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Electrospray Ionization Mass Spectrometry Investigation of Oligomers Prepared by Ring-Opening Metathesis Polymerization of Methyl *N*-(1-Phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate

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ABSTRACT: Electrospray ionization mass spectrometry (ESI-MS) was used for the characterization of oligomers which were prepared by ring-opening metathesis polymerization (ROMP) of methyl *N*-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate (**1**), employing molybdenum alkylidene initiators of the type Mo(CH(*t*-Bu))(NAr)(OR)$_2$ (Ar = 2,6-di(isopropyl)phenyl, R = C(CH$_3$)$_3$ (**I**), C$_{10}$H$_{17}$ (**II**), and CCH$_3$(CF$_3$)$_2$ (**III**)). ROMP was terminated with acetone/water (99/1, v/v), the solvent also used for ESI-MS. The oligomers (**2**) had different alkylidene end groups derived from the active species: neopentylidene (from the catalyst), isopropylidene (reaction with acetone) and (2-(methoxycarbonyl)-5-methyl-*N*-(1-phenylethyl)pyrrolid-3-yl)methylidene (reaction with water, hydrogenation product). Metathesis equilibration and intramolecular reactions of the active species with ester groups, resulting in the formation of cyclic products, were found. The influence of the initiator structure and the reaction time t_R is discussed.

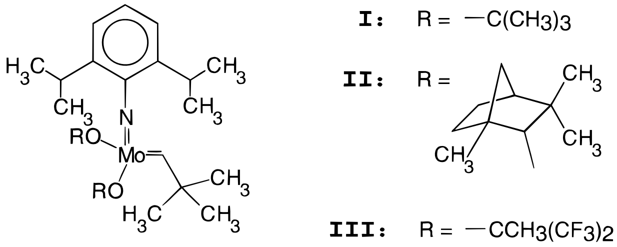
Introduction

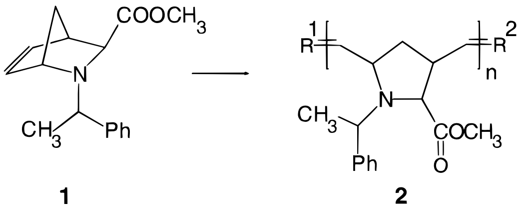
The interest in special techniques of mass spectrometry (MS) for the determination of the molecular weight of synthetic oligomers and polymers has increased in recent years. MS offers the advantage that the mass and/or the mass distribution can be determined more exactly than with other methods. Thus, detailed information can be obtained for samples containing various molecules with only small differences in mass. In addition, some problems that occur with other techniques can be avoided. In the case of size exclusion chromatography, the problem is to find a suitable standard polymer. In the case of multicomponent mixtures, spectroscopic techniques can provide only a superposition of the contribution of the components.

Suitable methods for the investigation of oligomers or polymers by means of MS are "soft" ionization techniques, for example laser desorption,[1] fast atom or ion bombardment,[2,3] or field desorption.[4] Recently, "extrasoft" techniques have become important. Examples are electrospray ionization (ESI)[5−9] and under suitable conditions matrix-assisted laser desorption/ionization (MALDI).[5,10,11] These techniques primarily result in the formation of pseudomolecular ions such as $[M + H]^+$ or $[M + Na]^+$ with little or no fragmentation. Multiple charged ions are also common (e.g., $[M + 8H]^{8+}$), especially in ESI-MS. Thus ESI-MS, until now mainly used successfully in biochemistry, allows investigation of thermally or chemically labile high molecular weight compounds with quadrupole or magnetic sector mass analyzers.

In this work, methyl *N*-(1-phenylethyl)-2-azabicyclo-[2.2.1]hept-5-ene-3-carboxylate (**1**) was polymerized employing the molybdenum alkylidene initiators **I**−**III** (Chart 1) as described previously.[12] Oligomers (**2**) were obtained by using low molar ratios of [**1**]/[initiator].

Chart 1. Molybdenum Alkylidene Initiators





1 **2**

Products **2** are not very stable thermally, but they are soluble in nonpolar and polar solvents. Therefore ESI-MS seemed to be the method of choice for investigation.

The aim of the present ESI-MS investigation was the determination of the chemical structure of the end groups R^1 and R^2 of oligomers **2**. Furthermore, we wished to investigate whether side reactions occurred with monomer **1**, the active species, or oligomers **2**. The reaction schemes presented below are a result of the ESI-MS investigation. For products prepared by ROMP employing molybdenum alkylidene initiators, corresponding experiments with other analytical techniques have been carried out in only a few cases.[13−15]

Experimental Section

A. Preparation of Samples. Various types of samples containing oligomers **2** were prepared at 20 °C, employing the initiators **I**−**III** and varying the reaction time t_R. For the assignment of the products, the indices I, II, or III (giving the

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Table 1. Preparation of Samples of Oligomers 2: Amounts of Initiator and Monomer 1 Used for the Polymerization

sample	initiator, μmol	**1**, μmol	molar ratio [**1**]/[initiator]	concn of **1**, mol/L
$\mathbf{2}_{\mathbf{I,S}}$	27	155	6	0.15
$\mathbf{2}_{\mathbf{I,M}}$	27	155	6	0.15
$\mathbf{2}_{\mathbf{I,L}}$	30	92	3	0.15
$\mathbf{2}_{\mathbf{II,S}}$	22	155	7	0.15
$\mathbf{2}_{\mathbf{II,M}}$	22	155	7	0.15
$\mathbf{2}_{\mathbf{II,L}}$	15	101	7	0.14
$\mathbf{2}_{\mathbf{III,L}}$	28	82	3	0.14

catalyst) and S (t_R = 7 min), M (t_R = 2 h), or L (t_R = 7 days) are used. For example, product $\mathbf{2}_{\mathbf{I,M}}$ is the oligomer **2** obtained with the catalyst **I** at t_R = 2 h.

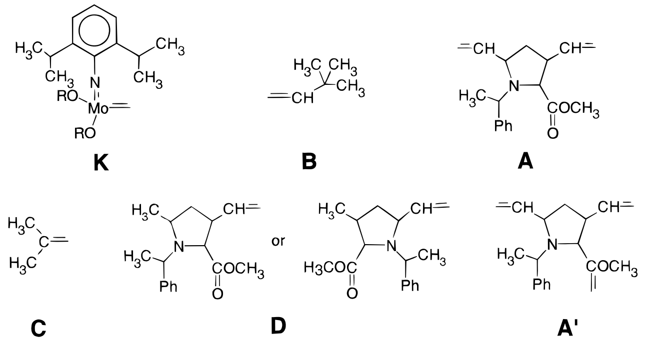
All polymerizations were carried out in a glovebox under dry nitrogen at 20 °C. As a general procedure, monomer and initiator (see Table 1), were dissolved separately in dry benzene or benzene-d_6 (for NMR control in the long-term experiments $\mathbf{2}_{\mathbf{I,L}}$, $\mathbf{2}_{\mathbf{II,L}}$, and $\mathbf{2}_{\mathbf{III,L}}$). The two solutions were mixed in a vial or an NMR tube. The decrease in the alkylidene signal in ^{1}H-NMR was taken as evidence for the consumption of active alkylidene species in the course of the reactions.

After the set reaction time t_R (7 min, 2 h, or 7 days), the reaction mixture was diluted with acetone/water (99/1, v/v) to a concentration of approximately 1 mmol/L (calculated on monomer **1**). Acetone or water terminate ROMP with molybdenum alkylidene initiators. In the 99/1 mixture, the water content is low enough to avoid problems with respect to the solubility of the samples, but high enough for a satisfactory ionization in subsequent ESI-MS. We also tried 95/5 and 90/10 mixtures, which lead to partial precipitation.

As shown below, traces of Na^+ in the acetone component of the mixture took part in ESI (attachment of Na^+ to molecules M gave pseudomolecular ions $[M + Na]^+$). For the samples with the index S or M, e.g. $\mathbf{2}_{\mathbf{I,S}}$ or $\mathbf{2}_{\mathbf{II,M}}$, acetone purum p.a. was used. For the investigation of the samples with the index L, e.g. sample $\mathbf{2}_{\mathbf{II,L}}$, the acetone was freshly distilled from P_2O_5 to remove traces of Na^+.

B. Mass Spectra. The spectra were recorded using a standard Kratos electrospray ion source fitted to a Kratos Profile double-focusing magnetic sector instrument with 2 kV acceleration voltage. The m/z range recorded was 25−2400, the scan speed 10 s/decade, and the resolution 1700 (10% valley definition). The potentials applied were 5.94 kV at the spraying capillary, 3.15 kV at the cylinder, and 2.43 kV at the end plate. The temperature of the electrospray ion source was 70 °C. The countercurrent flow of nitrogen was 50 mL/min. A Harvard Apparatus 22 syringe pump was used to deliver a constant solvent flow of 4 μL/min. The acetone/water solvent mixture (99/1, v/v) used was most satisfactory for ESI-MS in a series of experiments with different pure solvents and mixtures.

Chart 2. Definition of Units in the Products



The solutions were injected into the solvent flow of the electrospray system 15 min after dilution with acetone/water via a 100 μL sample loop. The signal-to-noise ratio was improved by averaging the scans of a measuring time of 30 min. The m/z values in Tables 2−4 give the most intense peak of any isotope distribution. The measured values of m/z corresponded to these theoretical values for resolved peaks within ±0.1 amu and for unresolved peaks within ±0.2 amu. Only peaks with a relative intensity >1% are reported.

Results and Discussion

A. General. To facilitate description, the products are formally subdivided into units ending in double bonds. These units are K, B, A, C, D, and A′ (Chart 2).

The initiators **I**−**III** are combinations of a unit containing the molybdenum (K) and a neopentylidene unit (B). Monomer **1** is polymerized forming dialky-

Table 2. Products Formed by Quenching Reactions of KA$_n$B with Acetone or Water: Ions Observed in the ESI Mass Spectra of Different Samples of 2 (See Figures 1−7)

			relative intensity in sample						
ions obsd	*n*	*m/z*	$\mathbf{2}_{\mathbf{I,S}}$	$\mathbf{2}_{\mathbf{I,M}}$	$\mathbf{2}_{\mathbf{I,L}}$	$\mathbf{2}_{\mathbf{II,S}}$	$\mathbf{2}_{\mathbf{II,M}}$	$\mathbf{2}_{\mathbf{II,L}}$	$\mathbf{2}_{\mathbf{III,L}}$
$[DA_nB + H]^+$	0	330.2	6	15	45	6	62	10	82
	1	587.4	100	67	50	100	87	11	75
	2	844.5	81	22	23	33	42	10	17
	3	1101.7	44	6	7	13	13	6	5
	4	1358.8	19	3	2	5	8	2	1
	5	1615.9	7	2		3	3		
	6	1873.1	3			2	1		
	7	2131.2	1						
$[DA_nB + Na]^+$	0	352.2	3	6		4	22		
	1	609.4	38	17		19	10		
	2	866.5	18	4		6	3		
	3	1123.7	7	1		6	2		
	4	1380.8	2			2			
	5	1637.9	1			2			
$[CA_nB + H]^+$	1	370.3	12	49	10	37	28	3	8
	2	627.4	38	100	12	13	11	4	2
	3	884.6	23	36	4	4	7	1	
	4	1141.7	16	16	2	2	3	1	
	5	1399.0	3	5		1	2		
	6	1657.0	4	2		1	1		
	7	1914.1	2						
	8	2171.3	1						
$[CA_nB + Na]^+$	1	392.3		5		4			
	2	649.4	4	8		2	1		
	3	906.5	3	2		1			
	4	1163.7	3	1					

Scheme 1. Quenching Reaction of KA_nB with Acetone or Water

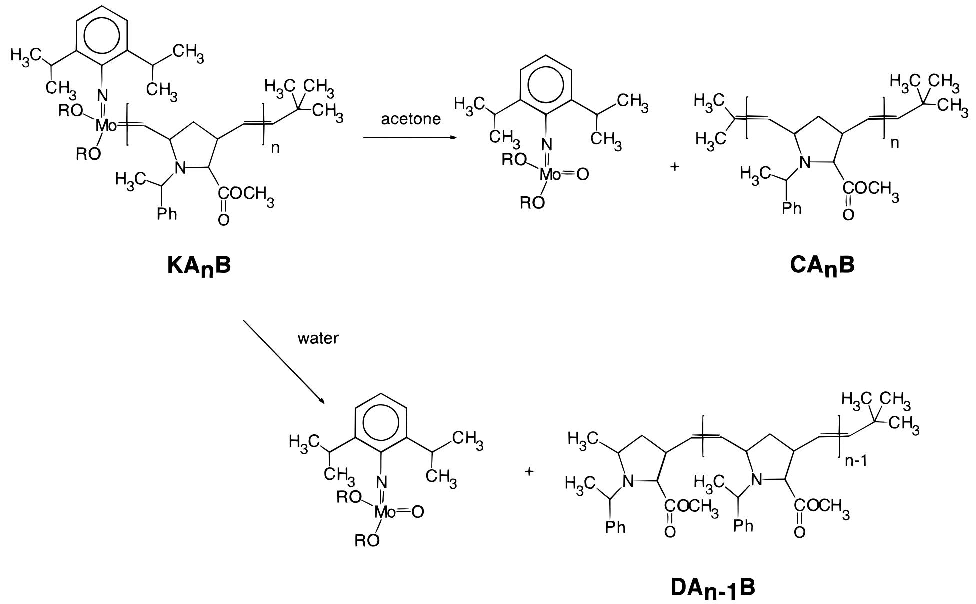


Table 3. Products Formed by Metathesis Equilibration: Ions Observed in the ESI Mass Spectra of Different Samples of 2 (See Figures 2, 3, 5, and 7)

			relative intensity in sample			
ions obsd	n	m/z	$2_{I,M}$	$2_{I,L}$	$2_{II,M}$	$2_{III,L}$
$[BA_nB + H]^+$	1	398.3	7	96		27
	2	655.5	3	100		24
	3	912.6	1	58		5
	4	1169.7		22		2
	5	1427.9		7		2
	6	1685.0		2		
$[CA_nC + H]^+$	1	342.2		14		1
	2	599.4	1	18	2	6
	3	856.6		6		
$[DA_nC + H]^+$	1	559.4		4		

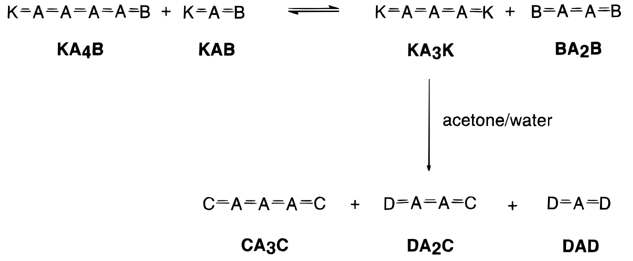
Table 4. Products Formed by Reactions Involving the Ester Group of the Monomeric Unit (Metathesis Cyclization): Ions Observed in the ESI Mass Spectra of Different Samples of 2 (See Figures 5–7)

			relative intensity in sample		
ions obsd	n	m/z	$2_{II,M}$	$2_{II,L}$	$2_{III,L}$
$[A_nA'B + H]^+$	1	569.4	100	100	100
	2	826.5	70	84	32
	3	1083.7	28	56	7
	4	1340.8	11	31	2
	5	1598.9	4	16	1
	6	1856.1	3	5	1
	7	2113.2	1	3	
	8	2370.4		1	
$[A_nA'B + 2H]^{2+}$	2	413.8	2	3	
	3	542.3	2	5	
	4	670.9	4	11	
	5	800.0	3	15	
	6	928.6	3	8	
	7	1057.1	1	7	
	8	1185.7	1	7	
	9	1314.8		4	
	10	1443.3		3	
	11	1571.9		3	
	12	1700.5		2	
	13	1829.0		1	

lidene units A. The growing polymer chain is KA_nB. The part K is removed in various termination reactions.

Quenching of the reaction with acetone gives an oligomer with an isopropylidene end group C. When the oligomerization is quenched with water, the CH= in the terminal monomer unit A next to unit K is transformed to CH_3 and an end group D results. The quenching reaction of KA_nB with acetone or water giving the products CA_nB and $DA_{n-1}B$ is shown in Scheme 1. The ions observed in the ESI mass spectra corresponding to these products are listed in Table 2.

Scheme 2. Metathesis Equilibration



In addition, metathesis equilibration reactions have been found, resulting in intermediates KA_nK and products BA_nB. Reactions of KA_nK with acetone/water should lead to products CA_nC, $DA_{n-1}C$ and —not found in this work—$DA_{n-2}D$. An example of this reaction sequence is given in Scheme 2. The ions observed in the ESI mass spectra corresponding to these products are listed in Table 3.

Further, an oxygen atom may be removed from the carbonyl group of A in a side reaction of the active species with A so that the trialkylidene group A′ results. Intramolecular reaction of the active species with the carbonyl group of a repeating unit leads to cyclization. As an example of a metathesis cyclization, the formation of the sequence $A_nA'B$ is shown in Scheme 3. The cyclized product is also termed $A_nA'B$ below. As far as we know, such reactions involving ester groups during ROMP with molybdenum alkylidene initiators have not yet been considered. However, molybdenum alkylidene complexes are known to react readily with aldehydes or ketones.[18] Thus reactions with esters, of course at much lower rates, can be expected. Furthermore, it is known from titanium complexes, which also initiate metathesis reactions, that esters can be transformed into vinyl ethers.[19] The ions observed in the ESI mass spectra corresponding to products containing unit A′ are listed in Table 4.

We found single- and double-charged pseudomolecular ions only ($[M + H]^+$, $[M + Na]^+$, $[M + 2H]^{2+}$), as might

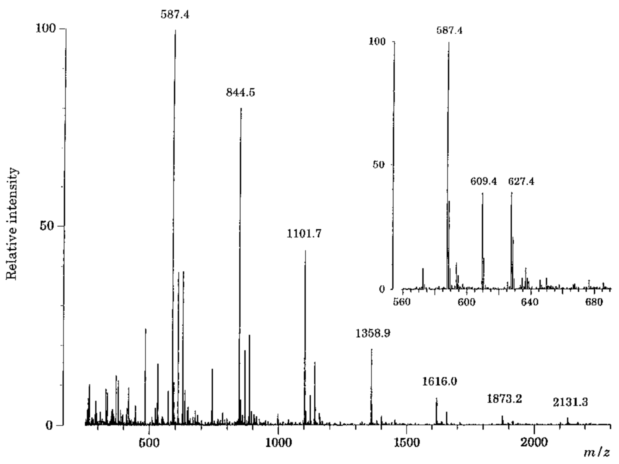
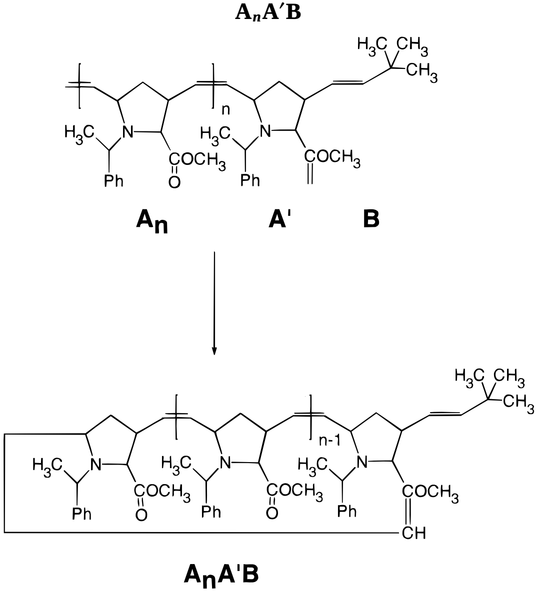


Figure 1. ESI mass spectrum of sample **2**$_{\rm I,S}$ (for *m/z* assignment of ions $[DA_nB + H]^+$, $[DA_nB + Na]^+$, $[CA_nB + H]^+$, and $[CA_nB + Na]^+$; see Table 2). Inset: expanded view of the mass region *m/z* 560−690 ($[DAB + H]^+$ (587.4), $[DAB + Na]^+$ (609.4), and $[CA_2B + H]^+$ (627.4)).

Scheme 3. Metathesis Cyclization of the Sequence $A_nA'B$



be expected for a solvent mixture with only 1% water, and because of the molecular weights which are relatively low for ESI conditions.

B. ESI Mass Spectra. Initiator I, t_R = 7 min. In this experiment, the polymerization was stopped before all monomer **1** was consumed. Figure 1 shows the ESI mass spectrum of sample **2**$_{\rm I,S}$.

The most intense signal was found at *m/z* = 587.4. The charge of this ion, identified by the isotope peaks, was *z* = 1. The ion is interpreted as $[DAB + H]^+$, the protonated product of the reaction of KA_2B with water (Scheme 1). The spectrum shows a series $[DA_nB + H]^+$ of corresponding oligomers with values of *n* up to 7 (see Table 2).

Another sequence of ions, found at *m/z* = 370.3, 627.4, etc., was identified as $[CA_nB + H]^+$. The highest value of *n* observed was 8. This sequence results from reactions with acetone (Scheme 1). The relative intensities of the series $[CA_nB + H]^+$ and $[DA_nB + H]^+$ show that the reaction of KA_nB with water is faster than with acetone.[13] A comparison of the intensities is possible since the chemical structure of the polymer backbone of both series is equal and dominates the behavior during the ESI process.

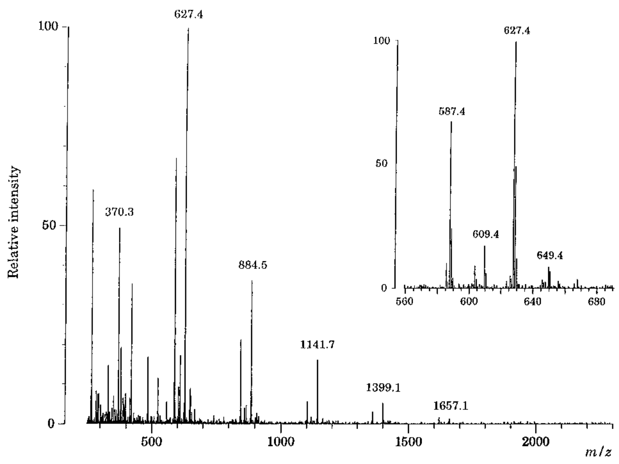


Figure 2. ESI mass spectrum of sample **2**$_{\rm I,M}$ (for *m/z* assignment of ions $[DA_nB + H]^+$, $[DA_nB + Na]^+$, $[CA_nB + H]^+$, $[CA_nB + Na]^+$, $[BA_nB + H]^+$, and $[CA_nC + H]^+$; see Tables 2 and 3). Inset: expanded view of the mass region *m/z* 560−690 ($[DAB + H]^+$ (587.4), $[DAB + Na]^+$ (609.4), $[CA_2B + H]^+$ (627.4), and $[CA_2B + Na]^+$ (649.4)).

Furthermore, a series at *m/z* = 609.4, 866.5, etc. was found corresponding to ions of the type $[DA_nB + Na]^+$. It is well known that even very low concentrations (<1 ppm) of cations like sodium can cause ionization of organic molecules during the ESI process. In the present case, the acetone purum p.a. was the source of the sodium ions.

In addition, some products were found with lower intensities, for example the series *m/z* = 483.3, 740.5, and 997.6 (probably $[DA_nB + H]^+$ where one phenyl-$CH(CH_3)$ group was removed, giving a secondary amine in the polymer backbone). These products are not discussed here, since they are not essential to compare the reactivity of the different initiators.

Initiator I, t_R = 2 h. The results with sample **2**$_{\rm I,M}$, shown in Figure 2, should give information about reactions occurring shortly after the end of the polymerization reaction.

DA_nB and CA_nB were found to be the most important products. DA_nB was identified by $[DA_nB + H]^+$ and $[DA_nB + Na]^+$, and CA_nB by $[CA_nB + H]^+$ and $[CA_nB + Na]^+$.

The relative intensities of $[DA_nB + H]^+$ and $[CA_nB + H]^+$ were different in **2**$_{\rm I,S}$ and **2**$_{\rm I,M}$. While $[DA_nB + H]^+$ was the most intense series of sample **2**$_{\rm I,S}$, the most intense series of sample **2**$_{\rm I,M}$ was $[CA_nB + H]^+$, although both reaction mixtures were diluted with the same mixture of acetone/water.

In comparison with **2**$_{\rm I,S}$, for sample **2**$_{\rm I,M}$ the fraction of oligomers with higher polymerization degree *n* is decreased. This can be explained by a slow metathesis equilibration of the oligomers according to Scheme 2, as soon as monomer **1** is consumed completely. Some products (especially BA_nB) that should be obtained by metathesis equilibration can be found in the ESI mass spectrum in Figure 2, but their relative intensities are very low.

Initiator I, t_R = 7 days. The ESI mass spectrum obtained for sample **2**$_{\rm I,L}$ is shown in Figure 3. To avoid ionization by Na^+, freshly distilled acetone was used instead of acetone purum p.a.

The most intense signal of the spectrum, interpreted as $[BA_2B + H]^+$, was found at *m/z* = 655.4 (*z* = 1). Other ions of the sequence $[BA_nB + H]^+$ (with *n* from 1 to 7) were also found (see Table 3).

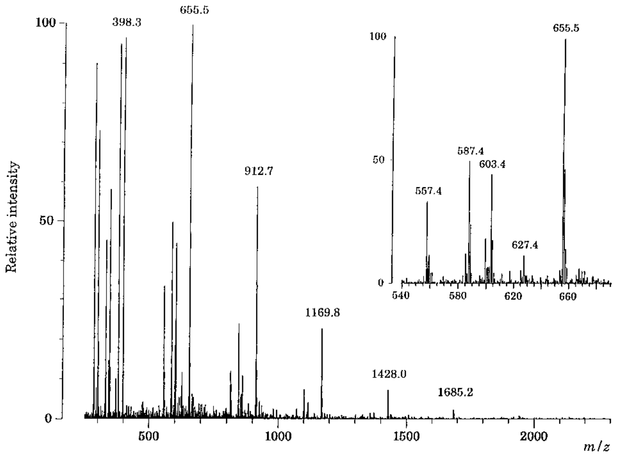


Figure 3. ESI mass spectrum of sample $\mathbf{2_{I,L}}$ (for *m/z* assignment of ions $[DA_nB + H]^+$, $[CA_nB + H]^+$, $[BA_nB + H]^+$, $[CA_nC + H]^+$, and $[DA_nC + H]^+$; see Tables 2 and 3). Inset: expanded view of the mass region *m/z* 540−690 ($[DAB + H]^+$ (587.4), $[CA_2B + H]^+$ (627.4), and $[BA_2B + H]^+$ (655.5)).

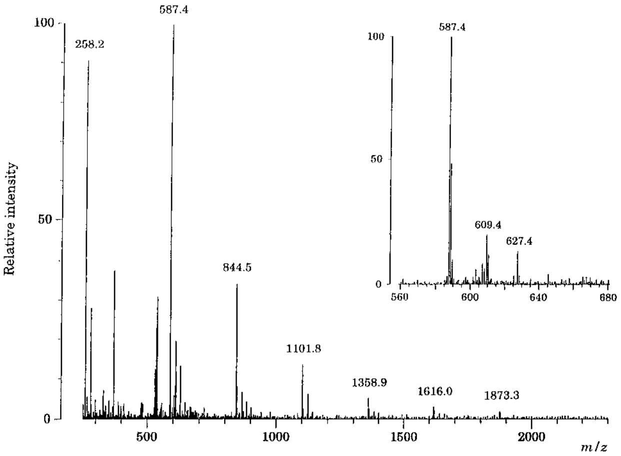


Figure 4. ESI mass spectrum of sample $\mathbf{2_{II,S}}$ (for *m/z* assignment of ions $[DA_nB + H]^+$, $[DA_nB + Na]^+$, $[CA_nB + H]^+$, and $[CA_nB + Na]^+$ see Table 2). Inset: expanded view of the mass region *m/z* 560−680 ($[DAB + H]^+$ (587.4), $[DAB + Na]^+$ (609.4), and $[CA_2B + H]^+$ (627.4)).

Three ions which can be interpreted as $[CA_nC + H]^+$ were observed ($n = 1-3$). Only one ion corresponding to $[DA_nC + H]^+$ was found, namely $[DAC + H]^+$ at *m/z* = 559.4 with approximately 4% relative intensity. It was not possible to find products of the type $[DA_nD + H]^+$.

These results show that equilibration according to Scheme 2 occurred. But the ratio of BA_nB to CA_nC and corresponding products implies that the main fraction of BA_nB should have been formed by bimolecular decomposition of the active species.[13]

The sequences $[DA_nB + H]^+$ and $[CA_nB + H]^+$ were also observed.

Initiator II, t_R = 7 min. Figure 4 shows the ESI mass spectrum obtained for sample $\mathbf{2_{II,S}}$. The results are similar to those obtained for $\mathbf{2_{I,S}}$. The oligomeric products identified are $[DA_nB + H]^+$, $[DA_nB + Na]^+$, $[CA_nB + H]^+$, and $[CA_nB + Na]^+$, respectively. The relative intensities found for oligomers with increasing *n* decreases in comparison with sample $\mathbf{2_{I,S}}$. On the other hand, the sample still contained high amounts of monomer **1**, identified as $[\mathbf{1} + H]^+$ and as $[\mathbf{1} + Na]^+$. In contrast to this, monomer **1** was detected only at low concentration in sample $\mathbf{2_{I,S}}$ which can be explained by different reactivities of the initiators **I** and **II**.[17]

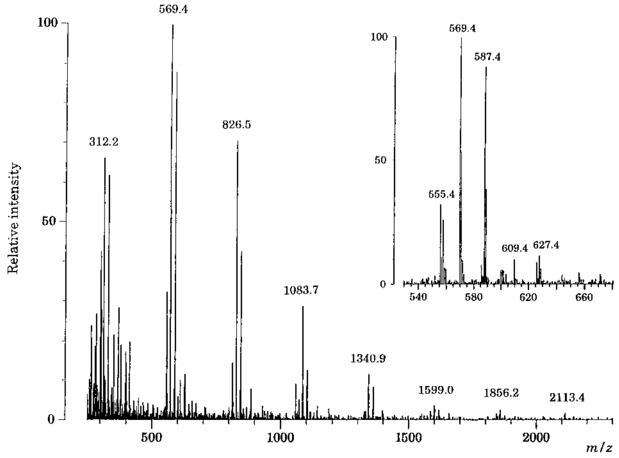


Figure 5. ESI mass spectrum of sample $\mathbf{2_{II,M}}$ (for *m/z* assignment of ions $[DA_nB + H]^+$, $[DA_nB + Na]^+$, $[CA_nB + H]^+$, $[CA_nB + Na]^+$, $[CA_nC + H]^+$, $[A_nA'B + H]^+$, and $[A_nA'B + 2H]^{2+}$; see Tables 2−4). Inset: expanded view of the mass region *m/z* 530−680 ($[AA'B + H]^+$ (569.4), $[DAB + H]^+$ (587.4), $[DAB + Na]^+$ (609.4), and $[CA_2B + H]^+$ (627.4)).

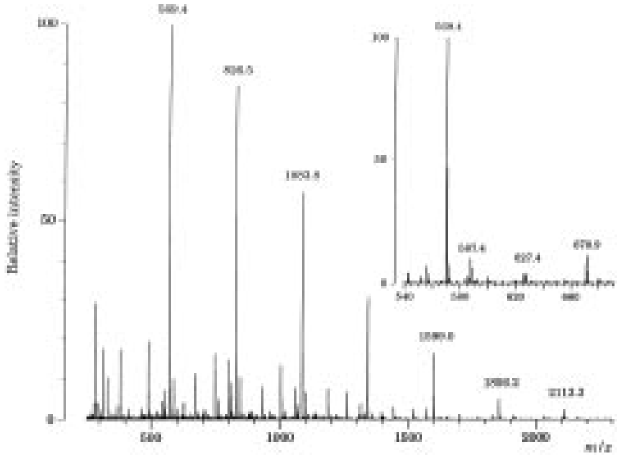


Figure 6. ESI mass spectrum of sample $\mathbf{2_{II,L}}$ (for *m/z* assignment of ions $[DA_nB + H]^+$, $[CA_nB + H]^+$, $[A_nA'B + H]^+$, and $[A_nA'B + 2H]^{2+}$; see Tables 2 and 4). Inset: expanded view of the mass region *m/z* 540−690 ($[AA'B + H]^+$ (569.4), $[DAB + H]^+$ (587.4), $[CA_2B + H]^+$ (627.4), and $[A_4A'B + 2H]^{2+}$ (670.9)).

Initiator II, t_R = 2 h. The results obtained for sample $\mathbf{2_{II,M}}$ are reproduced in Figure 5. $\mathbf{2_{II,M}}$ contained a new type of oligomer that was not detected in the samples described above. A series with *m/z* = 569.4 (base peak of the spectrum), 826.5, etc. was found. The highest mass corresponding to this series was found at *m/z* = 2113.2 (see Table 4). This series can be interpreted as $[A_nA'B + H]^+$ resulting from metathesis cyclizations according to Scheme 3. The sequence $A_nA'B$ with higher values of *n* could also be interpreted by $A_{n-1}A'AB$, $A_{n-2}A'A_2B$, etc., or by a mixture of these compounds. In the following, we describe all corresponding ions as $A_nA'B$.

The reaction of the ester groups seems to occur only at the end of the polymerization, when the concentration of monomer **1** has already been sufficiently decreased, but is faster than the metathesis equilibration observed for the samples prepared employing initiator **I**.

The ions known from sample $\mathbf{2_{II,S}}$ were also found, namely $[DA_nB + H]^+$, $[DA_nB + Na]^+$, $[CA_nB + H]^+$, and $[CA_nB + Na]^+$.

Initiator II, t_R = 7 days. The results obtained for sample $\mathbf{2_{II,L}}$ are shown in Figure 6. The ESI mass spectrum shows that $\mathbf{2_{II,L}}$ consists predominantly of

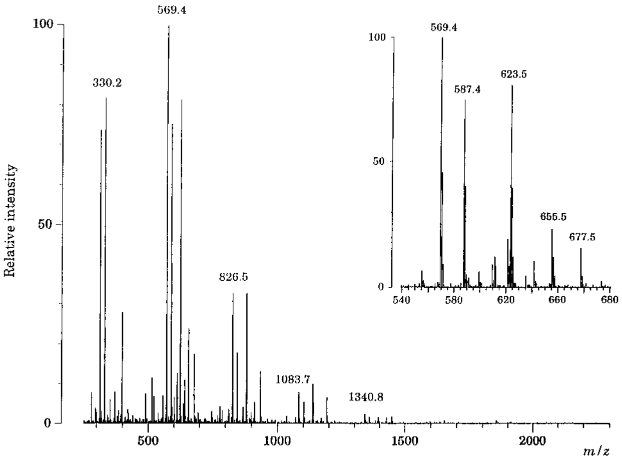


Figure 7. ESI mass spectrum of sample $\mathbf{2}_{\mathrm{III,L}}$ (for *m/z* assignment of ions $[DA_nB + H]^+$, $[CA_nB + H]^+$, $[BA_nB + H]^+$, $[CA_nC + H]^+$, and $[A_nA'B + H]^+$; see Tables 2–4). Inset: expanded view of the mass region *m/z* 540–680 ($[AA'B + H]^+$ (569.4), $[DAB + H]^+$ (587.4), $[(A'B)A'B + H]^+$ (623.5), and $[BA_2B + H]^+$ (655.5)).

oligomers of the type $[A_nA'B + H]^+$. The relative intensity of oligomers with rising *n* increases in comparison with the results found for sample $\mathbf{2}_{\mathrm{II,M}}$. The doubly charged ions at $m/z = 413.8$, 542.4, 670.9, 800.0, etc., correspond to $[A_nA'B + 2H]^{2+}$. The highest value of *n* observed for this series was 13.

The sequences $[DA_nB + H]^+$ and $[CA_nB + H]^+$ were again found, but with reduced intensity. No products giving evidence for a metathesis equilibration were observed. Thus the long-term behavior of ROMP with initiator **I** and initiator **II**, respectively, is different.

Initiator III, $t_R = 7$ days. Among the initiators used in the present investigation, initiator **III** is the most reactive in ROMP.[20] It is known from on-line NMR investigations that at a ratio of [**1**]/[initiator] = 400, full conversion is obtained within less than 2 min. For this reason, only the long-term experiment was carried out.

The ESI mass spectrum obtained for sample $\mathbf{2}_{\mathrm{III,L}}$ is reproduced in Figure 7. The ion found at $m/z = 569.4$ (base peak) belongs to the sequence $[A_nA'B + H]^+$.

Oligomers $[DA_nB + H]^+$ (e.g. for $n = 1$ at $m/z = 587.4$) resulting from the reaction of KA_nB with water were found.

The sequence resulting from the reaction with acetone instead of water (e.g. $[CA_2B + H]^+$ at $m/z = 627.4$) was also found, but only with very low intensity.

Further products observed result from metathesis equilibration. Examples are $[BA_nB + H]^+$ (e.g. for $n = 2$ at $m/z = 655.5$) or $[CA_nC + H]^+$ (for $n = 2$ at $m/z = 599.4$).

Nearly all additional ions of the spectrum can be interpreted assuming an increased reactivity of initiator **III** toward ester groups. It has to be mentioned that the ratio of the rate constants of propagation to initiation, k_p/k_i, is in the range of 50 for this system. Thus about 70% of unreacted initiator remains after full conversion of the monomer. If, for example, the cyclic product AA′B reacts with the initiator KB on the residual ester group, (A′B)A′B should be obtained. The protonated ion $[(A'B)A'B + H]^+$ has a calculated *m/z* of 623.46. This corresponds very well with one of the most intense peaks observed at $m/z = 623.5$. If one monomer unit A is added to (A′B)A′B, the cyclic product A(A′B)-A′B is obtained. Consequently, another signal found at $m/z = 880.6$ can be interpreted as $[A(A'B)A'B + H]^+$ (calculated *m/z* 880.60). A further reaction of the ester group in A(A′B)A′B with KB would give the product $(A'B)_3$. A corresponding protonated ion was found at $m/z = 934.6$ (calculated *m/z* 934.68). The ion found at $m/z = 641.5$ can be interpreted as $[D(A'B)B + H]^+$ (calculated *m/z* 641.47), etc.

Conclusions

The samples prepared by ROMP of monomer **1** employing the initiator **I**, **II**, or **III**, respectively, and using short, medium, or long reaction times t_R, were found to be complex mixtures of oligomeric compounds. Significant differences between the samples were observed depending on the initiator employed and on t_R.

Products typical for the reaction of the active species with ester groups of the monomeric unit were found when initiator **II** was employed. The reaction with ester groups was found to be faster than the metathesis equilibration, observed for initiator **I**. For initiator **III**, both metathesis equilibration and reaction of the active species with ester groups were observed.

The results are of general interest for ROMP, since these side reactions can occur immediately after full conversion of the monomer, and have an important influence on the product distribution.

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