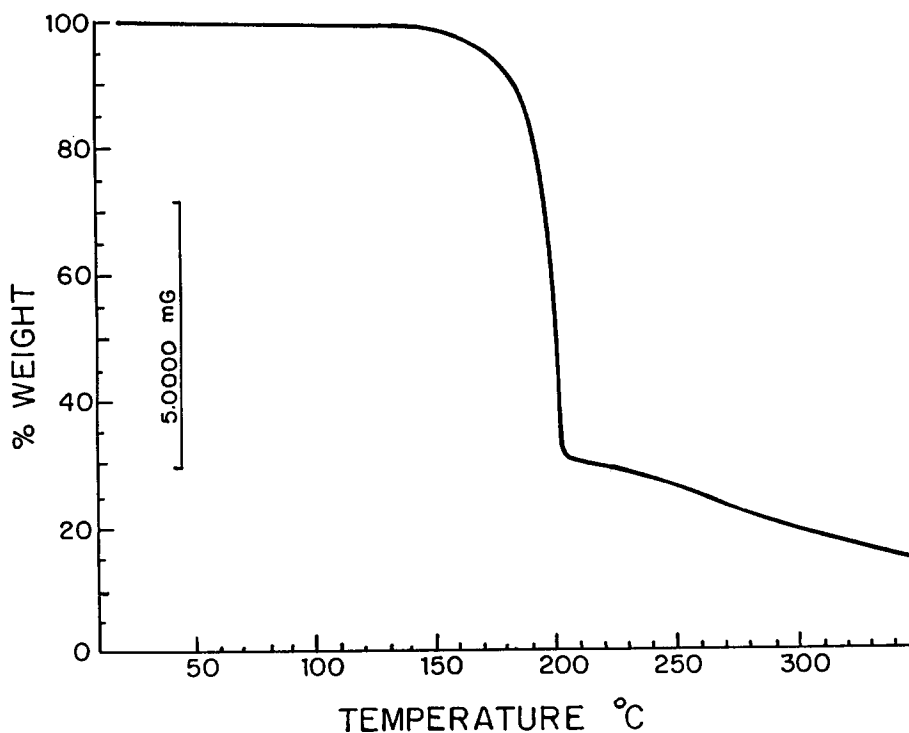
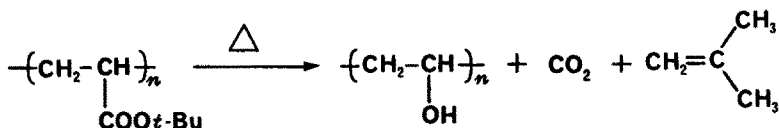


FIGURE 1. Thermogravimetric Analysis of Poly(vinyl t-butyl carbonate).

better results are obtained with benzoyl peroxide in bulk systems or in aromatic hydrocarbon solution near 100°. Due to its relatively high solubility in a variety of organic solvents the polymer is difficult to isolate in high yield. Typical processing may include dissolution in acetone followed by precipitation in hexane and brief vacuum drying at 110° to afford 30-60% of the purified polymer (Table 1). Alternately, freeze-drying in benzene affords a quantitative yield of a white material which contains significant amounts of lower molecular weight polymer and oligomers. As can be seen in Table 1 the molecular weight distributions of the precipitated polymers reflect the fractionation which inevitably occurs as the low molecular weight species have a very high solubility in hexane. Table 1 also shows the importance of the choice of initiator for bulk polymerizations as gel formation is observed in the solvent-free polymerizations involving either di-*t*-butyl peroxide or azobiscyclohexa-carbonitrile. The gel polymers had spectroscopic properties similar to those of their soluble counterparts.

The thermogravimetric analysis of poly(vinyl-*t*-butyl carbonate) (Fig. 1) afforded results which are comparable to those we obtained in our previous studies with *t*-BOC substituted vinyl phenol polymers [2,3]. The poly(vinyl-*t*-butyl carbonate) is stable to over 170° then undergoes rapid thermolytic loss of the *t*-BOC side-chains as carbon dioxide and 2-methyl propene are evolved (Scheme I).



Scheme I

As the temperature reaches 220° a sharp change in the thermogravimetric trace is seen; the weight loss observed at the outset of the side-chain decomposition is approximately 69.5% in close agreement to the calculated value. In some experiments involving polymers which had not been dried at 100-110° after precipitation a small loss of weight was observed near 100°. Such small loss of mass near 100° has also been observed by Gibson and Kurek in their work with somewhat similar polymers prepared using dicyclohexyl peroxydicarbonate as initiator [11]. GPC experiments were carried out to determine if the drying process was accompanied by significant changes in MW or distribution but the experiments proved inconclusive. Differential scanning calorimetry (Fig. 2) on poly(vinyl-*t*-butyl carbonate) show the occurrence of a large endothermic event corresponding to loss of the *t*-BOC protection centered at 218°C while a smaller endotherm near 80° was attributed to T_g. Again DSC experiments with polymers not dried at 110° after precipitation afforded different results with a small T_g endotherm near 72°. In the latter case, the endotherm moves to the higher temperature (80°) if the second heating is preceded by annealing at 110° for 10 min. DSC analysis of the insoluble polymer obtained by bulk polymerization with di-*t*-butyl peroxide shows a T_g at 117°C.

The thermal deprotection reaction is also easily followed by infrared spectrometry using a film of poly(vinyl-*t*-butyl carbonate) on sodium chloride window. The FT-IR spectrum of the starting polymer shows large bands at 2988, 1742 and 1287, 1253, 1170 cm⁻¹ corresponding to C-H

(t-butyl) C=O and multiple C-O-C bands respectively. Upon thermolysis these and other significant bands disappear completely while the remaining film shows an infrared spectrum identical to that of a fully hydrolyzed sample of poly(vinyl alcohol). Further monitoring of the thermolysis reaction by GC-MS analysis of the volatiles evolved at various temperatures confirms that carbon dioxide and 2-methyl propene are obtained under normal conditions while higher temperature degradations lead to more complex mixtures similar to those observed in the thermolysis of pure poly(vinyl alcohol). Similar polymers have recently been prepared by Harwood et al. [12] using t-butylperoxyvalate at 35°C. The polymers which were obtained had significantly higher molecular weights than ours and possessed similar thermal properties.

As is the case for other t-BOC protected hydroxylic polymers, the thermolysis reaction can be carried out at lower temperatures if acid is present [8]. This property of the polymer may prove useful in its application as an imaging material [9,10].

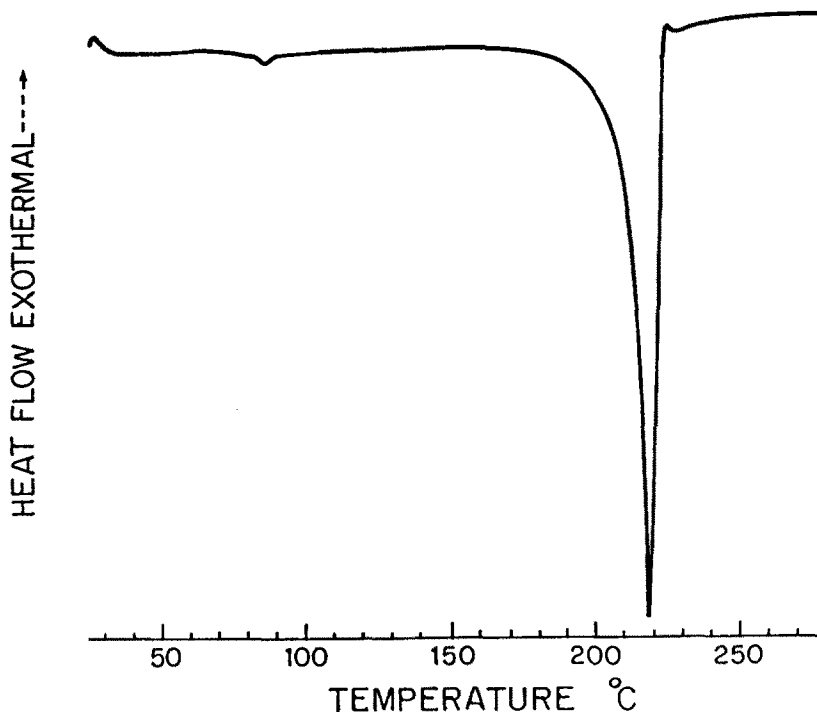


FIGURE 2. Differential Scanning Calorimetry on Poly(vinyl t-butyl carbonate)

EXPERIMENTAL

NMR spectra were recorded on a Varian XL300 spectrometer in CDCl_3 solution using TMS as internal standard. Infrared spectra were recorded on a Nicolet 10DX FT-IR using liquid cells or KBr pellets. Thermal

analyses were carried out on Mettler DSC and TG modules. GC-MS analyses were performed on VG-7070E double-focusing mass spectrometer using the normal thermal probe and 30 m capillary gas chromatographic columns. Molecular weight distributions and GPC data were obtained on a Waters model 150 gel permeation chromatograph using 5 microstyragel columns calibrated with polystyrene standards and THF as the mobile phase. Vinyl chloroformate obtained from SNPE (France) or from Sigma was purified by distillation immediately prior to use in the modification reactions.

Preparation of Vinyl t-Butyl Carbonate.

A mixture of 12 g of t-butyl alcohol (0.16 mole) and 8.6 g of pyridine (0.11 mole) which was dried and distilled over KOH was added dropwise with stirring into 10.4 g (0.1 mole) of vinyl chloroformate at 0°C. After half of the mixture had been added, the rest of the material is added as rapidly as possible, keeping the temperature below 10°C. Ten minutes later, the flask was brought to room temperature, after addition of dichloromethane and water the mixture was shaken then left standing overnight. The two layers were separated and the water layer was discarded away. The organic layer was then washed twice with 15% HCl then twice with 20% HCl. The organic phase was again separated then dried over MgSO₄. The distilled product is a colorless liquid (77% yield).

¹H NMR (chloroform-D) δ in ppm from TMS: 1.48 (s, 9H, CH₃, t-butyl); 4.48-4.50 and 4.82-4.87 (2d + 2d, 2H, =CH₂, vinyl); 6.99-7.06 (q, 1H, =CH-, vinyl).

FT-IR (in cm⁻¹): 1756 (C=O, stretch, carbonate); 1648 (C=C, stretch, vinyl); 1461, 1478 (-CH₃, antisymmetric deformation, t-butyl); 1371, 1396 (-CH₃, symmetric deformation, t-butyl).

Alternately, vinyl t-butyl carbonate was prepared as follows: a mixture of 10.85 g of vinyl chloroformate (0.102 mole), 20 mL of t-butanol (excess), and 20 mL (excess) dimethylaniline was stirred for 4 days in the presence of dimethylaminopyridine under nitrogen atmosphere. After reaction, work-up afforded 4.55 g of the desired product (31%). Polymerization of vinyl t-butyl carbonate.

All polymerizations were carried out as described in Table 1 under inert atmosphere. The temperatures indicated in Table 1 were the temperatures measured within the oil bath rather than within the polymerizing mixture. After polymerization, the polymer was dissolved in benzene and freeze-dried prior to precipitation. Alternately the polymer dissolved in toluene was precipitated in hexane. Due to the high solubility of the polymers, the yield of material was greatly affected by the conditions used in the precipitation. In some cases the precipitated polymers were dried in vacuo at 110° for 10-20 min.

¹H NMR (chloroform-D) δ in ppm from TMS: 1.47 (s, 9H, CH₃, t-butyl); 1.4-2.1 (broad m, 2H CH₂); 4.7-4.9 (broad m, 1H, CH).

FT-IR (in cm⁻¹): 2988 (C-H, t-butyl), 1742 (C=O), 1480-1460 (t-butyl), 1396, 1371, 1287, 1253, 1170.

Thermal analyses.

Thermal analyses carried out under nitrogen atmosphere on the various polymers afforded slightly different results depending on whether the polymers had been dried at 110° or at room temperature after precipitation.

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