Macromolecules **1992,** *25,* 2977–2984

Synthesis of Alternating Copolymers of 2,2-Dimethyltrimethylene Carbonate and ϵ-Caprolactam via Insertion of ϵ-Caprolactam into Poly(2,2-dimethyltrimethylene carbonate)[†]

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Received October 16, 1991; Revised Manuscript Received January 22, 1992

ABSTRACT: 2,2-Dimethyltrimethylene carbonate (DTC, **1**) was polymerized in toluene with dibutylmagnesium [$MgBu_2$, **5**] or aluminum tri-*sec*-butanolate [$Al(Osec\text{-}Bu)_3$, **6**] as initiator and was used as the initiating species for the polymerization of ϵ-caprolactam (EClam, **2**). The polymerization of EClam was performed in the melt at temperatures around 125 °C using *N*-(methoxycarbonyl)-ϵ-caprolactam (**3a**) as a cocatalyst. By this procedure, the carbonate groups of the initiating block were converted into ester and urethane groups by formal insertion of the ring-opened lactam moiety. As a consequence, an alternating copolymer of 2,2-dimethyltrimethylene carbonate and ϵ-caprolactam was obtained by successive addition of the monomers. Evidence for this reaction route was brought about by ^1H and ^{13}C NMR spectroscopy. A mechanism for the formation of the copolymer is proposed.

Introduction

It was our aim to prepare a block copolymer consisting of a polycarbonate and a polyamide block, two polar blocks suitable for interactions with enthalpic effects in polymer blend systems. The polymerization of cyclic carbonates has been studied in our laboratory since 1984, particularly with regard to the ring–chain equilibrium, the ceiling temperature,[1] and the active species in anionic polymerization.[2] Besides anionic initiators based on alkali metal compounds, initiators based on metal-free anions,[3] magnesium compounds,[4] and tetraphenylporphyrin–aluminum compounds[5] and initiators based on aluminum [$Al(Osec\text{-}Bu)_3$], zinc [$ZnEt_2$], or tin[6] [$Bu_2Sn(OMe)_2$] were investigated. It was found that initiators with Mg, Al, and Zn in the active site do not result in intermolecular transesterification reactions, while those with alkali metals and tin may show transesterification activity under certain reaction conditions.

A variety of block copolymers with an aliphatic polycarbonate block were prepared either by using anionic living polymers as initiating species for the ring-opening polymerization of the cyclic carbonate or by using the living polycarbonate species as initiator for the polymerization of a second monomer. Thus, poly(styrene)-*block*-poly(2,2-dimethyltrimethylene carbonate)[7] and poly(butadiene)-*block*-poly(2,2-dimethyltrimethylene carbonate)[8] were prepared by successive anionic polymerization of the monomers with an active site transformation from a carbanionic species to an alcoholate by using ethylene oxide. Poly(methyl methacrylate)-*block*-poly(2,2-dimethyltrimethylene carbonate)[9] could be prepared by successive group-transfer polymerization (GTP) and anionic metal-free polymerization. The silylketene acetal active species of the GTP was desilylated to form an enolate, which initiates the anionic polymerization of DTC. Block copolymers with an aromatic polycarbonate block and an aliphatic polyamide sequence are mentioned in the patent literature.[10–12] Also in the patent literature it is reported that the copolymerization of ϵ-caprolactam and cyclic aliphatic carbonates with sodium lactamate as the initiating species yields a copolymer with ester and urethane groups in addition to amide and carbonate functionality.[13–15] We have found[16] that under special reaction conditions the copolymerization yields cyclic oligomers with one ϵ-caprolactam unit and *n* units of the aliphatic carbonate ($n = 2$–10).

Table I
Elemental Composition of a DTC/EClam Copolymer (Molar Ratio 1.15:1) and Comparison with the Theoretical Value of a DTC/EClam Copolymer without and with Loss of CO_2

	calcd values for poly($C_5H_{10}O$-*co*-$C_6H_{11}NO$),[a] wt %	exptl values for a DTC/EClam copolymer, wt %	calcd values for poly($C_6H_{10}O_3$-*co*-$C_6H_{11}NO$),[b] wt %
C	66.91	58.71	59.24
H	10.82	8.99	8.70
O	16.51	26.98	26.30
N	5.76	5.32	5.76

[a] Represents structures **9** and **2**. [b] Represents structures **1** and **2**.

The literature gives examples of AB-block copolymers with an aliphatic amide block (B) and a block (A) consisting of a vinyl or diene polymer (e.g., poly(ethylene),[17] poly(propylene),[17] poly(isoprene),[18,19] poly(butadiene),[20] poly(styrene)),[18–23] a polyether (e.g., poly(ethylene oxide),[24] poly(propylene oxide),[17,24] polytetrahydrofuran[17,21]), and a polyester (e.g., poly(ϵ-caprolactone)).[17]

The strategy for the synthesis of these blocks is as follows. First the A-block is formed and capped with a lactam unit using toluylene 1,4-diisocyanate, *N*-(chlorocarbonyl)-ϵ-caprolactam, or terephthaloyl chloride as coupling species. With this polymeric "cocatalyst", the activated anionic ring-opening polymerization of ϵ-caprolactam is initiated. A prerequisite for the successful block copolymer synthesis is the stability of block A toward the active species in lactam polymerization.

This requirement could not be realized for the A-block poly(2,2-dimethyltrimethylene carbonate) poly(DTC) when using alkali metal counterions.[15,16] The reason was that the active species—the lactamate anion—reacts preferentially with the carbonate group of the polycarbonate block rather than with the activated ϵ-caprolactam moiety.

This paper presents experimental results on the polymerization of 2,2-dimethyltrimethylene carbonate and

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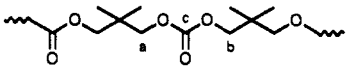
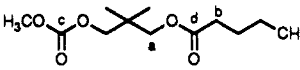
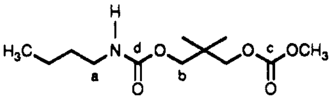
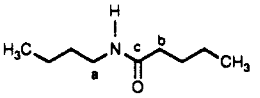
[†] Dedicated to Professor Walter Heitz on the occasion of his 60th birthday with our best wishes.

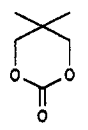
0024-9297/92/2225-2977$03.00/0

Table II

Model Compounds for DTC–DTC, DTC–EClam, EClam–DTC, and EClam–EClam Diads, ^{1}H NMR Assignment of the CH_2 Groups Adjacent to the Functional Groups, and ^{13}C NMR Assignment of the C=O Groups in a Carbonate, Ester, Urethane, and Amide Function[a]

		assignment of the methylene groups		assignment of the carbonyl groups	
diad	model compound	a	b	c	d
DTC–DTC		3.94 (s)	3.94 (s)	155.24	
DTC–EClam		3.86 (s)	2.30 (tr)	155.78	173.59
EClam–DTC		3.12–3.15 (m)	3.85 (s)	155.77	156.39
EClam–EClam		3.15–3.22 (m)	2.12 (tr)	173.13	

[a] For the complete NMR resonance values, see Experimental Section.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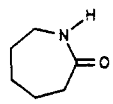
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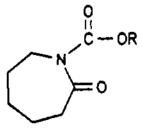
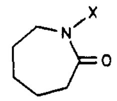

3a–b
a: R=CH$_3$
b: R=poly(DTC)


4a–c
a: X=MgBu
b: X=Al(OsecBu)$_2$
c: X=Li;Na;K

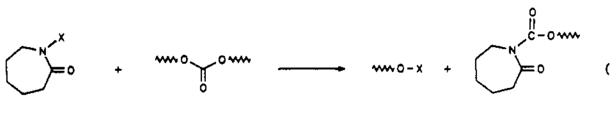
$Mg(CH_2CH_2CH_2CH_3)_2$
5

$Al(OCH(CH_3)CH_2CH_3)_3$
6

ε-caprolactam by successive addition of the monomers (first DTC and then EClam) with Bu_2Mg or $Al(OsecBu)_3$ as initiator. The mechanism of the reaction leading to an alternating copolymer is discussed.

Results and Discussion

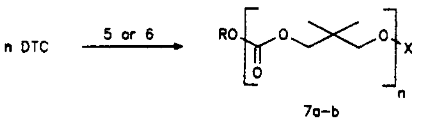
It is known from the patent literature[14,15] and from our laboratory[16] that the active species in the polymerization of ε-caprolactam (EClam) with lithium or potassium as counterion (**4c**) reacts with a carbonate group (of the monomer or the polymer) according to eq 1 rather than



(1)

with an activated ε-caprolactam moiety. Thus, copolymers with a polyamide and a polycarbonate block were not obtained. We found from the copolymerization of DTC and ε-caprolactone with different initiating species that lithium and potassium[6] alcoholates promote transesterification reactions to a large extent, while species containing aluminum[6] or magnesium[4] showed no transesterification activity. This behavior was attributed to the lower nucleophilicity of the aluminum- and magnesium-containing active sites as compared to those with lithium or potassium.

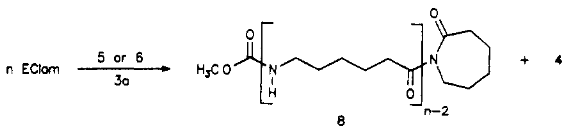
To obtain qualitative information on the behavior of aluminum and magnesium active sites in DTC polymerization, preliminary experiments were performed. The homopolymerization of DTC with dibutylmagnesium (**5**)[4] and aluminum tri-*sec*-butanolate (**6**)[6] in toluene at 20 °C resulting in good yields of poly(DTC) with polydispersity indexes of M_w/M_n = 1.32 and 1.17, respectively (eq 2). This result was not influenced by the addition of EClam (**2**) to the reaction mixture. However, by heating the active polymer solution to 90 °C in the presence of ε-caprolactam, complete degradation of poly(DTC) was observed within 24 h when the active site contained magnesium. In contrast, the polymer remained stable under the given reaction conditions when the active site contained aluminum.



(2)

7a–b
a: X=MgBu
b: X=Al(OsecBu)$_2$

Another series of preliminary experiments was concerned with the polymerization of ε-caprolactam with initiators containing magnesium and aluminum. It is known that *N*-acyllactams enhance the polymerization of lactams strongly. It was found that a solution of EClam in toluene, with *N*-(methoxycarbonyl)-ε-caprolactam (**3a**) as a cocatalyst and $MgBu_2$ (**5**) or $Al(OsecBu)_3$ (**6**), did not lead to the polyamide up to 100 °C. With the same reagents, however, in the melt at 125 °C the polyamide **6** was obtained in a yield of 60–70% for $MgBu_2$ and 15–20% for $Al(OsecBu)_3$ (eq 3). In the absence of cocatalyst **3a** no reaction occurred.



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(3)

On the basis of these preliminary experiments the following strategy for the reaction was developed: (i) First, DTC was polymerized in toluene with $MgBu_2$ or $Al(OsecBu)_3$ as initiator. (ii) Then ε-caprolactam and *N*-(methoxycarbonyl)-ε-caprolactam were added, the solvent was removed, and polymerization was performed in the melt at 125 °C.

The polymerization with $MgBu_2$ as initiator showed, in the second stage of the reaction, an increase in melt viscosity of the sample after 15–30 min, while with $Al(OsecBu)_3$ an increase in viscosity was observed only after 1 day. The polymer was isolated and separated from oli-

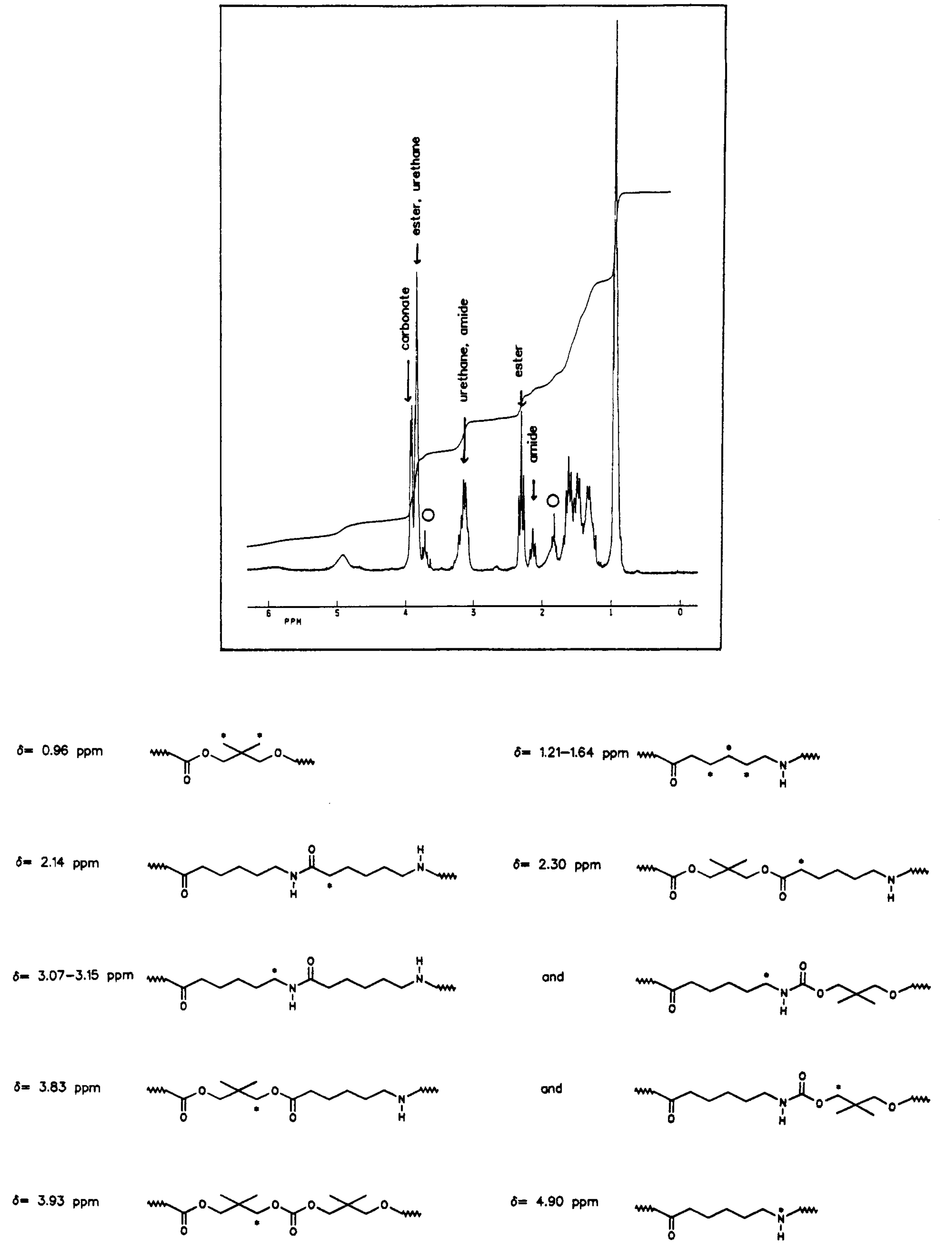


Figure 1. ^{1}H NMR spectrum of a DTC/EClam copolymer (molar ratio DTC:EClam = 0.87:1); assignment of the characteristic resonance lines (O, resonances of residual THF).

gomers and unreacted monomer by dissolution in THF and precipitation in water. The good solubility of the polymer in THF indicated that no long polyamide sequences were present in the polymer. Dilution of a THF solution with methanol did not lead to precipitation, indicating that no long polycarbonate sequences were present. The conclusion from this behavior was that neither homopolymers nor block copolymers were obtained.

It has been reported in the literature[13] that DTC in the presence of an alkali metal lactamate leads to decarboxylation at temperatures of 100–200 °C (cf. eq 4). The question arose whether decarboxylation plays a role or not in the present system. To investigate this possibility,

Table III
Relative Molar Composition of a DTC/EClam Copolymer, Molecular Weight, and Molecular Weight Distribution as a Function of Time, Initiator, and Presence of Cocatalyst (Molar Ratio of DTC/EClam in the Feed Is 0.87:1)[a]

expt 1[b]			expt 2[c]				expt 3[d]			
DTC:EClam[e]	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	DTC:EClam[e]	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	time,[f] min	DTC:EClam[e]	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	time,[g] min
	1.32	9000		1.30	9200	0		1.17	8000	
2:1	1.55	9200	4.6:1	1.45	9900	5				
1.4:1	1.62	9700	2:1	1.56	11300	30				
1:1	1.73	10200	1.8:1	1.60	12400	60	11.7:1	1.30	8100	120
1:1	1.78	10900	1.7:1	1.68	14000	180	4.3:1	1.42	8900	300
1:1	1.83	11900	1.4:1	1.72	15100	480	3.8:1	1.58	9100	660
1:1	1.86	12400	1.3:1	1.84	18900	1440	1.6:1	1.72	9500	1200
1:1	1.89	12400				2880	1.2:1	1.77	10000	2700

[a] Reaction conditions (for experiments 1–3): first step, solvent toluene, [DTC] = 0.731 mol/L, $[I]_0$ = 9.513 mmol/L; second step, addition of EClam (with and without cocatalyst, the concentration of cocatalyst = $[I]_0$), removal of the solvent, further reaction in the melt at 125 °C. [b] I = Bu_2Mg and cocatalyst. [c] I = Bu_2Mg. [d] I = $Al(OsecBu)_3$ and cocatalyst. [e] DTC:EClam ratio in the polymer as determined by ^1H NMR spectroscopy. [f] Time column for experiments 1 and 2. [g] Time column for experiment 3.

Table IV
Molecular Weight, Molecular Weight Distribution, and Composition of a DTC/EClam Copolymer as a Function of Monomer Ratio in the Feed and of Time

sample	DTC:Bu_2Mg, mol:mol	DTC:EClam,[a] mol:mol	poly(DTC) $\bar{M}_{GPC}$	poly(DTC-*co*-EClam) $\bar{M}_{GPC}$	DTC:EClam[b] $f(t_{p2})$	$\bar{M}_w/\bar{M}_n$	carbonate:ester: urethane:amide
1	77:1	1.76:1	8900	8900	5 min, 3.9:1	1.45	2.47:1.00:1.00:0.10
				9000	30 min, 3.6:1	1.50	2.25:1.00:1.00:0.17
				9200	90 min, 3.4:1	1.62	2.15:1.00:1.00:0.14
				9300	180 min, 3.2:1	1.68	2.03:1.00:1.00:0.15
				9300	420 min, 3.1:1	1.69	2.04:1.00:1.00:0.30
				9300	1440 min, 2.9:1	1.75	2.00:1.00:1.00:0.37
2	77:1	0.87:1	9000	9200	5 min, 2:1	1.55	0.67:1.00:1.00:0.40
				9700	30 min, 1.4:1	1.62	0.64:1.00:1.00:0.30
				10200	90 min, 1.1:1	1.73	0.31:1.00:1.00:0.30
				10900	180 min, 1:1	1.78	0.19:1.00:1.00:0.31
				11900	420 min, 1:1	1.83	0.12:1.00:1.00:0.18
				12400	1440 min, 1:1	1.86	0.08:1.00:1.00:0.20
3	77:1	0.43:1	8800	9500	5 min, 1.6:1	1.74	0.60:1.00:1.00:0.10
				10700	30 min, 1.1:1	1.86	0.39:1.00:1.00:0.12
				13000	90 min, 1:1	2.03	0.27:1.00:1.00:0.17
				13600	180 min, 0.9:1	2.37	0.17:1.00:1.00:0.09
				14700	420 min, 0.9:1	2.39	0.09:1.00:1.00:0.04
				15400	1440 min, 0.7:1	2.51	0.04:1.00:1.00:0.10

[a] Ratio in the feed. [b] Ratio in the copolymer.

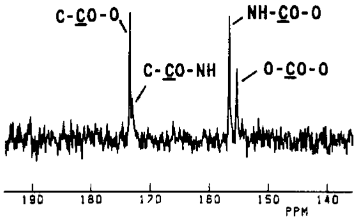
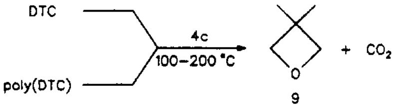


Figure 2. ^{13}C NMR spectrum of the carbonyl region of a DTC/EClam copolymer (molar ratio DTC:EClam = 0.87:1) assignment of the resonance lines.

DTC was polymerized with initiators based on Mg and Al, and the "living" polymers were heated with EClam and *N*-(methoxycarbonyl)-ε-caprolactam in the melt to 125 °C in a stream of dry nitrogen. The gas was then passed through a saturated solution of $Ba(OH)_2$ to bind CO_2, which may be formed. No trace of CO_2 could be detected over a period of 4 h. This result was confirmed by elemental analysis of the polymer obtained. The experimental results agree with the calculated values without loss of CO_2 (see Table I).



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(4)

Characterization of the Polymer by ^1H NMR and ^{13}C NMR Spectroscopy. The ^1H NMR spectrum of a typical copolymer (molar ratio of DTC:EClam = 0.87:1) is complex. The most indicative resonance lines stem from the methylene groups adjacent to functional groups. To assign these signals, model compounds for the different diads were prepared. Table II shows that for the methylene group in the 2,2-dimethyltrimethylene moiety the resonances are at δ 3.94 for a DTC–DTC diad (CH_2 adjacent to a carbonate group), at δ 3.86 for a DTC–EClam diad (CH_2 adjacent to an ester group), and at δ 3.85 for an EClam–DTC diad (CH_2 adjacent to a urethane group). For the CH_2 groups in the EClam moiety the signals at δ 2.30, 3.12–3.15, 3.15–3.22, and 2.12 correspond to the DTC–EClam, EClam–DTC, and EClam–EClam diads, respectively. The signals observed in the ^1H NMR of the copolymer agreed very well with those found in the model compounds (see assignment in Figure 1). The ^{13}C NMR spectrum (Figure 2) of the copolymer supports the assignment made by ^1H NMR. The most indicative signals for the structural composition of the copolymer are given by the carbonyl carbon atoms. The signals at δ 173.3, 172.9, 156.5, and 155.3 were assigned on the basis of the model compounds (Table II) to the DTC–EClam diad (ester carbonyl), EClam–EClam diad (amide carbonyl), EClam–DTC diad (urethane carbonyl), and DTC–DTC diad (carbonate carbonyl), respectively. From both the

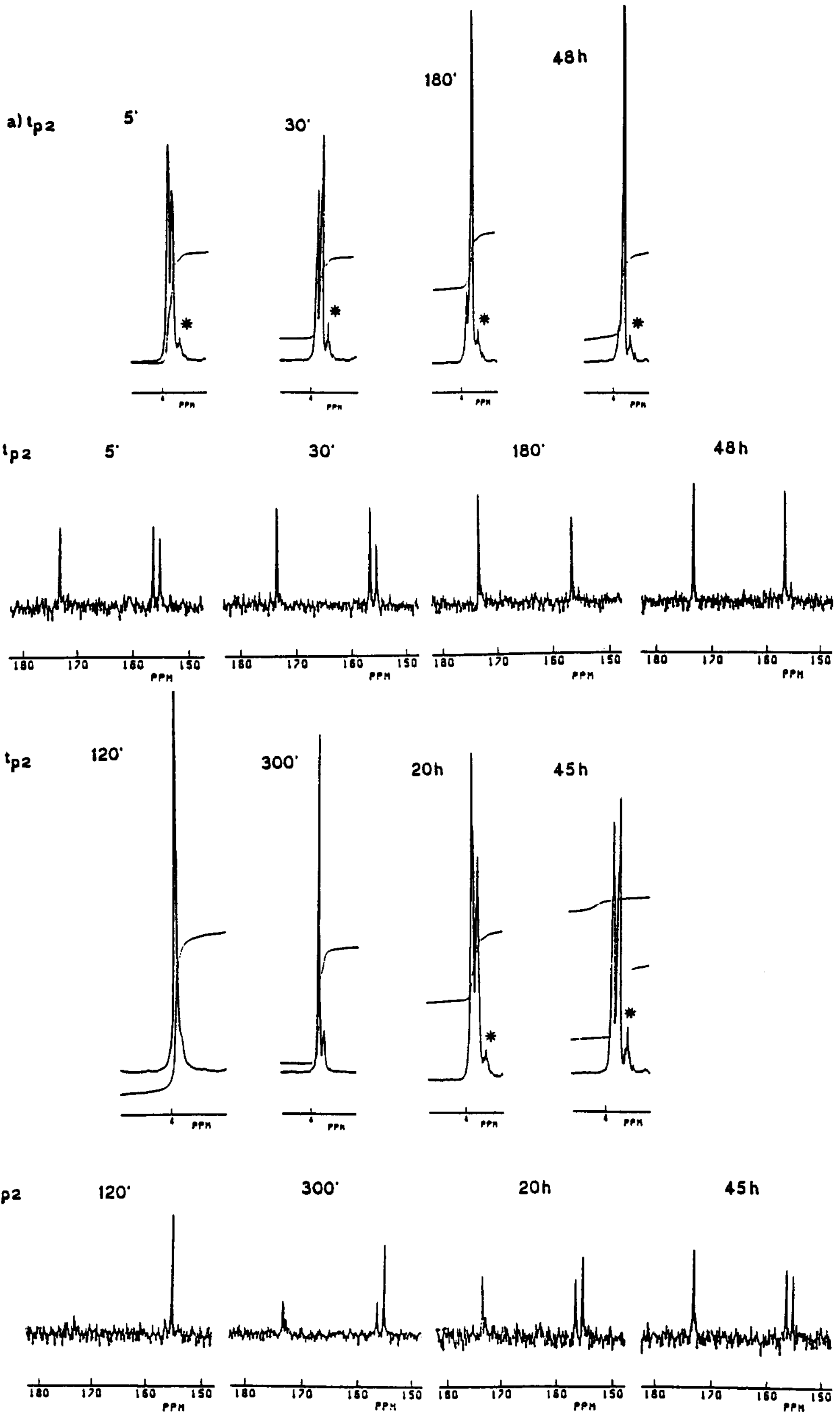
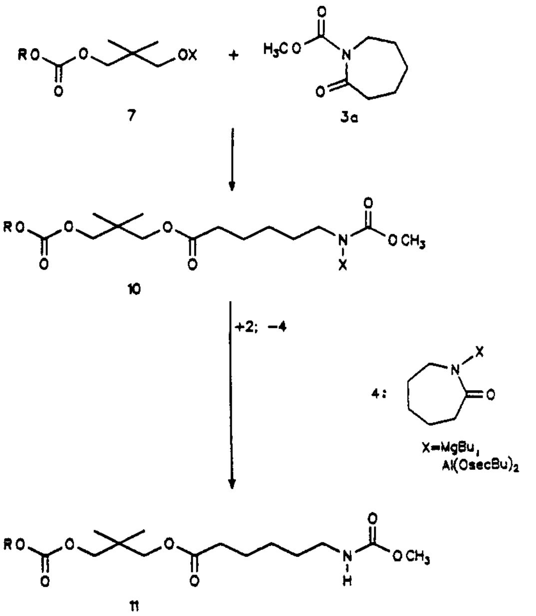


Figure 3. ^{1}H and ^{13}C NMR spectra of DTC/EClam copolymers as a function of time (t_{p2}): (a) MgBu in the active site (see experiment 1 in Table III); (b) Al(OsecBu)$_2$ in the active site (see experiment 3 in Table III).

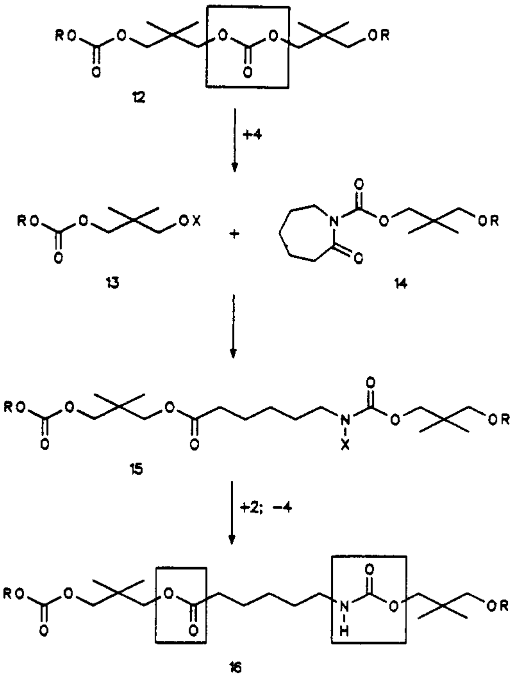
^{1}H and ^{13}C NMR the composition of the copolymer was determined by integration. For the example given, the molar ratio of DTC:EClam is 1.1 and the ratio of the diads DTC–EClam:EClam–EClam:EClam–DTC:DTC–DTC is 1:0.3:1:0.4. The fact that the molar content of ester and urethane groups is equal has utmost importance for a mechanism of this reaction.

To obtain more insight into the course of the reaction, the dependence of the copolymer composition, the molecular weight (M_{GPC}), and the polydispersity index (M_w/M_n) on reaction time was determined for both the Mg- and Al-containing active species. As shown in Table III for the Mg initiator (experiment 1), the rate of consumption of EClam was much higher than for the Al initiator

Scheme I
Initiation



Scheme II
Propagation



(experiment 3); in the first case, after 2 h the ratio of the repeating units DTC:EClam was 1, while in the second case, even after 45 h, this ratio was still in favor of DTC, i.e., 1.15. The analysis of the molecular weight (MW) and polydispersity index of a representative sample with a molar ratio of DTC:EClam of 0.87:1 in the feed revealed that the initiating poly(DTC) obtained with the Al initiator (M_{GPC} = 8000) shows M_w/M_n = 1.17; after the addition of EClam, the molecular weight increased to M_{GPC} = 10 000 and M_w/M_n = 1.77. A corresponding result was observed for the Mg initiator: M_w/M_n being 1.32 for the initiating poly(DTC) and 1.89 for the final polymer. For different molecular weights of the initiating poly(DTC) no distinctive difference in conversion or final structure of the polymer was observed; however, the rate of the reaction decreases with an increase in molecular weight of the initiating poly(DTC). This may be explained by the decrease of the concentration of the active species.

The ^{1}H NMR spectra (Figure 3) at different reaction times illustrate the decrease of carbonate groups (signal at δ 3.93, 4 H) and the increase in ester and urethane groups (signal at δ 3.83, 2 H + 2 H). In other words, DTC–DTC diads disappear in favor of DTC–EClam diads—ester groups—and EClam–DTC diads—urethane groups. This results is confirmed by the ^{13}C NMR analysis of the samples. Additionally, Figure 3 shows that, for the Mg initiator at a temperature of 125 °C after 180 min, the resonance for the carbonate groups (δ 155.24) had disappeared and only signals for ester and urethane (δ 173.3 and 156.5) moieties were observed. For the Al initiator after 45 h, an appreciable amount of DTC–DTC diads was still present. It turned out that the cocatalyst, which is essential for the homopolymerization of ε-caprolactam, does not have the same importance in the reaction presented here. The reaction took place in the absence of the cocatalyst but with lower rate (see Table III, experiment 2). The maximum conversions of EClam in the reaction with living poly(DTC) initiated with $MgBu_2$ and with $Al(Osec\text{-}Bu)_3$ were 85% and 75%, respectively. Thus, they are much closer than for the homopolymerization of the system EClam/*N*-(methoxycarbonyl)-ε-caprolactam, where the polymer yields were 60–70% and 15–20%, respectively.

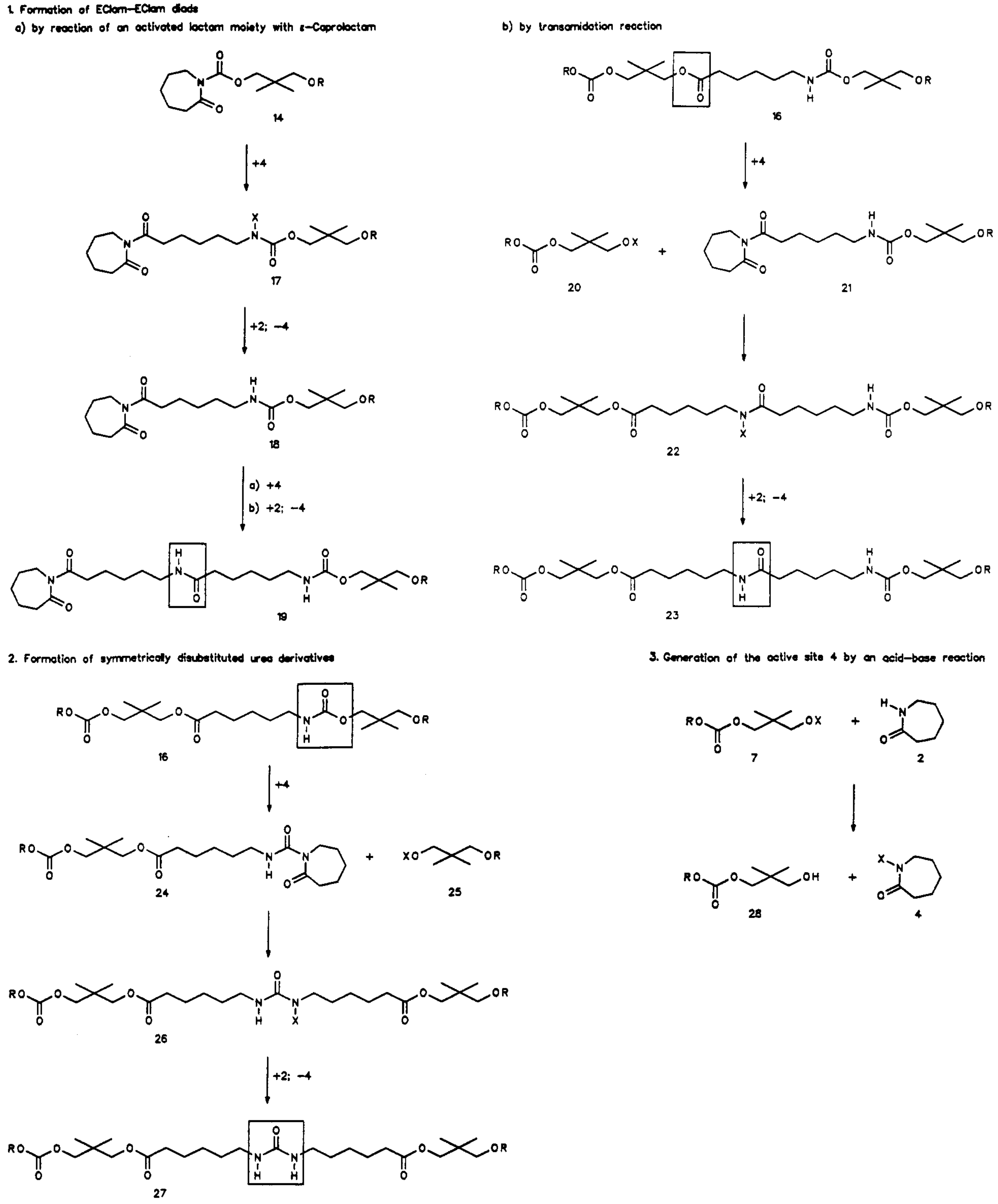
The influence of the ratio DTC:EClam in the feed on the composition of the copolymer, its molecular weight, and the polydispersity index gives additional information on the reaction mechanism as indicated in Table IV. The initiating poly(DTC) obtained with $MgBu_2$ shows M_{GPC} = 9000 and M_w/M_n = 1.32. With an equimolar amount of EClam, a final polymer was obtained with M_{GPC} = 12 400 and M_w/M_n = 1.86 (sample 2). The ratio DTC:EClam in the polymer was 1, and besides ester and urethane groups only a few amide groups were detected. Addition of a molar deficit of EClam (sample 1) led to a smaller increase in M_{GPC} and M_w/M_n. The polymer showed residual carbonate units. In contrast, when EClam was added in molar excess, all carbonate groups were consumed but no additional amide groups were formed. The increase in molecular weight and polydispersity index was unexpectedly high. This last result is not well understood. Finally, it should be mentioned that for samples with a ratio DTC:EClam > 1 the MWD was multimodal (di- or trimodal), while for all other samples a unimodal distribution was obtained.

Mechanistic Aspects of Copolymerization. To explain the structural elements found by means of NMR analysis, which are consistent with the properties of the copolymer, the following mechanism is proposed. In the initiating step (Scheme I) the active poly(DTC) species **7** reacts with the cocatalyst **3a** in a ring-opening way and the intermediate **10** reacts with ε-caprolactam (**2**) to form **11** and the active polymerization site **4** of the ε-caprolactam polymerization.

In the next step, the chain propagation reaction (Scheme II), **4** reacts with polymer **12** containing carbonate groups via nucleophilic addition to a carbonyl group, inducing the chain cleavage to form **13** and **14**. These fragments react in the sense shown in the initiating step (**7** + **3**) to give **16**. It is emphasized that in one such growing step a carbonate group reacts with the active species **4**, by formal insertion into the chain, with formation of one ester and one urethane group and generation of a new active species **4** by deprotonation of an ε-caprolactam molecule.

To some extent, besides this main reaction, side reactions (Scheme III) occur, leading to the formation of amide

Scheme III
Side Reactions



sequences, according to the generally accepted mechanism of lactam polymerization. Upon the first reaction of the lactamate **4** with the oxycarbonyllactam **14**, the new functional groups formed are a urethane and an acyllactam group **18**, which upon renewed reaction with the lactamate species yields an amide group **19**. Another pathway to form amide groups arises when the concentration of carbonate groups decreases and the concentration of ester/urethane groups increases. Now the probability of a nucleophilic attack of the lactamate active species at an ester carbonyl has increased; the result of this reaction is an acyllactam **21**, which upon ring-opening reaction with alcoholate **20** results in **23** with a newly formed amide group. Further, **21** may react with **4** to result in an amide group, too. The reaction of the acyllactam **21** with the alcoholate **20** may be degenerate, leading to the starting materials; this is the case when the exocyclic carbonyl group reacts with the alcoholate species.

Another center for nucleophilic attack of the lactamate is the urethane carbonyl group. This reaction, however, which would lead to a disubstituted urea **27**, was excluded, since no resonances were observed in the ^{13}C NMR spectra in the region δ 160–170, typical for the carbonyl group of symmetrically alkyl-disubstituted ureas, e.g., CH_3NH–

CO–NHCH$_3$ δ 165.4. Finally, it should be mentioned that in the absence of the cocatalyst an acid–base reaction between alcoholate **7** and EClam may lead to the active site **4** of lactam polymerization.

Conclusions. This paper describes the preparation of rather specific nearly alternating copolymers of 2,2-dimethyltrimethylene carbonate and ε-caprolactam by successive addition of monomers. The presented mechanism includes the complex reactions taking place in such systems and implies that the ε-caprolactam units should reside in alternating sequences with random head to tail (urethane–ester diad), head to head (urethane–urethane diad), and tail to tail (ester–ester diad) placement. In the future higher resolution NMR spectra will lead to further enlightening of the mechanism.

Experimental Section

Reagents. 2,2-Dimethyltrimethylene carbonate (DTC) (from Bayer AG) was sublimed, and ε-caprolactam (from Aldrich) was used without further purification, before polymerization. The initiators dibutylmagnesium (from Alfa Products), 1.1 M in heptane, and aluminum tri-*sec*-butanolate (from Merck-Schuchardt) were used without further purification. Toluene was freshly distilled from a solution of *sec*-butyllithium before use. Nitrogen and argon (both from Linde) were passed over molecular sieve (4 Å), finely distributed potassium on aluminum oxide, and reduced Phillips catalyst 800/350 (Cr^{II} on silica gel) for purification.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker CXP 200 FT-NMR spectrometer at 200 and 50 MHz, respectively. Deuterochloroform was used as solvent and TMS as internal standard. GPC analyses were carried out using a Waters apparatus with combined UV and RI detector. A combination of four columns was applied with PL gel (from Polymer Laboratories): length of one column, 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 polymers THF was the eluting solvent with a flow rate of 0.5 mL/min.

General Polymerization Procedure. All glass vessels were heated in vacuo before use, filled with inert gas, and handled in a stream of dry inert gas. Monomer and initiator solutions were added by syringe technique.

A solution of 5.0 g (0.038 mol) of DTC in 52.3 mL of toluene was treated with 0.5 mmol of initiator (MgBu$_2$ or Al(OsecBu)$_3$) and polymerized at 20 °C for 12 h. To the solution of the living poly(DTC) was added 4.35 g (0.038 mol) of ε-caprolactam and dissolved. Then 0.086 g (0.5 mmol) of *N*-(methoxycarbonyl)-ε-caprolactam was added and the solvent removed in vacuo. The solvent-free residue was heated to 120–125 °C for 4 (Mg initiator) and 24 h (Al initiator). The polymer was then dissolved in 50 mL of THF containing 2 mL of 5% H$_3$PO$_4$/CH$_3$OH. The polymer was isolated by precipitation into 200 mL of H$_2$O.

NMR Data of the Model Compounds. (a) DTC–DTC diad: ^{1}H NMR δ 3.94 (s, CH$_2$, 4 H), 0.96 (s, CH$_3$, 6 H); ^{13}C NMR δ 155.24 (C=O), 72.40 (CH$_2$O), 35.20 (C), 21.40 (2CH$_3$).

(b) DTC–EClam diad: ^{1}H NMR δ 3.93 (s, CH$_2$O, 2 H), 3.86 (s, CH$_2$O, 2 H), 3.74 (s, CH$_3$O, 3 H), 2.30 (t, CH$_2$CO, 2 H), 1.54–1.62 (m, CH$_2$, 2 H), 1.29–1.37 (m, CH$_2$, 2 H), 0.96 (s, 2CH$_3$, 6 H), 0.89 (t, CH$_3$, 3 H); ^{13}C NMR δ 173.59 (C=O), 155.78 (C=O), 77.01 (CH$_2$O), 68.74 (CH$_2$O), 54.70 (CH$_3$O), 34.83 (C), 33.97 (CH$_2$CO), 27.01 (CH$_2$), 22.22 (CH$_2$), 21.53 (2CH$_3$), 13.61 (CH$_3$).

(c) EClam–DTC diad: ^{1}H NMR δ 5.30 (s, NH, 1 H), 3.91 (s, CH$_2$O, 2 H), 3.85 (s, CH$_2$O, 2 H), 3.75 (s, CH$_3$O, 3 H), 3.14 (dt, CH$_2$NH, 2 H), 1.21–1.54 (m, 2CH$_2$, 4 H), 0.94 (s, 2CH$_3$, 6 H), 0.88 (t, CH$_3$, 3 H); ^{13}C NMR δ 156.39 (C=O), 155.77 (C=O), 76.98 (CH$_2$O), 69.18 (CH$_2$O), 54.61 (CH$_3$O), 40.68 (CH$_2$NH), 35.00 (C), 31.98 (CH$_2$), 21.41 (2CH$_3$), 19.77 (CH$_2$), 13.59 (CH$_3$).

(d) EClam–EClam diad: ^{1}H NMR δ 5.54 (s, NH, 1 H), 3.19 (dt, CH$_2$NH, 2 H), 2.12 (t, CH$_2$CO, 2 H), 1.24–1.61 (m, 4CH$_2$, 8 H), 0.88 (t, CH$_3$, 6 H); ^{13}C NMR δ 173.13 (C=O), 39.06 (CH$_2$NH), 36.41 (CH$_2$CO), 31.62 (CH$_2$), 27.83 (CH$_2$), 22.28 (CH$_2$), 19.95 (CH$_2$), 13.61 (2CH$_3$).

Acknowledgment. The financial support of the Bundesministerium für Forschung und Technologie (Project O3M 4031 6) is gratefully acknowledged. B.W. is indebted to the Fonds der Chemischen Industrie for a Kekulé scholarship.

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Registry No. **1**, 3592-12-9; **2**, 105-60-2; **3a**, 22366-95-6; (**1**)(**2**) (copolymer), 82613-72-7; MgBu$_2$, 1191-47-5; Al(O-*sec*-Bu)$_3$, 2269-22-9.