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Tertiary Amine-Initiated Zwitterionic Polymerization of Pivalolactone—A Reinvestigation by Means of MALDI-TOF Mass Spectrometry[a]

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When pyridine, 4-methylpyridine (4-MP) and 4-(N,N-dimethylamino)pyridine (DMAP) were used as initiators for the polymerization of pivalolactone in N-methylpyrrolidone, linear chains having one pyridinium ion and one $CO_2^{\ominus}$ ion as endgroups were found to be the main reaction products. The absence of cyclic oligolactones, even at temperatures up to 140°C, proves that the chain growth of the zwitterionic chains proceeds exclusively by anionic ring-opening polymerization. When dichloromethane was used as a reaction medium, part of the polylactone chains had $-CO_2CH_2Cl$ endgroups due to side reactions with the solvent. With diazabicyclooctane as initiator, a clean zwitterionic polymerization was found in NMP. With triethylamine or 2-ethyloxazolidine as initiators, the zwitterionic/anionic ring-opening polymerization was again the prevailing process, but significant side reactions also took place. In the case of 2-ethyloxazolidine, these side reactions included the formation of cyclic oligolactones. In the case of β-propiolactone, complete elimination of the pyridinium ions with formation of acrylate chain ends was observed.

Keywords pivalolactone, ring-opening polymerization, zwitterions, MALDI-TOF

Introduction

About three to five decades ago, ring-opening polymerizations of β-lactones and other heterocycles involving chains with one positively charged endgroup and one negatively charged chain end were intensively studied by a number of research groups.[1–19] For several reasons, the course of such zwitterionic polymerizations may be very complex. For instance, the chain growth may proceed as an ionic ring-opening polymerization (typically anionic) involving a chain growth kinetic. Alternatively, the zwitterionic monomers or dimers may react with each other by a polycondensation or polyaddition process involving a step-growth kinetic. Furthermore, elimination reactions at the cationic chain end may result in unsaturated, dead endgroups. Moreover, cyclization reactions may take place with cancellation of both charges. The characterization of

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isolated polymers in previous studies was based on molecular weight measurements (VPO or SEC) and on IR- and ^{1}H NMR spectroscopy. Neither method allows for a clear cut detection of cyclic oligomers or polymers in complex reaction mixtures. In this context, the present work was designed as a reinvestigation of tertiary amine-initiated polymerizations of β-pivalolactone and β-propiolactone with the purpose to elucidate the formation of cyclic oligo- and polyesters by means of MALDI-TOF mass spectrometry.

Experimental

Materials

Pivalolactone (PiL) was kindly supplied by E. I. Dupont (Wilmington, DE). Pyridine, 4-methylpyridine (4-MeP), 4-N,N-dimethylaminopyridine (DMAP), diazabicyclooctane (DABCO), 2-ethyloxazoline (2-EOX) and β-propiolactone (PrL) were purchased from Aldrich Co. (Milwaukee, WI). Pyridine, 4-methylpyridine, 2-ethyloxazoline, triethylamine and both β-lactones were distilled over freshly powdered calcium hydride. DMAP was dried in a desiccator over P_4O_{10} *in vacuo.* DABCO was used as received. N-Methylpyrrolidone (NMP) (a gift of BASF AG, Ludwigshafen, Germany) was also distilled over P_4O_{10} *in vacuo* and dichloromethane was distilled over P_4O_{10} at atmospheric pressure.

Pyridine-Initiated Polymerization of Pivalolactone (Table 1)

Pivalolactone (40 mmol) was weighed in a 50 mL Erlenmeyer flask having silanized glass walls, the solvent (20 mL) was added and the initiator (0.4 mL of a 1 M solution in CH_2Cl_2 or in dioxane) was injected by means of a syringe. The reaction vessel was closed with glass stopper and steel spring and immersed into a preheated oil bath (see Table 1). Finally, the reaction mixture was poured into methanol and the isolated polylactone was

Table 1
Pyridine-initiated polymerizations of pivalolactone

Exp. no.	Initiator	Solvent	Temp. (°C)	Time (h)	Yield (%)	η_{inh}[a] (dL/g)
1	Pyridine	CH_2Cl_2	20	48	78	0.09
2	Pyridine	NMP	20	48	93	0.09
3	Pyridine	NMP	60	24	100	0.17
4	Pyridine	NMP	100	24	100	0.20
5	Pyridine	NMP	140	24	100	0.63
6	4-Methylpyr.	CH_2Cl_2	20	48	65	0.07
7	4-Methylpyr.	NMP	20	48	76	0.08
8	4-Methylpyr.	NMP	60	24	95	0.10
9	4-Methylpyr.	NMP	100	24	100	0.19
10	4-Methylpyr.	NMP	140	24	100	0.25
11	DMAP	CH_2Cl_2	20	48	93	0.09
12	DMAP	NMP	20	48	87	0.28
13	DMAP	NMP	60	24	95	0.33
14	DMAP	NMP	100	24	98	0.37

[a]Measured at 20°C with c = 2 g/L in CH_2Cl_2/TFA (8 : 1).

dried at 60°C *in vacuo.* All experiments listed in Table 1 were performed analogously. However, the DMAP-initiated experiments were repeated and precipitated into diethyl ether.

DABCO-Initiated Polymerizations of Pivalolactone (Table 2)

Pivalolactone (40 mmol) was weighed into a 50 mL Erlenmeyer flask having silanized glass walls, dry NMP (20 mL) was added, and pyridine (0.4 mL of a 1 M solution in dry dioxane) was injected by means of a syringe. The reaction vessel was closed with glass stopper and steel spring and thermostated at 20°C (48 h) or 100°C (24 h). Finally, the reaction mixture was poured into methanol, and the isolated polylactone was dried at 60°C *in vacuo.*

The triethylamine-initiated polymerizations were conducted analogously.

Polymerization of Pivalolactone with 2-Ethyloxazoline

Pivalolactone (20 mmol) and 2-ethyloxazoline (20 mmol) were weighed into a 50 mL Erlenmeyer flask, having silanized glass walls and dry NMP (20 mL), was added. The closed reaction vessel was thermostated at 20 or 100°C. Finally, the reaction mixture was precipitated into diethyl ether, the product was isolated by centrifugation and dried at 40°C *in vacuo.*

Pyridine-Initiated Polymerizations of β-Propiolactone

β-Propiolactone (40 mmol) was weighed into a 50 mL Erlenmeyer flask having silanized glass walls, and pyridine (0.4 mL of a 1 M solution in dry dioxane) was injected. The reaction vessel was closed with a glass stopper and steel spring, and thermostated at 20 or 60°C for 48 h. Afterwards, the reaction mixture was poured into diethyl ether.

Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20°C. The 400 MHz ^{1}H NMR spectra were recorded with a Bruker "Avance 400" FT NMR spectrometer in 5 mm o.d. sample tubes using $CDCl_3$/TMS as solvent and shift reference. The MALDI-TOF mass spectra (m.s.) were recorded with a Bruker Biflex III equipped with a nitrogen laser ($\lambda = 335$ nm). All spectra were measured in the reflection

Table 2
Zwitterionic polymerization of PiL initiated with various tertiary nucleophiles in NMP

Exp. no.	Initiator	Temperature (°C)	Time (h)	Yield (%)	η_{inh}[a] (dL/g)
1	Dabco[b]	20	48	97	0.40
2	Dabco[b]	100	24	100	1.03
3	Triethylamine	20	48	3	—
4	Triethylamine	100	24	98	0.58
5	2-Ethyloxazoline	20	48	16	0.07
6	2-Ethyloxazoline	100	24	50	0.12

[a]Measured at 20°C with c = 2 g/L in CH_2Cl_2/TFA (volume ratio 8 : 1).
[b]Diazabicyclooctane.

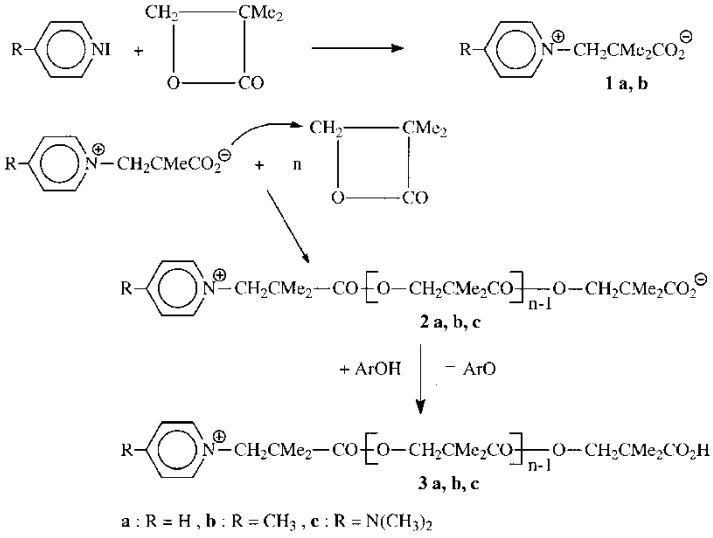
mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from $CHCl_3$ solutions containing 10 vol% of trifluoroacetic acid. The IR spectra were recorded from KBr pellets on a Nicolet "Impact 410" FT IR spectrometer.

Results and Discussion

Pyridine-Initiated Polymerization of PiL

The pyridine-initiated polymerizations of PiL were conducted in two solvents of different polarity, namely in dichloromethane and in NMP (Table 1). In addition to pyridine, 4-methylpyridine and DMAP were used as initiators. Both basicity and nucleophilicity increase in the above given order of the initiators. This variation had the purpose to find out if these properties have an influence on the structure of the reaction products. The monomer/initiator ratio (M/I) was fixed at 100/1 for all polymerizations, but the temperature was varied.

With pyridine as initiator, a uniform reaction product was obtained which was identified as linear chains of structure **3a** by MALDI-TOF mass spectroscopy (Fig. 1). Even when the temperature was raised to 140°C, formation of cyclic oligo-/polylactones was not detectable. This result proves that a zwitterionic polymerization took place in such a way that the initiation step was followed by an anionic ring-opening polymerization (Sch. 1). A polycondensation process (with step-growth kinetic) involving a nucleophilic attack of the $CO_2^{\ominus}$ anion onto the pyridinium group with elimination of pyridine should automatically result in the formation of cyclic oligo- and polylactones. We have recently demonstrated[20] that any kinetically controlled polycondensation (no equilibration) involves a permanent competition between cyclization and chain growth at any concentration and at any stage of the polycondensation. Therefore, the absence of cycles necessarily rules out a significant contribution of condensation steps, and it rules out that "back-biting degradation" occurred.



Perfectly analogous results were found for 4-methylpyridine as initiator (Nos. 6–10, Table 1). Regardless if pyridine or its 4-methyl derivative was used, the ^{1}H NMR-spectra

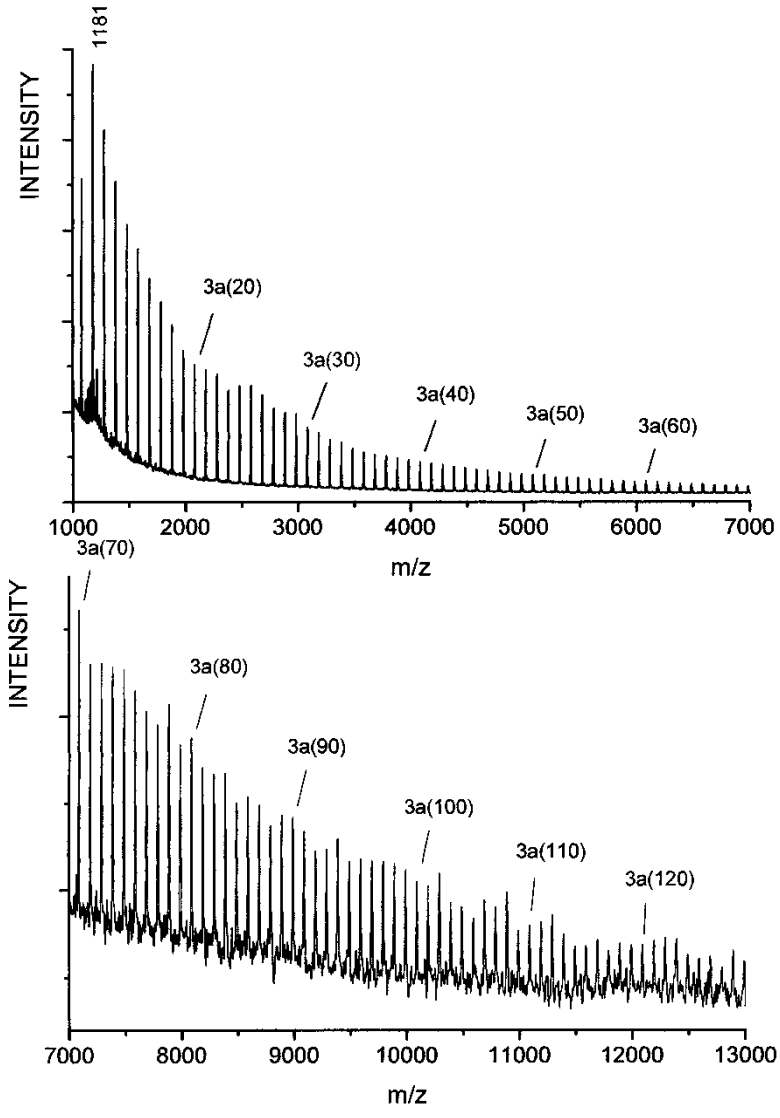
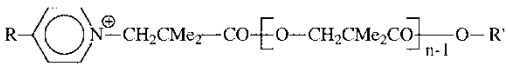


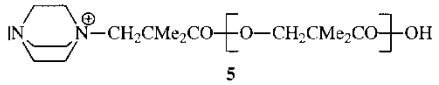
Figure 1. MALDI-TOF m.s. of a pyridine-initiated polypivalolactone (**3a**, No. 3, Table 1) prepared in NMP at 60°C (the number in brackets indicates the DP).

proved the covalent incorporation of pyridinium endgroups (Fig. 2). The formation of a CO_2H endgroup (structure **3b**) in the MALDI-TOF m.s. may be explained by proton transfer from the matrix (dithranol) to the $CO_2^{\ominus}$ ion of the zwitterionic chain of structure **2** (Sch. 1).

With DMAP as initiator in NMP, polylactone chains of Struct. **3c** were the only reaction product at 100°C (No. 14, Table 1), and they were the predominant product at 60 or 20°C. From this point of view, the DMAP-initiated polymerizations agreed well with the pyridine and 4-MeP-initiated ones. However, at these lower temperatures, chains having an additional mass of 14 Da were also observed. Such mass peaks may either result from $K^{\oplus}$-doped cyclic oligo-/polylactones or from linear chains having



4a : R' = CH_3 **4b** : R' = CH_2Cl



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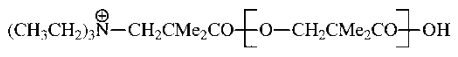

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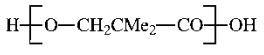

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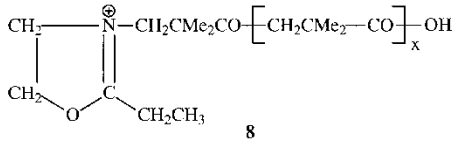

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Scheme 1.

one methyl ester endgroup and one dimethylaminopyridinium endgroup. In order to clarify the origin of these mass peaks, the measurements were repeated with $Li^{\oplus}$ doping. In contrast to the linear chains intramolecularly "doped" by pyridinium endgroups, the peaks of the cycles should shift to lower masses by 32 Da ($K^{\oplus}$-$Li^{\oplus}$). However, such a shift was not observed. Therefore, the MALDI-TOF m.s. with $Li^{\oplus}$ doping suggest that linear chains with methyl ester endgroups are present (Struct. **4a**) (Sch. 2). The methyl ester endgroups may be formed when the polylactones precipitated into methanol are heated for drying. When the virgin reaction products of repeated syntheses were precipitated into diethyl ether, methyl ester endgroups were absent, and the MALDI-TOF m.s. displayed the mass peaks of chains with Struct. **3c** exclusively.

Furthermore, it should be mentioned that the MALDI-TOF m.s. of all polylactones prepared in dichloromethane showed a species corresponding to chains of Struct. **3** with an additional mass of 48–49 Da. This linear species was assigned to Struct. **4b** resulting from the reaction of the carboxylate anions (Struct. **2**) with the solvent (see Fig. 3). Finally, it should be mentioned that the Structures **3a**, **3b**, and **3c** were confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of all polylactones listed in Table 1 displayed the aromatic protons of the pyridinium endgroups as exemplarily illustrated by Fig. 3 for a DMAP-initiated polylactone.

Initiation with Tertiary Alkylamines

Three aliphatic tertiary amines of largely different structure were selected as initiators for the second part of this work, namely DABCO, triethylamine and 2-EOX. To avoid side reactions with the solvent, all polymerizations were conducted in NMP (Table 2). The MALDI-TOF m.s of the polylactones initiated by DABCO exclusively displayed mass peaks of linear chains having the Struct. **5**. This result ruled out that both nitrogens of

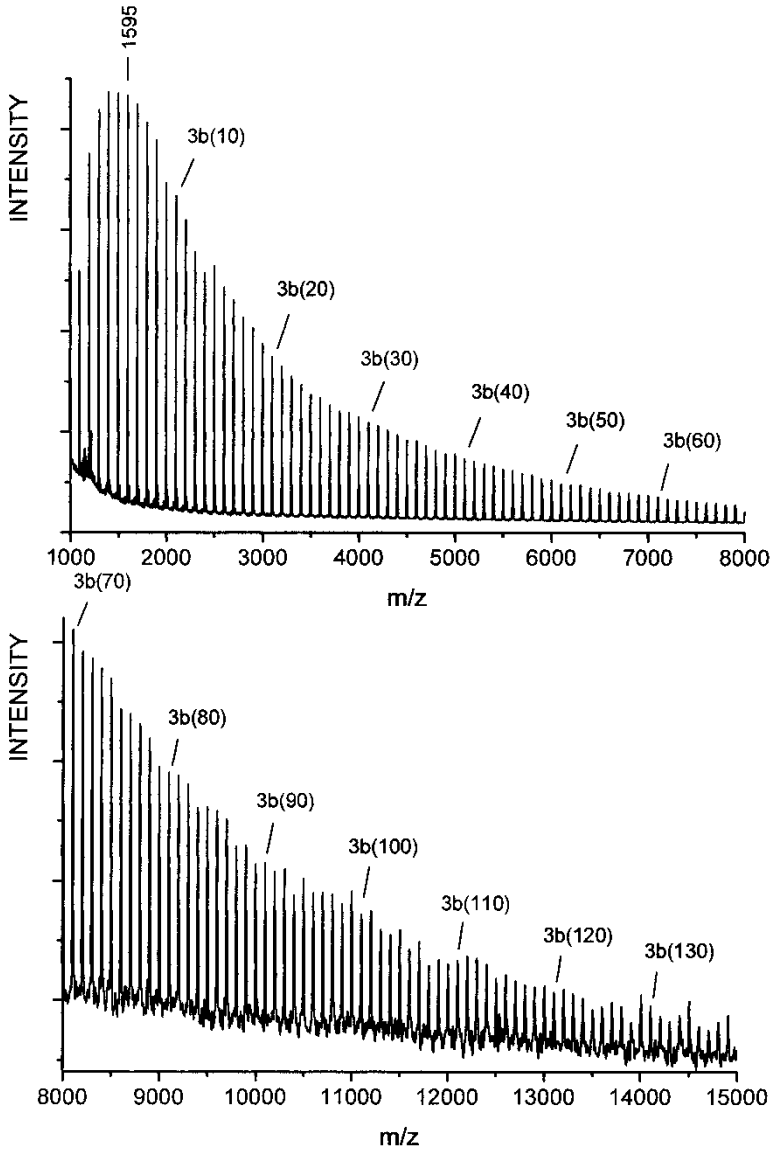
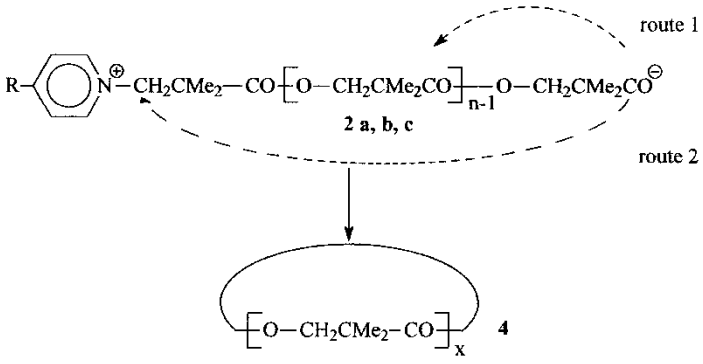


Figure 2. MALDI-TOF m.s. of a 4-methylpyridine-initiated polypivalolactone (**3b**, No. 8, Table 1) prepared in NMP at 60°C (the number in brackets indicates the DP).

DABCO started a chain growth in "both directions". The absence of cyclic oligolactones also proves that no or only few (poly)condensation steps occurred in perfect agreement with the pyridine-initiated polymerizations.

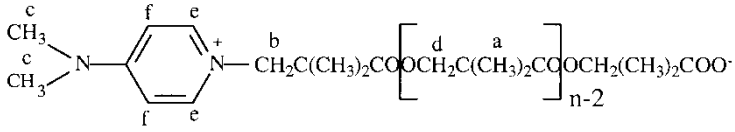
With triethylamine, rather complex reaction products were obtained. The main product found in the MALDI-TOF m.s. had the Struct. **6** resulting from zwitterionic polymerization analogous to the pyridine-initiated polylactones. Cyclic oligolactones were absent, indicating that frequent condensation steps had not occurred. However, a byproduct was detected having the Struct. **7** resulting from an initiation by $OH^{\oplus}$. The origin of the traces of water, which played the role of coinitiators is not clear at this



Scheme 2.

time, since all reagents were carefully dried. A third type of linear species, which was present in small quantities, was not identified with regard to its endgroups.

From initiation with 2-ethyloxazolidine again a complex reaction product was obtained. Both ^{1}H NMR and IR spectra clearly proved that polypivalolactone was formed and no copolymers. This point needs to be emphasized because it is known from the work of Saegusa et al. [9–11] that the unsubstituted oxazolidine yields an alternating copolymer when heated with PiL in equimolar ratios. The MALDI-TOF mass spectra



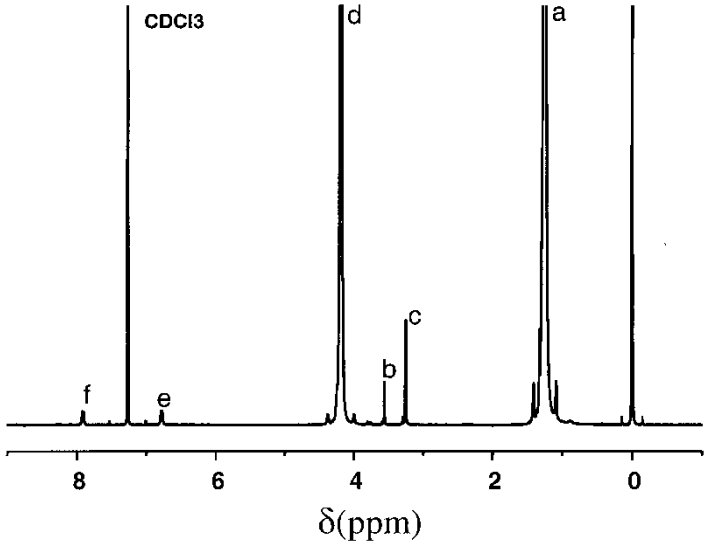
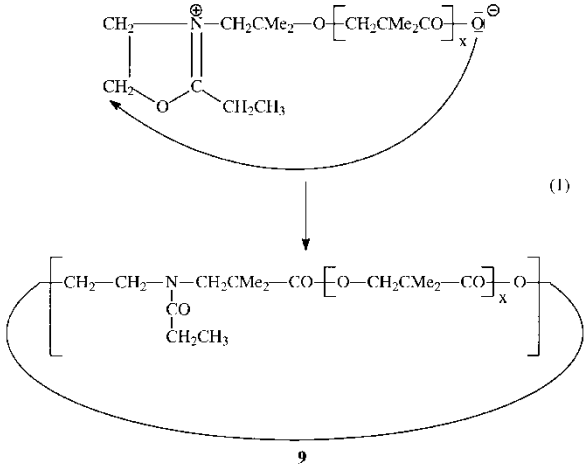


Figure 3. 400 MHz ^{1}H NMR spectrum of a DMAP-initiated polypivalolactone (**3c**, No. 12, Table 1) prepared in NMP.

prove that chains of Struct. **8** were the main products in all three samples. In other words, a normal zwitterionic polymerization of PiL has occurred. Furthermore, the $K^{\oplus}$-doped peaks of cyclic oligolactones were detectable in contrast to all other reaction products discussed above. However, in the case of initiation with 2-ethyloxazolidine, an end-to-end cyclization may take place as outlined in Eq. (1). Such a cyclization mechanism cannot exist for the other amine initiators studied in this work, and thus the unique formation of cycles in 2-ethyloxazolidine-initiated polymerization and the absence of cycles in all other samples has a plausible explanation.

Pyridine-Initiated Polymerizations of β-Propiolactone

For comparison, two pyridine-initiated polymerizations of β-propiolactone were performed with $M/I = 100$ in NMP at 20 and 60°C. The MALDI-TOF m.s. of the isolated polylactones displayed a clean course of both polymerizations. Only one kind of polylactones was formed. The mass peaks corresponded to $K^{\oplus}$–doped cycles. Pyridinium endgroups were totally absent. The ^{1}H NMR spectra displayed the presence of acrylate endgroups. Therefore, these polylactones should have the linear Struct. **10**, which is isomeric to cyclic oligo- and polylactones. In other words, the initially formed pyridinium groups were quantitatively eliminated and the resulting acrylate ions played the role of initiators. This result is in good agreement with studies of other research groups[3] which were published before MALDI-TOF mass spectroscopy was available.



(1)

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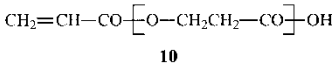

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Conclusions

The MALDI-TOF mass spectroscopic measurements conducted in this work proves that both pyridine-type initiators and trialkylamine initiate a zwitterionic polymerization of pivalolactone. With the exception of initiation with 2-ethyloxazoline, no cyclic oligolactones were found. This finding proves that the chain growth almost exclusively proceeds via an anionic ring-opening polymerization of the lactone. However, it was also observed that the molecular weights increased in NMP at higher temperatures, also the conversions

were high at all temperatures. In other words, the molecular weights did not parallel the conversions. This finding suggests that at least a few condensation steps involving the anionic chain ends contributed to the chain growth after the anionic ring-opening polymerization was almost complete. In the case of initiation with 2-ethyloxazoline, cyclization via a special mechanism was also observed.

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