Design, Synthesis, and Study of Novel, Thermally Depolymerizable Polycarbonates

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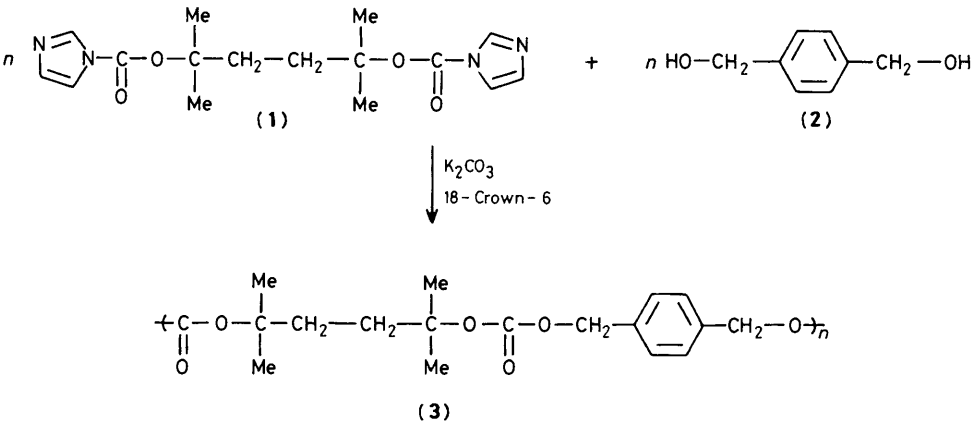
Novel polycarbonates containing tertiary or secondary benzylic diol structures are prepared *via* their bis-carbonylimidazolide derivatives under phase transfer conditions; these polycarbonates are designed to undergo a near instantaneous depolymerization to volatile monomeric species when heated to a critical temperature.

Thermally or photochemically labile polymers which undergo drastic changes in properties when exposed to heat or radiation are finding increasing applications in areas as varied as coatings, additives, or imaging materials. We have recently developed a new class of polycarbonates which undergo a unique thermally induced depolymerization process when heated to 190—210 °C.

Our design of the thermally depolymerizable polycarbonates described in this communication is based on the initial observation of the thermolytic cleavage of t-butyl carbonates of alcohols or phenols.[1] For example while it is convenient to protect the phenolic groups of *p*-hydroxystyrene[1a] with t-butoxycarbonyl (t-BOC) moieties to effect its free radical polymerization, the resulting poly(*p*-t-butoxycarbonylhydroxystyrene) can be easily deprotected to the free and unoxidized phenolic polymer by heating to 190 °C. Similarly, our work on simple t-BOC derivatives of alcohols, phenols, and enols[2] has confirmed that thermal cracking of the t-butoxycarbonyl groups results in the clean liberation of the starting hydroxy compound with evolution of carbon dioxide and 2-methylpropene. Based on these observations, it was expected that a polycarbonate containing tertiary diols in its repeating unit would behave in the same way as the t-BOC protected moieties, exhibiting great thermal lability and undergoing multiple chain scission with total breakdown of the polymer chains when heated to a certain



Scheme 1

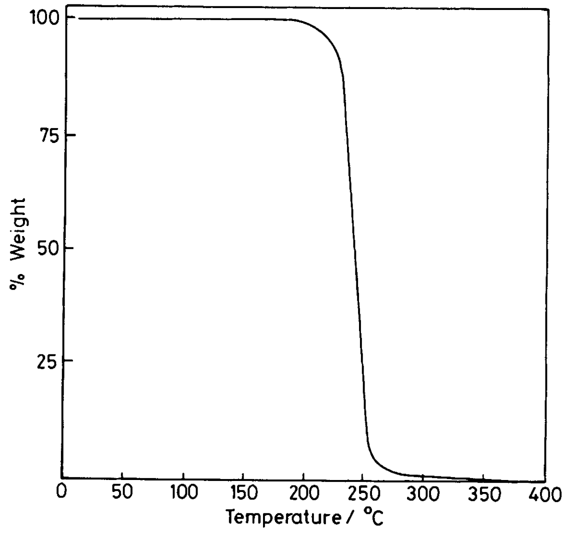


Figure 1. TGA of the alternating polycarbonate (**3**) of 2,5-dimethylhexane-2,5-diol and *p*-benzenedimethanol.

critical temperature. Scheme 1 shows the preparation of the first known example of such a polycarbonate containing tertiary diol units.

Owing to the well documented[3] lack of stability of tertiary chloroformates such as t-butylchloroformate, it appeared futile to attempt a synthesis using a tertiary bis-chloroformate. Similarly, the relatively low reactivity of t-butyl alcohol precluded the use of a tertiary diol with a pre-formed bis-chloroformate as such a synthesis would, at best, lead to oligomeric materials. In contrast, the work of Staab[4] with t-butylcarbonylimidazole, a stable analogue of t-butyl chloroformate, appeared to be well suited for our purpose as imidazole is displaced by reaction of t-butylcarbonylimidazole with an alcohol in presence of the corresponding alcoholate to afford good yields of t-butyl carbonates. The choice of tertiary diol is dictated by the need to avoid the possible formation of a five or six membered ring carbonate. Thus, the bis-carbonylimidazolide of 2,5-dimethylhexane-2,5-diol (**1**) is prepared in excellent yield by reaction of the parent diol with carbonyl di-imidazole in the presence of a small amount of sodium or potassium. Reaction of (**1**) with any simple diol such as *p*-benzenedimethanol (**2**) is best carried out under phase transfer conditions† in dichloromethane using powdered anhydrous potassium carbonate as the base and a catalytic amount of 18-crown-6.

This reaction leads to useful polymeric materials with molecular weights (M_n) ranging from 7000 to 50 000. The physical properties of the polymers, such as melting point (T_m), glass transition temperature (T_g), and solubility, are greatly affected by the nature of the co-monomer (**2**). For example, replacement of all or part of the *p*-benzenedimethanol by its *meta* isomer results in large increases in solubility but significant decreases in T_g and T_m as the percentage of *meta* alcohol is increased.

While numerous polymers such as poly(α-methylstyrene) are known to undergo a slow and reversible thermolysis when heated above their ceiling temperature, polymer (**3**) and analogues are characterized by their near instantaneous, irreversible, and quantitative decomposition into volatile materials when heated to 200—210 °C. Figure 1 shows a thermogravimetric analysis (TGA) trace of polymer (**3**) heated from room temperature to above its decomposition point. Thus, the thermolysis of (**3**) is easily followed by g.c.–mass spectrometry (m.s.) and affords the results shown in the first part of Scheme 2. As expected carbon dioxide evolution accompanies the liberation of the starting benzenedimethanol (**2**) while the starting tertiary diol is released as the corresponding diene (**4**) together with the two other possible isomeric dienes.

Consideration of the likely mechanism of thermolysis of both t-BOC protecting groups and tertiary polycarbonates led us to speculate that structures containing the 1-phenylethoxycarbonyl (PEOC) moiety should undergo a similar thermolytic cleavage. This assumption was confirmed in a study of model compounds such as 1-phenylethoxycarbonylphenol which undergoes both thermolysis and acidolysis to afford phenol, styrene, and carbon dioxide. Other model studies[5] with alcohols and amines have confirmed that the PEOC group can be used as a substitute for the t-BOC group in the protection of these functionalities. The labile PEOC structure can readily be incorporated in a polycarbonate such as (**5**) using the phase transfer catalysed polycondensation of

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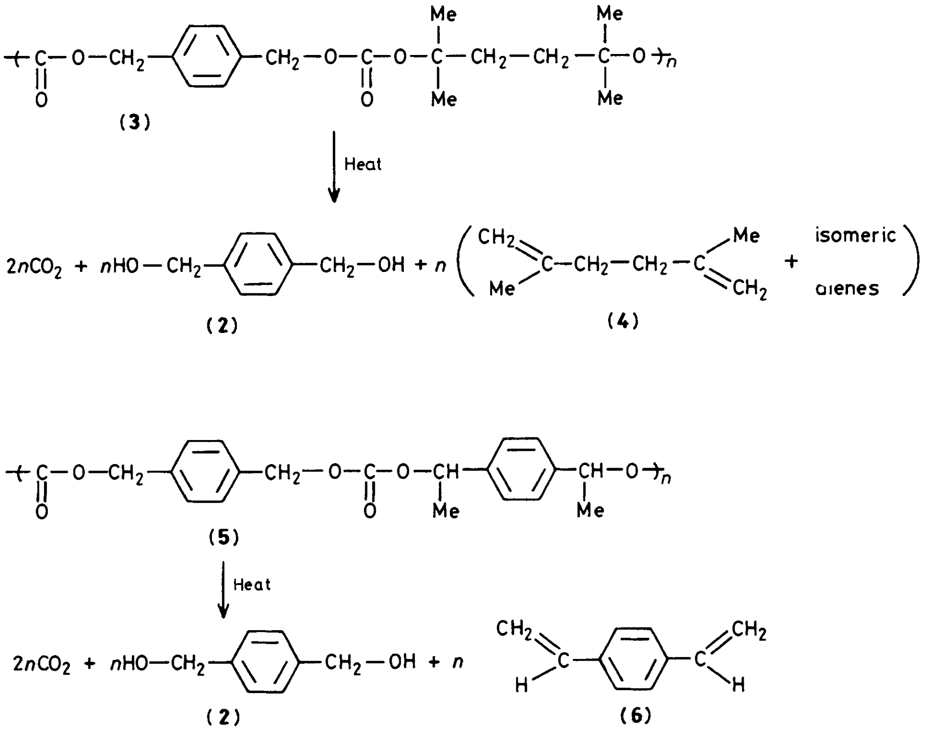
† The reaction is carried out in dry tetrahydrofuran or CH_2Cl_2 using equimolar amounts of (**1**) and (**2**) in the presence of 5 mol% 18-crown-6 and an excess of finely powdered K_2CO_3. The mixture is stirred at 60 °C for 3—15 h, the solution is filtered, and, after concentration, the polymer is precipitated in MeOH. After washing and reprecipitation a white solid material is isolated in 60—85% yield. The molecular weight of the polymer can be determined by osmometry, gel permeation chromatography, or by end-group analysis in a g.c.–m.s. study. The thermolytic behaviour of the polymer is followed by TGA on a DuPont 1030 instrument.



Scheme 2

1,4-bis(1-hydroxyethyl)benzene with a diol bis-carbonylimidazolide as in the preparation of (**3**). As expected, polymer (**5**) is stable when heated until the critical decomposition temperature of 210 °C is reached. At this point complete and near instantaneous thermolysis is observed with quantitative liberation of divinylbenzene (**6**) as shown in Scheme 2. This finding is of some interest as polymer (**5**) can be considered as a stable precursor to divinylbenzene and can find some applications in thin film technology.

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