Tetraphenylporphyrin-aluminium compounds as initiators for the ring-opening polymerization of 2,2-dimethyltrimethylene carbonate: synthesis of homopolymers and copolymers with ε-caprolactone, ethylene oxide and propylene oxide

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Insertion polymerization of 2,2-dimethyltrimethylene carbonate (DTC) with initiators based on tetraphenylporphyrin-aluminium (TPPAl-R) results in high yields of poly(2,2-dimethyltrimethylene carbonate) without cyclic oligomers being formed. This indicates that back biting does not take place. The polymerization reaction is slow in methylene chloride or toluene at room temperature; the reaction rate increases with increasing temperature. Tetraphenylporphyrin-alkoxides (TPPAl-OR), the most active initiators for DTC polymerization, from a mixture of DTC and ε-caprolactone (ECL) yield a statistical copolymer, indicating poor selectivity towards these monomers. The initiator, however, is well suited for block copolymer synthesis upon stepwise addition of the monomers, e.g. poly(ECL-*block*-DTC), poly(ethylene oxide-*block*-DTC) and poly(propylene oxide-*block*-DTC). The thermal properties of poly(propylene oxide-*block*-DTC) as a function of composition are reported. Copolymers with a high propylene oxide content show a pronounced glass transition temperature for the polyether block; all copolymers show only one melting transition which is assigned to that of the polycarbonate block.

(Keywords: tetraphenylporphyrin-aluminium compounds; initiators; ring-opening polymerization; 2,2-dimethyltrimethylene carbonate)

INTRODUCTION

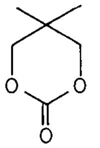
Block copolymers containing a hydrophobic and a hydrophilic block are of interest for membrane technology. Block copolymers of styrene, isoprene and ethylene oxide (EO) were prepared by anionic polymerization[1].

Oxiranes such as EO—which is considered in this work for the build up of a hydrophilic block—or propylene oxide (PO) are well suited monomers for ring-opening polymerization. The polymerization reaction is highly exothermic and if the heat of polymerization is not removed explosions may occur[2].

The cationic polymerization of oxiranes always leads to an equilibrium between the polymer and the 1,4-dioxanes with a back-biting reaction[3]. As a consequence, the polymer yields and the molecular weights which can be achieved are both low. Anionic polymerization with alkoxides as initiators has the advantage that back-biting reactions leading to 1,4-dioxanes are much slower than in cationic polymerization; but proton transfer reactions—especially if an α-hydrogen atom to the oxirane ring is present—lead to chain termination reactions. Due to these reactions nucleophilic initiators are not well suited for copolymer synthesis[3].

Insertion polymerizations are characterized by the interaction of the monomer with a covalent bond as active site which may be a metal–carbon or a metal–oxygen bond. The metal is often aluminium but can also be zinc, tin or iron, with ligands such as O-alkyl or a halogen[3,4]. Special initiators of this kind, which have been extensively studied by Inoue and co-workers, are based on tetraphenylporphyrin-aluminium (TPPAl-R) compounds[5,6]. Epoxides[5], lactones[7] and even methacrylates[8] were successfully polymerized with these initiators. Copolymers of the above-mentioned monomers and special copolymers of oxiranes with phthalic anhydride[9] or carbon dioxide[10] were also obtained. The molecular weight distributions were always narrow ($M_w/M_n \leqslant 1.1$).

In the present paper we report on the polymerization of a cyclic carbonate, 2,2-dimethyltrimethylene carbonate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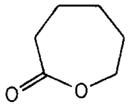
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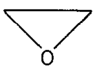
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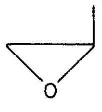
PO

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(DTC), with a TPPAl-R compound as initiator. In order to obtain some information on the activity and selectivity of TPPAl-R initiators, the copolymerization of DTC with ε-caprolactone (ECL) was investigated. The synthesis and some properties of poly(EO-*block*-DTC) and poly(PO-*block*-DTC) are reported.

EXPERIMENTAL

Reagents

DTC (Bayer AG) was sublimed, ECL (Aldrich) and PO (Merck) were distilled over calcium dihydride, and EO (Merck) was distilled before use. Tetraphenylporphyrin ($TPPH_2$) (Aldrich) was used without further purification for the synthesis of the initiators. Toluene was freshly distilled from a solution of sec-butyllithium and methylene chloride was distilled from calcium dihydride. Nitrogen and argon (Linde) were passed over a molecular sieve (4 Å), finely distributed potassium on aluminium oxide and reduced Phillips catalyst 800/350 (Cr(II) on silica gel) for purification.

Measurements

^1H and ^{13}C n.m.r. spectra were recorded on a Bruker CXP 200 FT n.m.r. spectrometer at 200 and 50 MHz, respectively. Deuterochloroform was used as solvent and tetramethylsilane as internal standard.

Thermoanalytical measurements were recorded on a differential scanning calorimeter (Perkin-Elmer DSC-7). Each sample was heated from −110 to 160°C (first heating cycle). The heating and cooling rates were $20\,K\,min^{-1}$.

G.p.c. analyses were carried out using a Waters apparatus with a combined u.v. and RI detector. A combination of four columns was applied with PL-gel (Polymer Laboratories): column length, 300 mm; diameter, 7.0 mm; diameter of the gel particles, 5 μm; pore width, 100, 500, 10^3 and 10^4 Å. For all copolymers the eluting solvent was THF and a flow rate of $0.5\,ml\,min^{-1}$ was used.

General polymerization procedure

All glass vessels were heated *in vacuo* before use, filled with inert gas and handled only in a stream of dry inert gas. Monomer and initiator solutions were added in the desired order. The polymerization was terminated by addition of H_3PO_4/methanol solution.

Polymerization of 2,2-dimethyltrimethylene carbonate. The time–conversion plot (*Figure 1*) was obtained by quenching samples with H_3PO_4 methanol at different polymerization times, followed by evaporation of the solvent and analysis of the residue by ^1H n.m.r. spectroscopy.

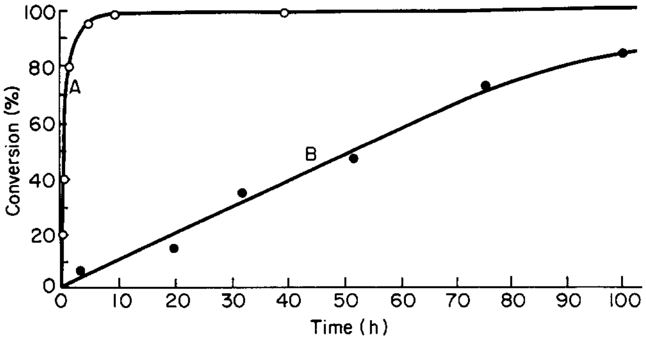


Figure 1 Polymerization of DTC (A) in toluene at 50°C and (B) in methylene chloride at 20°C. $[DTC]_0 = 1.9\,mol\,l^{-1}$; $[TPPAl\text{-}(OCH(CH_3)\text{-}CH_2)_2\text{-}Cl]_0 = 12.5\,mmol\,l^{-1}$

*Poly(ε-caprolactone-*block*-2,2-dimethyltrimethylene carbonate).* Initial conditions—first step: solvent, toluene; temperature, +50°C; $[TPP\text{-}Al\text{-}(OCH(CH_3)\text{-}CH_2)_2\text{-}Cl]_0$, $12.5\,mmol\,l^{-1}$; $[ECL]_0$, $2.2\,mol\,l^{-1}$; time, 15 h; second step: addition of DTC to obtain $[DTC]_0$, $1.9\,mol\,l^{-1}$; reaction time, 15 h. The polymer was isolated by precipitation in methanol/H_3PO_4. Yield 91%.

Molar composition (^1H n.m.r.): ECL/DTC repeat units: 56/44.

^1H n.m.r. ($CDCl_3$): $\delta = 0.97$ (s, 6H, DTC), 1.4 (m, 2H, ECL), 1.6 (m, 4H, ECL), 2.27 (t, 2H, ECL), 3.93 (s, 4H, DTC), 4.02 (t, 2H, ECL) ppm.

^{13}C n.m.r. ($CDCl_3$): $\delta = 21.32$ (2C, DTC), 24.53 (1C, ECL), 25.49 (1C, ECL), 28.31 (1C, ECL), 34.07 (1C, ECL), 35.12 (1C, DTC), 64.07 (1C, ECL), 72.42 (2C, DTC), 155.29 (1C, DTC), 173.44 (1C, ECL).

*Poly(ε-caprolactone-*stat*-2,2-dimethyltrimethylene carbonate).* Initial conditions—solvent, toluene; temperature, +50°C; $[TPPAl\text{-}(OCH(CH_3)\text{-}CH_2)_2\text{-}Cl]_0$, $12.5\,mmol\,l^{-1}$; $[ECL]_0$, $2.2\,mol\,l^{-1}$; $[DTC]_0$, $1.9\,mol\,l^{-1}$; reaction time, 15 h. The polymer was isolated by precipitation in methanol/H_3PO_4. Yield 88%.

Molar composition (^1H n.m.r.): ECL/DTC repeat units: 55/45.

^{13}C n.m.r. ($CDCl_3$): in addition to the signals for the block copolymer two new signals for heterodiads appear at $\delta = 67.78$ (ECL–DTC diad) and 68.87 (DTC–ECL diad) ppm.

*Poly(ethylene oxide-*block*-2,2-dimethyltrimethylene carbonate).* Initial conditions—first step: solvent, methylene chloride; temperature, 20°C; $[TPP\text{-}Al\text{-}Cl]_0$, $12.5\,mmol\,l^{-1}$; $[EO]_0$, $10.8\,mol\,l^{-1}$; reaction time, 48 h; second step: addition of a solution of DTC to obtain $[DTC]_0 = 7.6\,mol\,l^{-1}$; reaction time, 72 h. Yield 90%.

Molar composition (^1H n.m.r.): EO/DTC repeat units: 48/52.

^1H n.m.r. ($CDCl_3$): $\delta = 0.97$ (s, 6H, DTC), 3.61 (s, 4H, EO), 3.93 (s, 4H, DTC) ppm.

^{13}C n.m.r. ($CDCl_3$): $\delta = 21.33$ (2C, DTC), 35.13 (1C, DTC), 70.55 (2C, EO), 72.43 (2C, DTC), 155.25 (1C, DTC) ppm.

*Poly(propylene oxide-*block*-2,2-dimethyltrimethylene carbonate).* Initial conditions—first step: solvent, methylene chloride; temperature, 20°C; $[TPPAl\text{-}Cl]_0$, $0.05\,mol\,l^{-1}$; $[PO]_0$, $7.41\,mol\,l^{-1}$; reaction time, 72 h; second step: all volatile materials are removed *in vacuo* and the polymer redissolved in toluene to obtain the same concentration; a solution of DTC is added to obtain $[DTC]_0 = 3.1\,mol\,l^{-1}$; temperature, 50°C; reaction time, 12 h. Yield 80%.

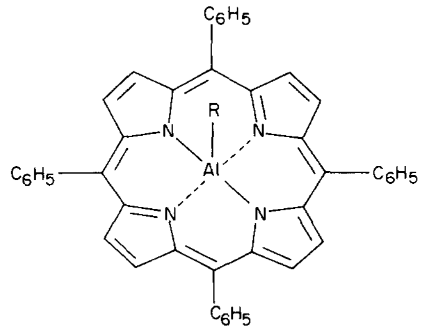
Molar composition (^1H n.m.r.): PO/DTC repeat units: 26/74.

^1H n.m.r. ($CDCl_3$): $\delta = 0.98$ (s, 6H, DTC), 1.10 (d, 3H, PO), 3.40 (m, 1H, PO), 3.53 (m, 2H, PO), 3.94 (s, 4H, DTC).

^{13}C n.m.r. ($CDCl_3$): $\delta = 17.42$ (1C, PO), 21.34 (2C, DTC), 35.14 (1C, DTC), 72.45 (2C, DTC), 73.39 (1C, PO), 75.52 (1C, PO), 155 (1C, DTC).

RESULTS AND DISCUSSION

The initiators based on TPPAl-R differ in the R substituent and are prepared from $TPPH_2$



R = Cl (**1**)
$-CH_3$ (**2**)
$-OCH_3$ (**3**)
$-OCH_2CH_2OC_6H_5$ (**4**)
$\{OCH(CH_3)CH_2\}_2Cl$ (**5**)
$-O(CH_2)_2OC_6H_4C(CH_3)_2C_6H_4O(CH_2)_2\cdot$ OAlTPP (**6**)

with either diethylaluminium chloride (equation (1)) or trimethyl aluminium (equation (2)).

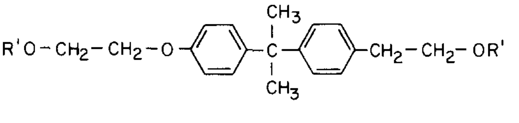
$$\text{TPPH}_2 + (\text{CH}_3\text{CH}_2)_2\text{AlCl} \rightarrow \underset{\mathbf{1}}{\text{TPPAl-Cl}} + 2\text{C}_2\text{H}_6 \tag{1}$$

$$\text{TPPH}_2 + (\text{CH}_3)_3\text{Al} \rightarrow \underset{\mathbf{2}}{\text{TPPAl-CH}_3} + 2\text{CH}_4 \tag{2}$$

$$\underset{\mathbf{2}}{\text{TPPAl-CH}_3} + \text{CH}_3\text{OH} \rightarrow \underset{\mathbf{3}}{\text{TPPAl-OCH}_3} + \text{CH}_4 \tag{3}$$

$$\underset{\mathbf{2}}{\text{TPPAl-CH}_3} + \text{C}_6\text{H}_5\text{-OCH}_2\text{CH}_2\text{OH} \rightarrow \underset{\mathbf{4}}{\text{TPPAl-OCH}_2\text{CH}_2\text{OC}_6\text{H}_5} \tag{4}$$

$$\underset{\mathbf{1}}{\text{TPPAl-Cl}} + 2\,\boxed{\text{CH(CH}_3\text{)-CH}_2\text{-O}} \rightarrow \underset{\mathbf{5}}{\text{TPPAl-[OCH(CH}_3\text{)CH}_2]_2\text{-Cl}} \tag{5}$$



6 (R' = TPPAl), **7** (R' = H)

Both initiators **1** and **2** can be transformed into TPPAl-alcoholates by either reaction with alcohols (equations (3) and (4)) or with epoxides (equation (5)).

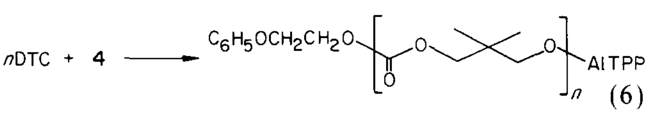
Initiator **4** has a u.v.-active aromatic group, which if incorporated in the polymer can easily be detected, leading to information on the mechanism involved.

A bifunctional initiator **6** was prepared based on the diol **7**.

Insertion polymerization of 2,2-dimethyltrimethylene carbonate with initiators based on tetraphenylporphyrin-aluminium

To our knowledge cyclic carbonates have not previously been polymerized with initiators based on TPPAl-R. In preliminary experiments it was shown that the initiators **1** and **2**, which were successfully applied by Inoue to oxirane polymerization[5], are not active in the polymerization of DTC. Using a 1.9 M solution of DTC in toluene at 50°C after 5 days of reaction with initiator **2** no polymer was obtained but with initiator **1** a polymer yield of 17 wt% was obtained. The molecular weight of the polymer was higher by a factor of 5 than expected from the monomer to initiator ratio. With initiator **1**, initiation is slow compared to propagation.

Initiators **3**, **4** and **5** show no difference in their reactivity with respect to DTC. Apart from the typical solvents of anionic polymerization such as toluene and tetrahydrofuran, methylene chloride can also be used. Thus DTC was reacted with **4** in methylene chloride to form a polymer (equation (6)); no cyclic oligomers were observed, which leads to the conclusion that no ring-chain equilibrium is established.



(6)

G.p.c. analysis of the polymer initiated with **4** shows a unimodal and narrow distribution with u.v. absorption, indicating that the aromatic residue of the initiator is incorporated into the polymer. The reaction time is very long at room temperature; after 100 h a yield of 85% polymer was obtained. In toluene the reaction time can be significantly reduced by increasing the temperature to 50°C. *Figure 1* shows the time–conversion curve of the polymerization of DTC initiated by **5** in methylene chloride at 20°C and in toluene at 50°C. For some cases of block copolymer synthesis, e.g. poly(EO-*block*-DTC), the disadvantage of a slow reaction in methylene chloride at 20°C must be tolerated for the benefit of a homogeneous reaction; poly(ethylene oxide) (PEO) is insoluble in toluene.

Copolymers of 2,2-dimethyltrimethylene carbonate and ε-caprolactone

Previous results[11] on copolymers of DTC and ECL have shown that initiation of a mixture of DTC and ECL with sec-butyllithium or potassium dihydronaphthylide at room temperature leads to polymers of the A–X–B type, where A represents a poly(2,2-dimethyltrimethylene carbonate) (PDTC) block, B represents a poly(ε-caprolactone) block and X stands for a tapered segment containing the two monomers with a compositional gradient. This result indicates that the active species shows a selectivity towards the monomers. Stepwise addition of the monomers to the above-mentioned initiators based on lithium and potassium yields copolymers with pure block structure, if the temperature is kept below 20°C. Statistical copolymers are obtained if the temperature is raised due to transesterification reactions. With initiators of the type TPPAl-OR pure A–B block copolymers are obtained by stepwise addition of the monomers to the initiator, at both low temperatures and at temperatures as high as 80°C. ^{13}C

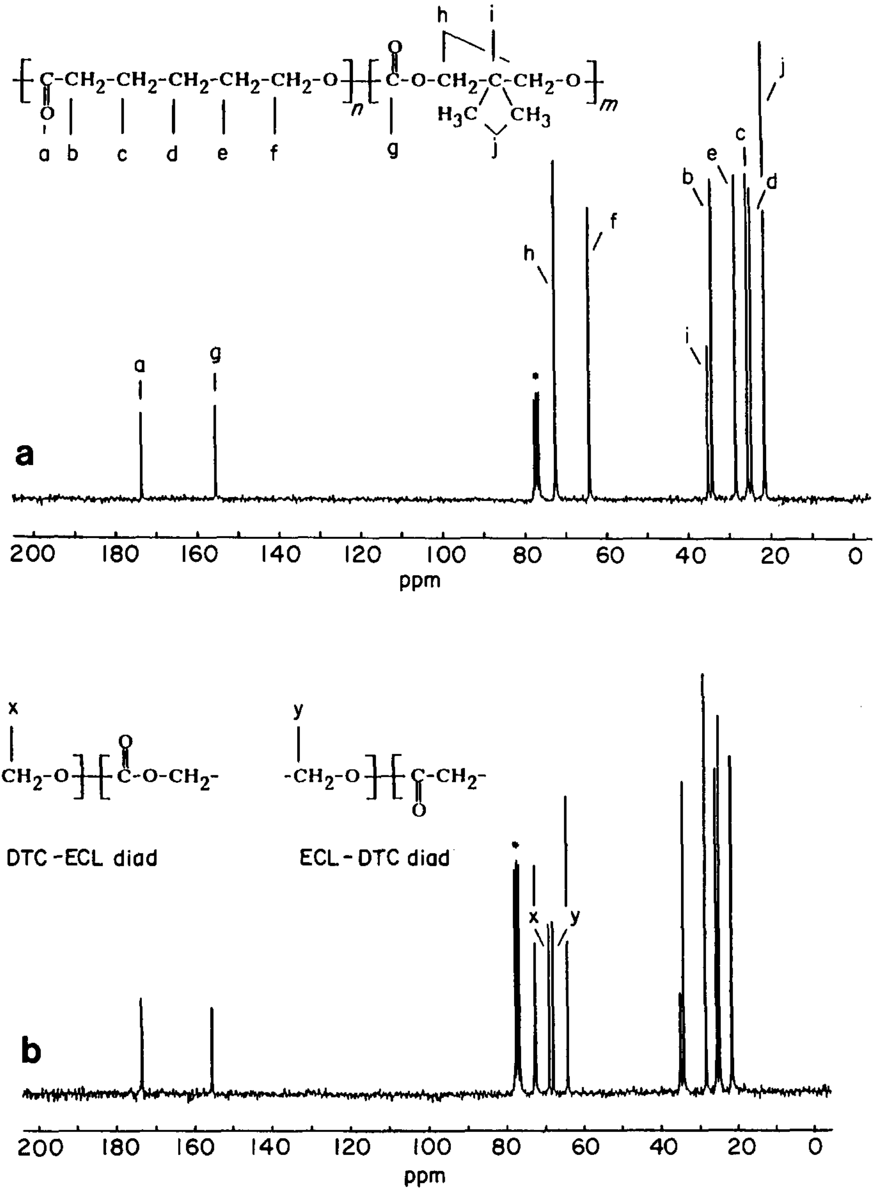


Figure 2 ^{13}C n.m.r. spectra of (a) poly(ECL-*block*-DTC) and (b) poly(ECL-*stat*-DTC)

n.m.r. analysis (*Figure 2a*) of these copolymers show only signals corresponding to the homodiads AA and BB.

A mixture of the monomers, however, in toluene solution with $[ECL]_0 = 2.2$ mol l^{-1}, $[DTC]_0 = 1.9$ mol l^{-1} and an initial concentration of **5** = 12.5 mol l^{-1} at 50°C results in a copolymer in a yield of 93% within 15 h. ^{13}C n.m.r. analysis (*Figure 2b*) confirms the statistical structure of the copolymer. The most sensitive carbon atom for sequence analysis is the CH_2 carbon neighbouring the alcoholate oxygen: for the carbonate and ester homodiads the signals were assigned at $\delta = 72.42$ and 64.07 ppm, respectively, while for the ester-carbonate and carbonate-ester diads the signals at $\delta = 67.78$ and 68.87 ppm were assigned, respectively, on the basis of model compounds[12].

Copolymers of 2,2-dimethyltrimethylene carbonate with ethylene oxide and propylene oxide

The synthesis of block copolymers with a polycarbonate block and a PEO or poly(propylene oxide) (PPO) block was of interest.

As initiator TPPAl-Cl (**1**) was chosen; this initiator was used by Inoue for EO and PO polymerization. In the first step the epoxide was polymerized and in the second the cyclic carbonate. For the synthesis of poly(EO-*block*-DTC) the solvent used was methylene chloride, because of the solubility of PEO. Several samples (*Table 1*) with different monomer ratios were prepared, with the molecular weight of the polycarbonate block being kept constant at 20000.

The formation of the block copolymer could not be followed by g.p.c. in THF, since PEO was insoluble in this solvent. However the g.p.c. of the copolymer showed a unimodal and narrow distribution. To verify the block copolymer structure, fractional precipitation of the polymer was performed. A blend of PEO and PDTC dissolved in methylene chloride was separated by dilution with THF; PEO precipitates under these conditions if the molecular weight is >5000. By dilution of the expected block copolymer solution in methylene chloride with twice the volume of THF, no precipitate was observed, showing that all the TPPAl-PEO initiated the DTC polymerization. Even by removing methylene chloride the polymer remained soluble in THF. Addition of twice the volume of methanol to this solution gave no precipitate [as should be the case when homo-PDTC is

Table 1 Preparation conditions and data for poly(EO-*block*-DTC)

Initial conditions				Molecular weight of		Block copolymer		PEO block yield[b] (wt%)	PDTC block yield[c] (wt%)
$[EO]_0$ (mol l^{-1})	$[I]_0$ (mmol l^{-1})	$[DTC]_0$ (mol l^{-1})	EO/DTC (mol mol^{-1})	PEO block	PDTC block	Yield (wt%)	EO/DTC[a] (wt%)		
2.25	50	3.85	23/77	1800	20000	92	13/87	56	96
5.5	50	3.85	42/58	4400	20000	88	20/80	36	99
10.8	50	3.85	59/61	8600	20000	90	48/52	65	100
21.3	50	3.85	74/26	17000	20000	88	68/32	75	98

[a] Molar composition from ^1H n.m.r.
[b] PEO in the block copolymer
[c] PDTC in the block copolymer

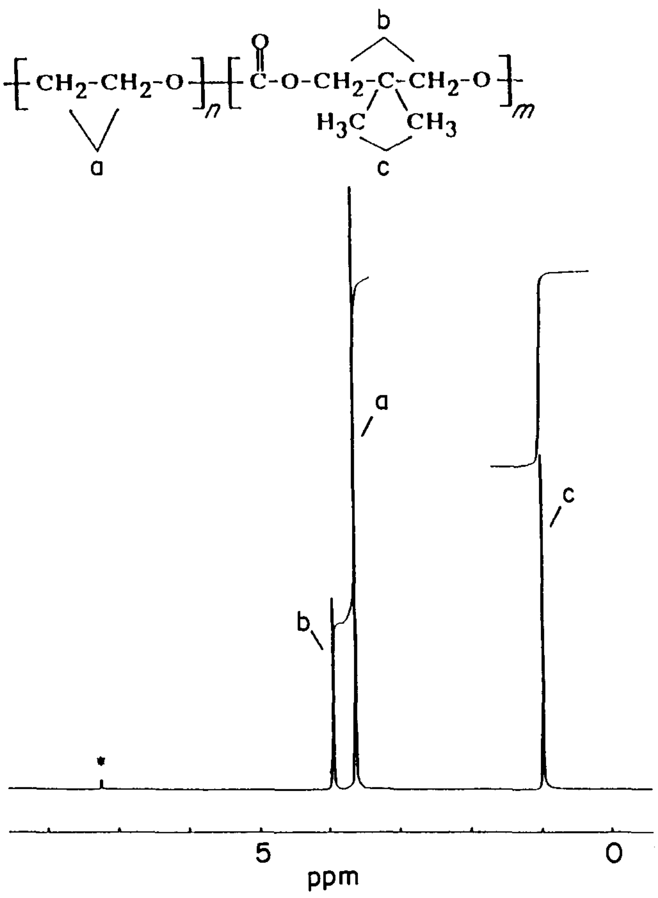


Figure 3 ^1H n.m.r. spectrum of poly(EO-*block*-DTC)

present]. Addition of more methanol leads to precipitation, if the molar composition of the copolymer EO:DTC is <2:1.

Table 1 summarizes the results obtained for four copolymers with different compositions. The monomer ratio in the feed does not show good agreement with the ratio of the repeat units in the copolymer. This is mainly due to the low polymer yield in the first step of the reaction. The overall polymer yield is in the range of 88–92% due to the quantitative polymerization of the cyclic carbonate. The composition of the copolymers was determined by ^1H n.m.r. analysis (*Figure 3*). The spectrum shows three singlets, two for the DTC repeating units at $\delta = 0.97$ and 3.93 ppm assigned to the methyl and methylene groups, respectively, and a singlet at $\delta = 3.61$ ppm assigned to the two methylene groups of the EO repeat unit. The ^{13}C n.m.r. spectrum (*Figure 4*) confirms the A–B block structure of the copolymer. All signals appear as singlets, which is evidence for the existence of only AA and BB diads within the limits of experimental error; one AB diad per polymer chain cannot be detected in the spectrum.

The synthesis of poly(PO-*block*-DTC) follows the same order of monomer addition. First PO is polymerized in methylene chloride with TPPAl-Cl as initiator. Then the solvent is changed to toluene, DTC is added and polymerized at 50°C, in order to increase the polymerization rate.

Again copolymers with different repeat unit ratios were prepared with the carbonate block having a molecular weight of 20000. Since PPO is soluble in THF, the formation of the copolymer with homo-PPO being used

Table 2 Preparation conditions and data for poly(PO-*block*-DTC)

Initial conditions				Molecular weight of		Block copolymer		PPO block yield[b] (wt%)	PDTC block yield[c] (wt%)
$[PO]_0$ (mol l^{-1})	$[I]_0$ (mmol l^{-1})	$[DTC]_0$ (mol l^{-1})	PO/DTC (mol mol^{-1})	PPO block	PDTC block	Yield (wt%)	PO/DTC[a] (wt%)		
1.55	50	1.54	17/83	1800	20000	92	5/95	44	96
3.79	50	1.54	33/67	4400	20000	86	10/90	30	99
7.41	50	1.54	49/51	8600	20000	80	26/74	37	98
14.66	50	1.54	66/35	17000	20000	75	45/55	45	100
29.31	50	1.54	79/21	34000	20000	72	66/34	53	100

[a] Molar composition from ^1H n.m.r.
[b] PPO in the block copolymer
[c] PDTC in the block copolymer

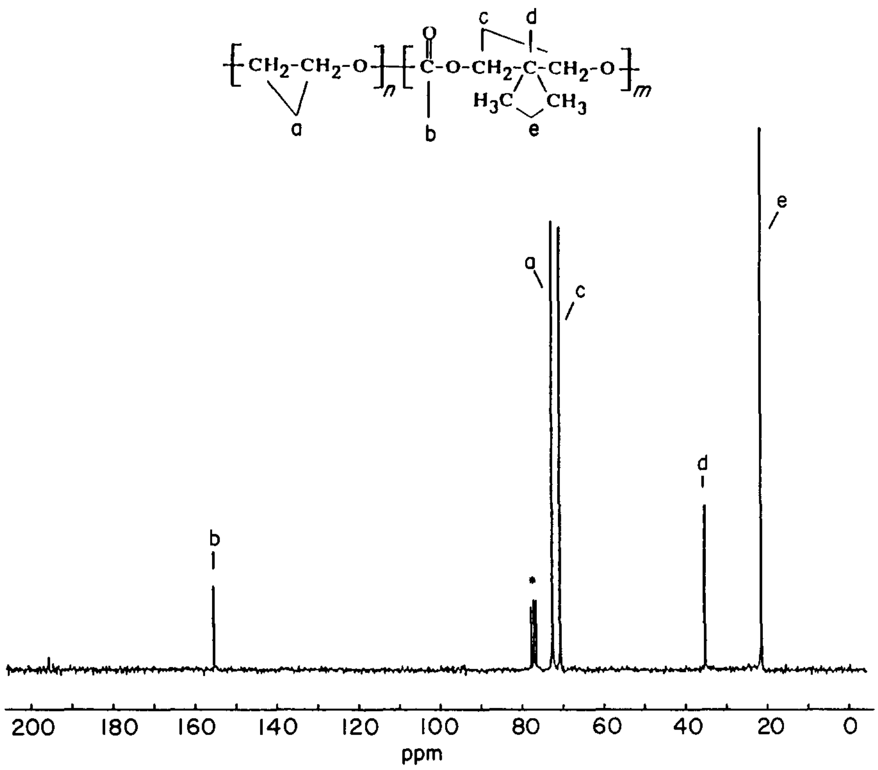


Figure 4 ^{13}C n.m.r. spectrum of poly(EO-*block*-DTC)

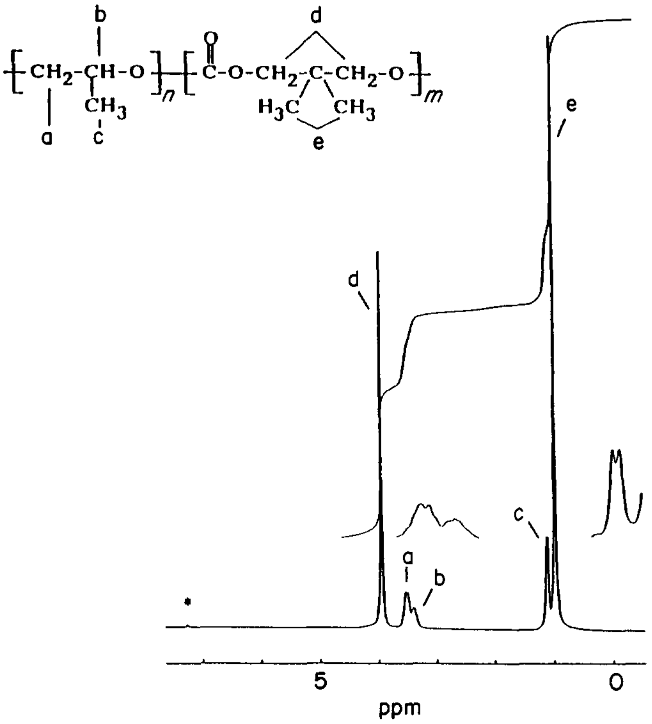


Figure 5 ^{1}H n.m.r. spectrum of poly(PO-*block*-DTC)

as initiator can be followed by g.p.c. analysis. All copolymer samples show a unimodal distribution of the molecular weight. The reaction conditions for the preparation of the copolymer as well as the yields are summarized in *Table 2*. The ratio of monomers in the feed is different from the ratio of the repeat units in the copolymer. This difference is attributed to the low yield of PPO in the first step. The yield of the polycarbonate is between 96% and 100%. The composition of the copolymer was determined by ^{1}H n.m.r. spectroscopy (*Figure 5*). The signals of the DTC repeating units were found to be identical with those of the poly(EO-*block*-DTC); the signals of the PO repeating unit appear at $\delta = 1.10$, 3.53 and 3.40 ppm for the methyl, methylene and methine units, respectively. The ^{13}C n.m.r. spectrum (*Figure 6*) shows the signals for the PO unit at $\delta = 17.42$ (CH_3), 73.39 (CH_2) and 75.52 (CH) ppm and those for the DTC repeat unit at $\delta = 21.33$ (CH_3), 35.13 (C), 72.43 (CH_2) and 155.25 (C=O) ppm, all being singlets, in accordance with the existence of only AA and BB diads in the A–B block copolymer. It should be mentioned that all copolymers prepared in this work are coloured materials, even after repeated purification by precipitation. Colourless materials were obtained by treatment of a methylene chloride solution of the polymer with an O_3/O_2 mixture. Under these conditions the $TPPH_2$ system responsible for the colour is oxidized to non-coloured products. The polymer is not affected by this treatment.

*Thermal characterization of poly(propylene oxide-*block*-2,2-dimethyltrimethylene carbonate)*

The thermal behaviour of some polymers prepared, have already been described, e.g. PDTC[13], poly(ECL-*stat*-DTC)[11], poly(EO-*block*-DTC)[14]. *Table 3* summarizes the results of the thermal analysis of poly(PO-*block*-DTC) with different compositions (see also *Table 2*) by d.s.c. For comparison the transition temperatures of the homopolymers are given: for PPO $T_g = -75°C$ and $T_m = 74°C$[15]; for PDTC $T_g = 27°C$ and $T_m = 123.5°C$[11]. A block copolymer with a high PO content shows a T_g at $-65°C$ and a T_m of 110°C, at first heating and of 91°C at second heating. For a lower PO content the T_g of the PPO block is barely detectable. PDTC shows two

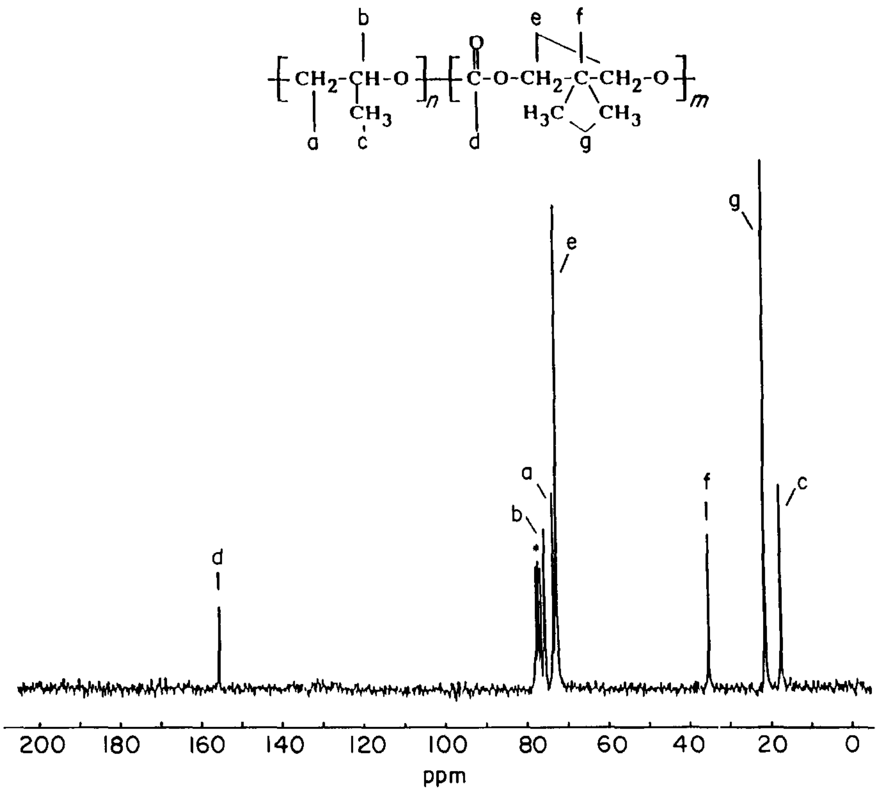


Figure 6 ^{13}C n.m.r. spectrum of poly(PO-*block*-DTC)

Table 3 D.s.c. measurements on poly(PO-*block*-DTC)

Molar composition (PPO/PDTC)	Heating cycle	T_g (°C)	T_{m1} (°C)	ΔH (J g^{-1})	T_{m2} (°C)	ΔH (J g^{-1})
5/95	1st heating	–	+99	44	(+111)	(2)
	2nd heating	–	–	–	+107	18
10/90	1st heating	–	+96	44	(+109)	(1)
	2nd heating	–	–	–	+103	18
26/74	1st heating	–	+98	43	(+113)	(1)
	2nd heating	–	–	–	+104	16
45/55	1st heating	–	+94	41	–	–
	2nd heating	–	–	–	+90	12
66/34	1st heating	−65	+110	17	–	–
	2nd heating	−64	–	–	+91	8

melting transitions upon first heating at +86°C ($\Delta H = 29.7$ J g^{-1}) and 121.5°C ($\Delta H = 23.0$ J g^{-1}); upon second heating only one melting transition at 123.5°C ($\Delta H = 22.6$ J g^{-1}) is observed[11]. All poly(PO-*block*-DTC) samples show one melting transition upon first and second heating. With low PO content the T_m increases upon second heating whilst at higher PO content the T_m decreases compared with the first heating.

CONCLUSIONS

TPPAl-alcoholates are well suited initiators for the polymerization of DTC. In copolymerization with lactones, both block and statistical copolymers are obtained depending on the preparation technique: statistical copolymers are obtained when the initiator is added to the monomer mixture. This is a consequence of the fact that the active species show no selectivity towards the monomers, in contrast to initiators based on alkali metal compounds[11]; block copolymers are obtained by a stepwise addition of the monomers to the initiator. Since no transesterification occurs over a large temperature range the initial block structure is maintained in contrast to initiators based on alkali metal compounds, where transesterifications at higher temperatures lead to statistical copolymers.

Initiators based on TPPAl-R have revealed a new synthetic route to poly(ether-*block*-carbonate) structures. These compounds have potential for materials in membrane technology and for solid electrolytes.

Polymers prepared with initiators based on TPPAl-R are coloured materials. We found that treatment of the polymer solutions with an O_3/O_2 mixture leads to oxidation of the dye with the formation of colourless products, without affecting the polymer structure.

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