

Synthesis and characterization of halato-telechelic bisphenol-A polycarbonates

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Abstract

Interfacial polycondensation of bisphenol-A and phosgene is a well-known way to prepare bisphenol-A polycarbonate, the molecular weight of which can be controlled by the addition of suitable amounts of phenol. When the chain stopper is a bifunctional compound, the way is open to the synthesis of telechelic polycarbonates. 4-Hydroxybenzoic acid, 4-hydroxybenzenesulfonic acid, 4 N,N'-dimethylaminophenol and the iodoammonium derivative have been used as bifunctional chain stoppers in the synthesis of acid and amino telechelic polycarbonates. The n.m.r. analysis of the final products has provided evidence for the successful synthesis of α,ω -tertiary amino and α,ω -quaternary ammonium polycarbonates. In contrast, fast transesterification reactions prevent α,ω -carboxylic and sulfonic acid polycarbonate from being prepared in a controlled way.

Keywords: bisphenol-A; polycarbonate; telechelic

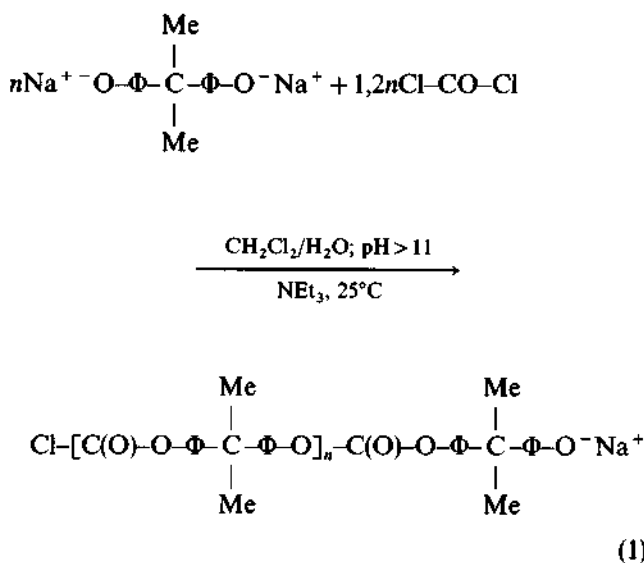
INTRODUCTION

Polymers bearing functional groups, and in particular telechelic polymers, are currently used as precursors for a large range of organic materials. For instance, telechelic polymers play a critical role in the synthesis of multiblock copolymers. The functional end-groups can either initiate the polyaddition of a second monomer or participate in coupling reactions or in a stepgrowth polymerization process. In the first case, the telechelic polymer is simply a macroinitiator, whereas in the third instance it is used as a macromonomer. Moreover, neutralization of acidic or basic end-groups generates ion pairs, the association of which promotes unusual solution and bulk properties¹⁻³. Halato-telechelic polymers (HTPs) have been produced according to this pathway as models for the more complex ionomers. In a medium with a low dielectric constant, the ionic end-groups behave as dipoles, the mutual interactions of which promote thermoreversible crosslinking. Indeed, the ion-pair association results in a microphase separation which engages the linear macromolecules in a threedimensional network. Actually, ionic multiplets, which may contain up to 20 dipoles, are organized in a liquid manner in the organic polymer matrix. However, at a high enough temperature, the ionic multiplets dissociate, releasing the individual macromolecules. The ionic multiplets are thus thermally slipping crosslinks.

Two main reaction pathways have been reported for producing bisphenol-A polycarbonate (PC): the interfacial polycondensation of bisphenol-A and phosgene⁴, and the melt reaction of bisphenol-A and diarylcarbonate^{5,6}.

Due to the toxicity of phosgene, several substitutes have been used: *N,N'*-carbonyl diimidazole⁷, bis(*o*-nitrophenyl)carbonate^{8,9}, triphosgene and trichlorophenylcarbonate¹⁰.

According to the Schotten-Bauman interfacial polycondensation, an aqueous alkaline solution containing the disodium salt of bisphenol-A is intimately mixed with an organic phase in which phosgene, triethylamine (catalyst) and the reaction products are soluble:



In order to control the molecular weight and the termination reaction, it is necessary to add a monofunctional compound reactive towards either chloroformate (-Ar-O-C(O)Cl) or phenolate (-Ar-O⁻Na⁺) end-groups¹¹. Phenol and aromatic acid chloride are recommended when the thermal stability of PC is a major concern. Recently, several patents have claimed the use of some difunctional aromatic compounds of the general formula HO-Φ-X, in order to end-cap PC with either an acid group (X=-COOH¹²⁻¹⁴, -COOtBu¹⁵, -SO₃H¹⁶) or an amino function (X=-NR₂¹⁷). This clearly implies that the phenolic group is the unique reactive function in the polycondensation reaction.

This paper reports the efficiency of the previously mentioned functional terminating agents where X is -COOH-, -SO₃H-, -N(CH₃)₂ and -N⁺(CH₃)₃I⁻, in the synthesis of α,ω-X functional PC.

EXPERIMENTAL

Materials

4,4'-Isopropylidenediphenol (bisphenol-A), 4-hydroxybenzoic acid (HBA), 4-hydroxybenzenesulfonic acid (HBSA), 4-*N,N'*-dimethylaminophenol, triethylamine, iodomethane and tetrachlorobenzoquinone (chloranil) were purchased from Aldrich and used without further purification. Phosgene solution in toluene (1.93 M) was purchased from Fluka. Toluene and tetrahydrofuran (THF) were dried by refluxing over calcium hydride and a benzophenone Na complex, respectively.

Polymerization procedure

Interfacial polycondensation was carried out at room temperature in a two-necked flask with a stopcock-equipped septum inlet and a cold finger condenser at -78°C . A mixture of bisphenol-A (6.57×10^{-2} mol), NaOH (3.24×10^{-1} mol), 100ml water and various amounts of the terminating agent was introduced into the reactor and stirred in the presence of 100 ml of CH_2Cl_2 containing triethylamine (6.57×10^{-4} mol). A phosgene solution (40 ml) in toluene (7.89×10^{-2} mol) was then carefully added. Thirty minutes later, the reaction mixture was transferred into a separating funnel. The organic layer was extracted, treated three times with water, and PC was finally precipitated in acetone.

Quaternization of 4-*N,N'*-dimethylaminophenol

The reaction was conducted in a two-necked flask with a stopcock-equipped septum inlet and a Liebig condenser. 4-*N,N'*-Dimethylaminophenol was previously dried by two azeotropic distillations with toluene. It was then added with dry THF and a 10-fold molar excess of iodomethane and refluxed for 24 h under anhydrous conditions. The solid reaction product was recovered by solvent evaporation and characterized by ^1H n.m.r. α,ω -Dimethylamino PC was quaternized under the same experimental conditions. The ^1H n.m.r. spectrum of the product showed that no reaction had occurred. The use of a greater excess of iodomethane ($50 \times$) did not improve the situation.

Characterization

^1H n.m.r. spectra were recorded in CDCl_3 using a Bruker AM 400 apparatus. Size exclusion chromatography (s.e.c.) was performed in THF at 45°C using a Hewlett-Packard 1090 liquid chromatograph equipped with an HB 1037 A refractometer index detector and four columns of various pore sizes (10^5 , 10^3 , 500 and 100 \AA). Molecular weight and molecular weight distribution were calculated by reference to a calibration curve built up with polystyrene and bisphenol-A PC standards. I.r. spectra were recorded using a Perkin-Elmer 1600 FT i.r. spectrometer.

RESULTS AND DISCUSSION

Synthesis of α,ω -acid functional polycarbonate

The first question to address is whether HBA and HBSA selectively react as monofunctional terminating agents in the interfacial polycondensation of bisphenol-A and phosgene. *Figure 1* shows a linear dependence of the number-average molecular weight (\bar{M}_n) of PC on the HBA/bisphenol-A and HBSA/bisphenol-A molar ratios. Since the chain length decreases as the amount of the functional phenol compared to bisphenol-A is increased, it is obvious that HBA and HBSA act as chain stoppers. Although the experimental data of *Figure 1* are in favour of the synthesis of acid-terminated PC, the ultimate evidence for this achievement has to be found in the presence of the acid end-groups on PC.

Several techniques have been used to analyse the structure of the PC chains. Non-aqueous titration of the purified PC with tetramethylammonium hydroxide has proved the absence of acid group attached to the polymer backbone. I.r. spectroscopy confirms the titration data since no absorption characteristic of the acid groups can be detected. On the other hand, the i.r. spectrum of a short PC chain prepared in the presence of HBA shows an additional absorption at 1740 cm^{-1} , typical of an aromatic ester function (*Figure 2*). In addition to the i.r. analysis, the ^1H n.m.r. spectrum of the same PC sample shows two minor resonances that can be assigned to aromatic protons in the β position of a phenylester group (δ_{Ha} : 8.26 ppm) and to aromatic protons in the β position of a hydroxyl function (δ_{Hc} : 6.71 ppm) (*Figure 3*). From the \bar{M}_n of PC (s.e.c. calibrated with PC standards) and the relative intensity of protons a and c (see *Figure 3*) compared to protons of the PC backbone (IH_a/IH_b; IH_c/IH_b), it appears that two phenol groups and two diphenylester functions exist per chain. Finally, the ^1H n.m.r. spectrum of PC synthesized with HBSA as a terminating agent agrees with the presence of aromatic protons in the β position of a hydroxyl group (δ_{Hb} : 6.71 ppm) (*Figure 4*). On the assumption that there are two phenol end-groups per PC chain, the relative intensity of protons b and a is quite consistent with the molecular weight determined by s.e.c. (7500 versus 7300).

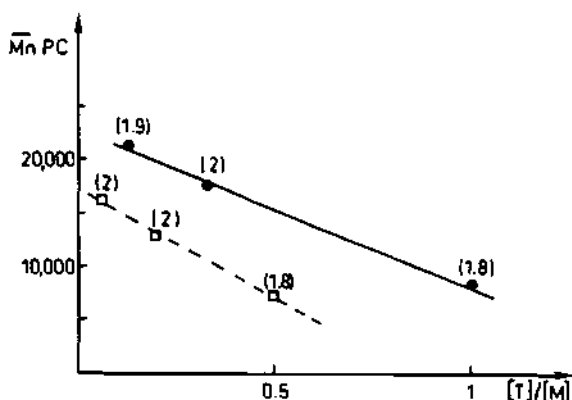
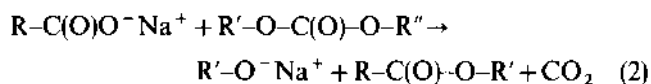


Figure 1 Dependence of the number-average molecular weight (as determined by size exclusion chromatography using polystyrene calibration) on the HBA/bisphenol-A molar ratio (●) and the HBSA/bisphenol-A molar ratio (□). The polydispersity is given in parentheses

A possible explanation for the i.r. and ^1H n.m.r. data could be found in a reaction of the acid end-groups (which should be salts at the pH of the polycondensation) with the carbonated subunits leading to the concomitant formation of esters within the chain and phenoxide end-groups. Equation (2) schematizes transesterification which is expected to occur as side reactions of the polycondensation process:



Gallez *et al.*¹⁸ give credit to the assumption of transesterification of PC by acid functions. These authors reported that the crystallization of PC is increased by several orders of magnitude in the presence of alkali arylcarbonates, such as sodium benzoate. This kinetic effect has been accounted for by a chemical reaction in the PC-salt system¹⁹⁻²¹, which would proceed through a nucleophilic attack of the carbonate subunits by the benzoate groups. A chain terminated with a sodium phenoxide is formed together with a mixed carboxylic carbonic anhydride, which is rapidly decarboxylated. This reaction scheme has been confirmed in solution (anhydrous cyclohexanone) at various temperatures (90-140°C) in the presence of minute amounts of different salts (e.g. benzoate, carbonate)²². In the melt, the chemical attack of the carbonate groups is complicated by additional reactions that lead to a complex process of crosslinking and chain scission.

In order to ascertain the instability of PC in the presence of acids and salts, PC samples were dissolved in a mixture of CH_2Cl_2 and THF (1:1) and added with HBA, HBSA and the related salts, respectively. Acids and salts were used in an 18-fold molar excess compared to PC, which corresponds to a telechelic PC with a molecular weight of 5000 carrying an acid or a salt group at both ends. From *Table 1* it is clear that PC is unstable under very mild conditions, since the acid and the related salt promote a partial degradation within the time required for polycondensation (30 min). The reaction mechanism is presumably a transesterification, as previously proposed (equation (2)). If so, carboxylic and sulfonic acid telechelic PC cannot be prepared in the presence of unprotected chain terminators. It is worth pointing out that acrylic acid has recently been reported as a chain stopper in the synthesis of α,ω -acrylate telechelic PC²³.

Synthesis of α,ω -quaternary amino polycarbonate

Besides acid phenols, *N,N'*-dimethylaminophenol has been used as a chain terminator in the synthesis of α,ω -tertiary amino PC. Tertiary amines are known to be chemically inert towards carbonates. Furthermore, they can be converted into quaternary ammonium salts, i.e. ion pairs able to self-associate in a medium of low polarity²⁴. *Table 2* illustrates the efficiency of *N,N'*-dimethylaminophenol as a chain stopper in the synthesis of bisphenol PC.

The \bar{M}_n of PC has been measured by s.e.c. (PC calibration) and found to decrease as the terminator/bisphenol-A molar ratio increases. The ^1H n.m.r. spectrum of the purified PC shows two minor resonances assigned to the dimethylamino group (δ_{Ha} : 2.98 ppm) and to aromatic protons in the β position of an amine (δ_{Hb} : 6.62 ppm) (*Figure 5*). It is interesting to point out that \bar{M}_n as calculated from the ^1H n.m.r. spectra (IHa/IHc) on the assumption of two *N,N'*-dimethylamino groups per chain, is in close agreement with the s.e.c. value (*Table 2*). This observation ascertains the quantitative end-functionalization of PC.

Table 1 Number-average molecular weight of a PC in relation to time and nature of the additive in solution (CH₂Cl₂ and THF, 1:1) at room temperature

Reaction time (min)	Number-average molecular weight × 10 ⁻³			
	HBSA	HBA	HBS·Na ⁺	HB·Na ⁺
0	45	45	45	45
30	43	40	40	35

Table 2 Dependence of the number-average molecular weight of PC on the *N,N'*-dimethylaminophenol/bisphenol-A molar ratio ([T]/[M])

[T]/[M]	\bar{M}_n (¹ H n.m.r.)	\bar{M}_n (s.e.c.)	\bar{M}_w/\bar{M}_n (s.e.c.)
1/3	2500	2600	1.6
1/10	6700	7000	1.8
1/30	21 000	21 000	1.9

As a qualitative confirmation of the amino functionalization of PC, the chloranil test proved to be positive²⁵. Indeed, coloured products (emerald green) are formed when the purified amino telechelic PC is added with chloranil, as expected for any tertiary amine.

In a further step, we investigated the quaternization of α,ω -tertiary amino PC by methyl iodide. However, the aromatic tertiary amine attached at both ends of PC is a poor nucleophile due to the withdrawing effect of the carbonated group in the *para* position, and the quaternization failed. As an alternative, *N,N'*-dimethylaminophenol was quaternized in a preliminary step and the related *N,N',N''*-trimethylaminophenol iodide was used as a terminating agent in PC formation (a terminating agent/bisphenol-A molar ratio of 0.2 was used). The recovered polycarbonate was characterized by ¹H n.m.r. and a peak assigned to the (CH₃)₃N⁺ end-groups was detected at 3.90 ppm (Figure 6). The absence of protons in the β position of hydroxyl end-group at 6.71 ppm suggests that a quaternary amine actually caps both ends of PC chains. As a result, the relative intensity of protons of the polymer backbone (Hb) and those associated to (CH₃)₃N⁺-(Ha) allows the \bar{M}_n to be calculated ($\bar{M}_n=25000$). This value has not been checked by s.e.c. due to problems of adsorption of amino compounds on the chromatographic support.

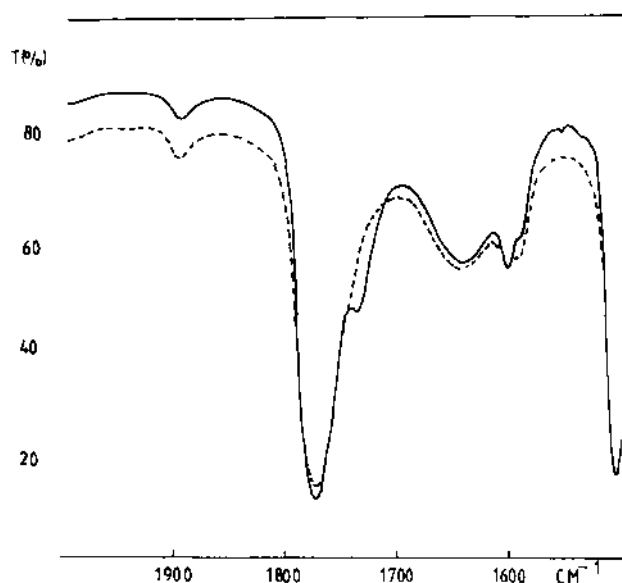
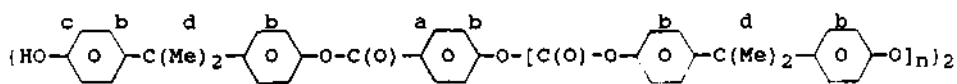


Figure 2 Comparison of the i.r. spectra of PC prepared in the presence (, $\bar{M}_n=8200$) and absence (, $\bar{M}_n=7200$) of HBA



Assignments	δ (ppm)	Intensity
a	8.26	0.45
b	7.24	65.20
c	6.71	0.45
d	1.70	48.00

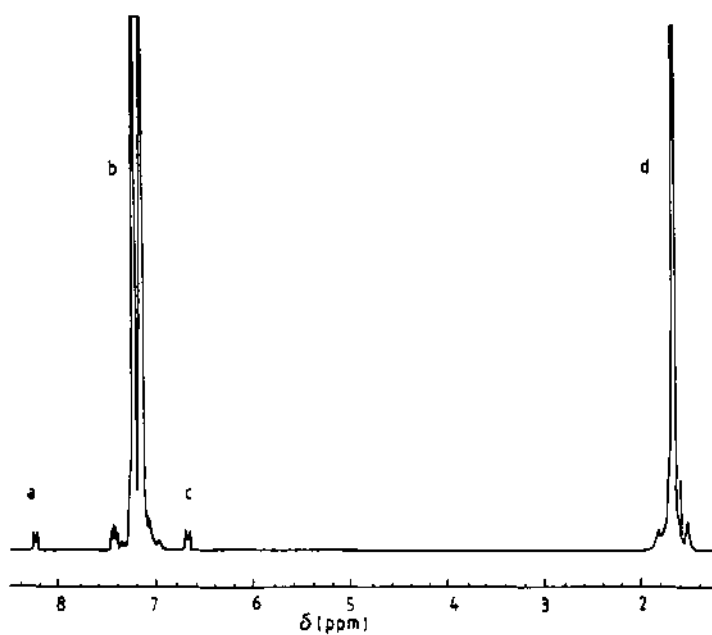
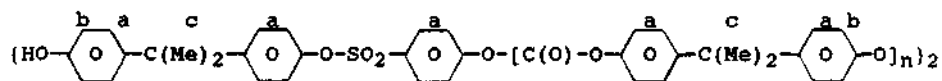


Figure 3 ^1H n.m.r. spectrum of a PC sample prepared in the presence of HBA as a chain terminator ($\bar{M}_n = 18000$)



Assignments	δ (ppm)	Intensity
a	7.24	54.06
b	6.71	0.93
c	1.70	40.52

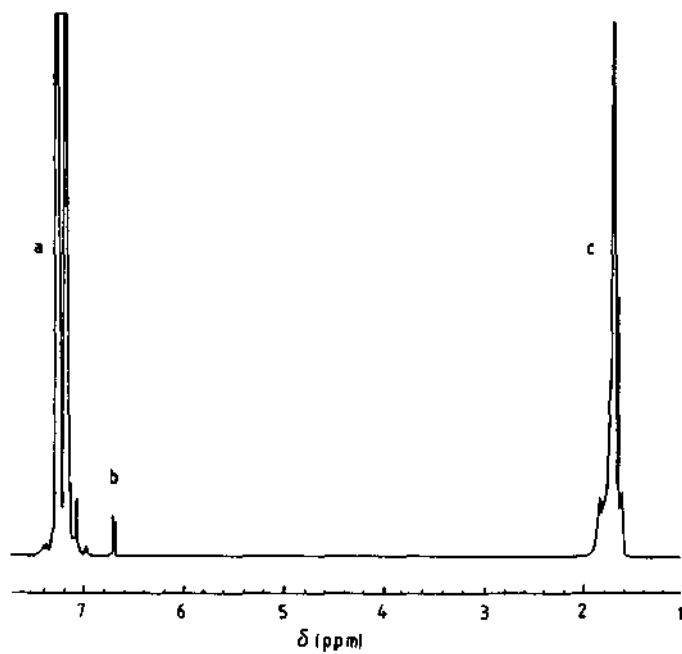
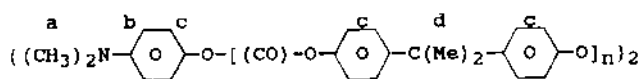


Figure 4 ^1H n.m.r. spectrum of a PC sample prepared in the presence of **HBSA** as a chain stopper ($\bar{M}_n=7500$)



Assignments	δ (ppm)	Intensity
a	2.98	7.28
b	6.62	2.42
c	7.24	40.17
d	1.70	30.50

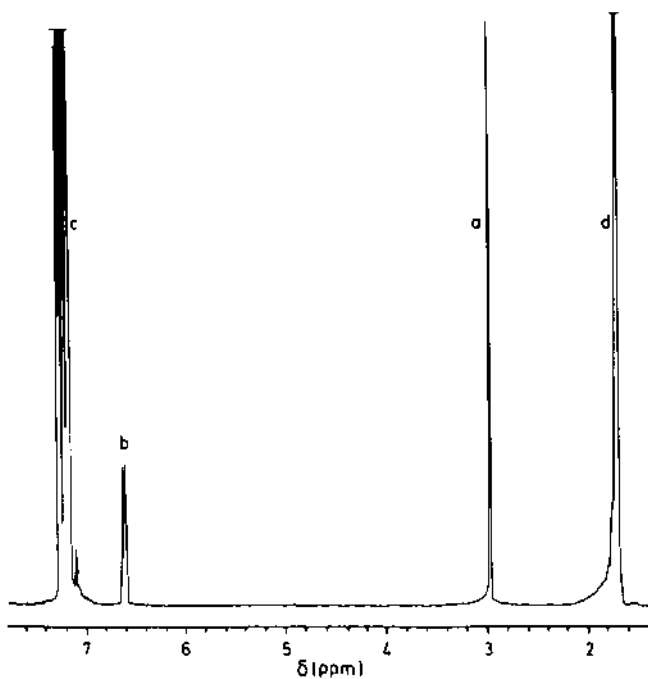
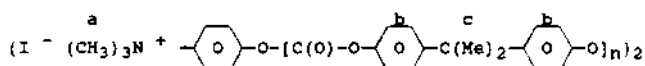


Figure 5 ¹H n.m.r. spectrum of α,ω -*N,N'*-dimethylamino PC ($\bar{M}_n=2500$)



Assignments	δ (ppm)	Intensity
a	3.90	1.31
b	7.24	56.02
c	1.70	41.21

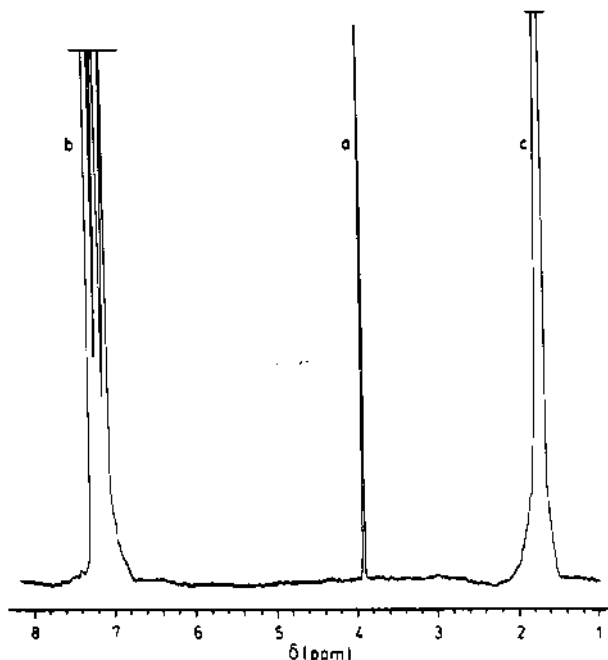


Figure 6 ^1H n.m.r. spectrum of α,ω - N,N',N' -trimethylamino PC ($M_n=25000$)

CONCLUSIONS

Although several patents have claimed the formation of carboxylic and sulfonic acid telechelic PC when HBA or HBSA are used as chain terminators, it has been proved in this paper that a fast transesterification reaction is promoted by an acid or the related salt, which prevents the telechelic PC from being synthesized. The use of a protected acid derivative, e.g. 4-hydroxytertbutylbenzoate, might be an alternative. Unfortunately, the deprotection of the terminal ester group with release of the acid will restore the instability of PC. Neutralization of the acid end-groups in the preparation of halato-telechelic PC will not improve the situation.

In contrast to acid phenols, 4- N,N' -dimethylaminophenol and the related quaternary ammonium iodide are very effective terminating agents that allow the synthesis of amino and quaternary ammonium telechelic PC to be carried out over quite a large range of molecular weights.

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