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Anionic polymerization of phenyl glycidyl ether

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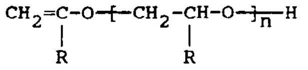
In the anionic polymerization of phenyl glycidyl ether (PGE) initiated by sodium caprolactam (NaCL) or sodium caprolactam/*N*-acetyl caprolactam (NaCL/AcCL), oligo(hydroxy ethers) with different structures and distributions are formed depending on the temperature and concentration of the initiating system. The progress of the reaction was followed by using epoxide titration and high-performance liquid chromatography. The properties of the reaction products were determined by means of vapour-phase osmometry. The melting ranges of the isolated products were found to be from 72 to 120°C and molar masses from 340 to 4000 g mol^{-1}.

(Keywords: phenyl glycidyl ether; anionic polymerization; oligo(hydroxy ethers))

INTRODUCTION

The anionic polymerization of glycidyl ethers can be initiated by nucleophilic initiators, such as tertiary amines, hydroxides and alkoxides. For tertiary amines, the mechanism was established by Shechter *et al.*[1]. The main products from phenyl glycidyl ether (PGE) at temperatures below 100°C can be represented by structure **1** ($CH_2{=}CRO(PGE)_n$):

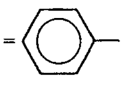


$CH_2{=}C(R){-}O{-}[CH_2{-}CH(R){-}O]_n{-}H$

1

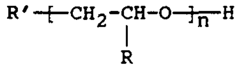
R = Ph-O-CH$_2$-

Ph =



Further oligomers with PhO– and HO– terminal groups ($PhO(PGE)_n$, $HO(PGE)_n$) are formed at temperatures above 100°C[2,3].

The reaction of hydroxides and alkoxides as initiators yield oligo(hydroxy ethers) with the following structure[4]:

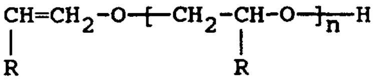


$R'{-}[CH_2{-}CH(R){-}O]_n{-}H$

R′ = HO–, C_nH_{2n+1}–O–

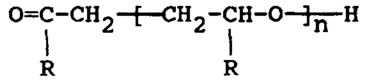
2

Alcohols are often used as solvents in these reactions owing to the poor solubility of the initiators in other solvents with less polarity. In the presence of alcohols and also in the absence of a suitable solvent, chain transfer reactions give rise to a decrease in the degree of polymerization. Consequently, the formation of oligomers with aliphatic double bonds (**1**, **3**) and carbonyl groups (**4**) can be observed[5–12]:



$CH(R){=}CH_2{-}O{-}[CH_2{-}CH(R){-}O]_n{-}H$

3



$O{=}C(R){-}CH_2{-}[CH_2{-}CH(R){-}O]_n{-}H$

4

The ratio of chain propagation reactions to chain transfer reactions depends on the temperature and concentration of the solvent and on the structure of the initiator (considering the polarity of the solvent and charge separation of the alkoxide ions). Furthermore, the nucleophile is able to open the epoxide ring between the oxygen atom and the α-carbon atom ('normal' ring-opening reaction) or between the oxygen atom and the β-carbon atom ('anomalous' ring-opening reaction). The ratio of the products obtained depends strongly on the reaction conditions. The 'normal' ring-opening reaction is preferred if no solvent is used.

The polymerization of lactams, e.g. ϵ-caprolactam (CL), can be initiated by the same anionic initators or one of their mixtures to form polyamide-6 (nylon-6). Special initiating systems have to be used to meet the conditions for an activated anionic polymerization of CL at temperatures below 180°C. A suitable initiator is a mixture of sodium caprolactam (NaCL) and *N*-acetyl caprolactam (AcCL) in given ratios. The reaction mechanism was established by several authors[13–21]. They found the formation of polyamide with one *N*-acetyl and one *N*-carbonyl caprolactam terminal unit per chain.

A lot of papers deal with the external flexibilization of epoxy resins[22–25]. Interpenetrating polymer networks are another way to improve the mechanical properties of

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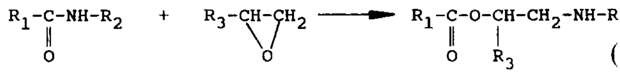
*To whom correspondence should be addressed polymers. Increased adhesion, flexibility and increased stress–strain properties can be expected for polyamide-modified epoxy resins. There are few papers in the literature on one-pot reactions of glycidyl ethers and ϵ-caprolactam and their polymerization products under anionic conditions. The crosslinking of epoxy resins in the presence of low-molar-mass polyamides was investigated[26–29]. Other authors described epoxies as additives for nylon-6[30] or grafting reactions of styrene oxide onto nylon-6[31]. As shown in equation (1), Prime[32] and Komarova *et al.*[33] found an insertion reaction resulting in the formation of an ester group:



$$R_1\text{-}\underset{\underset{O}{\|}}{C}\text{-NH-}R_2 + R_3\text{-}CH\overset{O}{\frown}CH_2 \longrightarrow R_1\text{-}\underset{\underset{O}{\|}}{C}\text{-O-}\underset{\underset{R_3}{|}}{CH}\text{-}CH_2\text{-NH-}R_2 \qquad (1)$$

R_1, R_2, R_3 = aromatic substituents

Reactions subsequent to the secondary amine are still unknown. CL and its derivatives have been used also as catalysts for the crosslinking of epoxy resins[34–36] or as additives[37,38]. Soluble terpolymers from PGE, hexahydrophthalic acid anhydride and CL with a molar mass of 2000 g mol^{-1} and a softening point of 50°C are described[39]. But there have been no investigations of the reaction of glycidyl ethers in a mixture with CL polymerized by using anionic initiators.

Thus, it would be of interest to monitor the reaction behaviour of PGE in a polymerizing CL–polyamide system initiated by NaCL or a NaCL/AcCL mixture. Previous measurements of the reaction rates of CL and PGE in separated homopolymerization reactions at temperatures of 100°C and 120°C revealed nearly equal values for both monomers[40]. This paper presents the results of investigating the product formation and kinetic aspects for the reaction of PGE with NaCL and NaCL/AcCL. To avoid chain transfer the reactions were carried out without a solvent.

RESULTS AND DISCUSSION

Reaction of PGE with catalytic amounts of sodium caprolactam (NaCL) and N*-acetyl caprolactam (AcCL)*

Figure 1 shows the relation between the degree of conversion and the polymerization time for PGE at various temperatures. The concentration of NaCL and AcCL was 1 mol% each. The resulting reaction rates are higher than those for the reaction of PGE with aliphatic tertiary amines as initiators under the same reaction conditions[1–3].

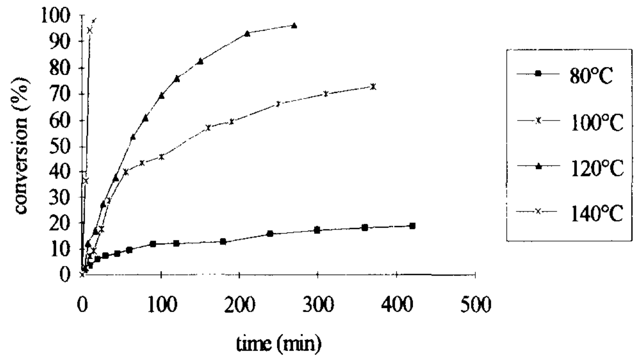
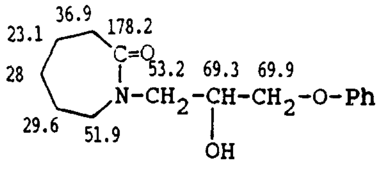


Figure 1 Conversion of PGE as a function of the reaction time at different reaction temperatures. Molar ratio of PGE : NaCL : AcCL = 1 : 0.01 : 0.01

The structure of the products obtained and their distribution depend on the polymerization temperature. Investigations by h.p.l.c. showed different chromatograms at temperatures of 80°C (*Figure 2*) and 140°C (*Figure 3*). The main products were separated by using preparative h.p.l.c. and identified by ^{13}C n.m.r. spectroscopy and mass spectrometry.

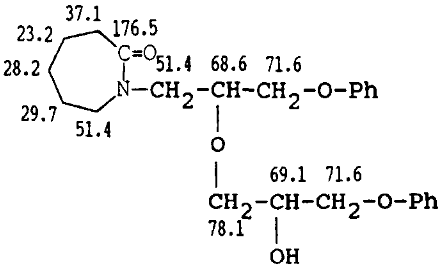
Peak 1 in *Figure 2* represents the following structure (the figures are resonances in the ^{13}C n.m.r. spectrum):



5

Mass spectrum: m/z = 263 (M$^+$), 245, 170, 156, 126, 98, 44.

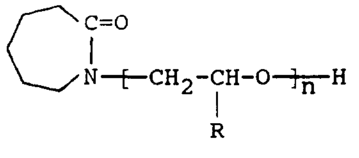
The same measurements were performed for the compounds from peak 3 (**6**) and following peaks 5, 7 and 9:



6

Mass spectrum: m/z = 413 (M$^+$), 320, 306, 245, 163, 132, 84, 58.

Thus, the main oligomeric structure at 80°C can be represented by structure **7** (*Figure 2*, peak numbers 1, 3, 5, 7, 9, 11, 13, 15). Structure **7** corresponds to a structure CL(PGE)$_n$, where n is the number of repeat units. For CL(PGE)$_n$, n was found to range from n = 1 (peak 1) to n = 8 (peak 15).



7

The structure of peaks 4, 6, 8, 10, 12, 14 and 16 corresponds to the general oligomeric structure **10** (AcCL(PGE)$_n$). It can be concluded that this is derived from the reaction product between AcCL and NaCL (equations (2)–(4)). During reactions in the absence of AcCL such products are not formed.

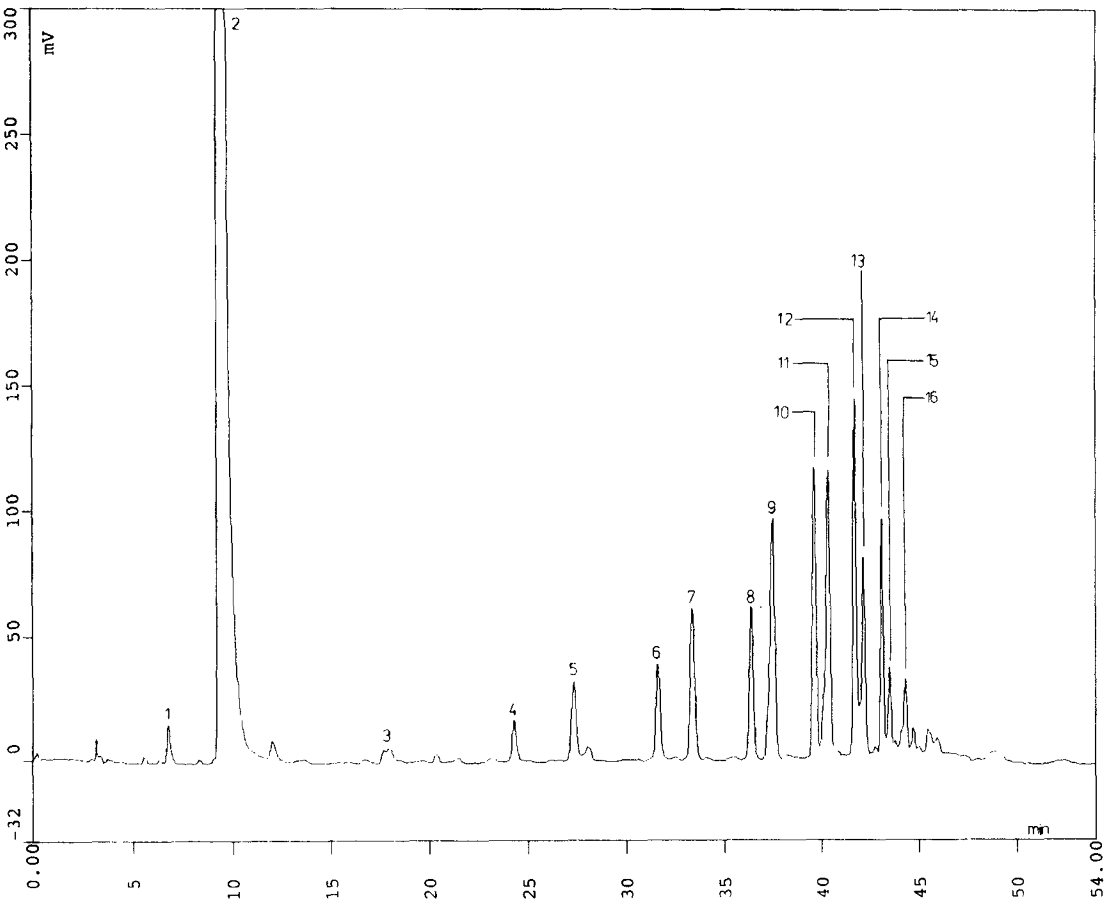


Figure 2 H.p.l.c. of products at 80°C according to *Figure 1*

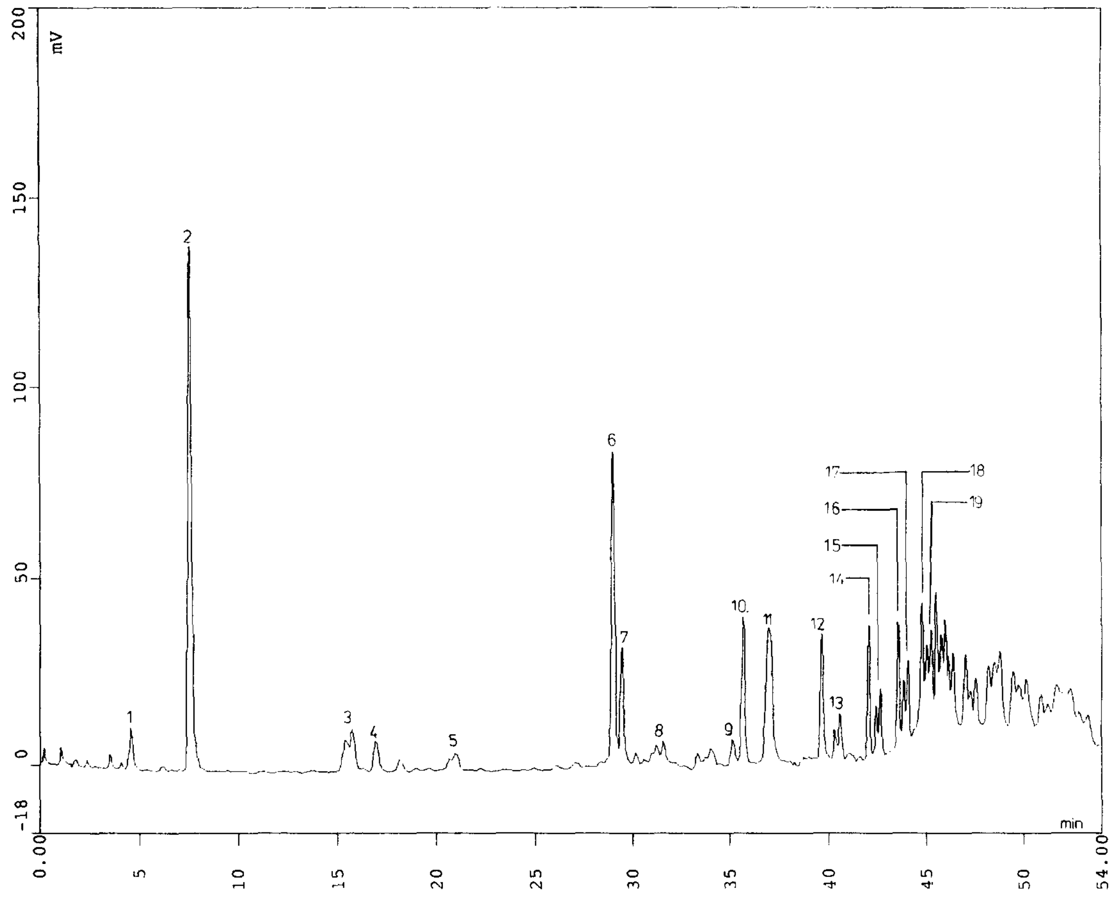
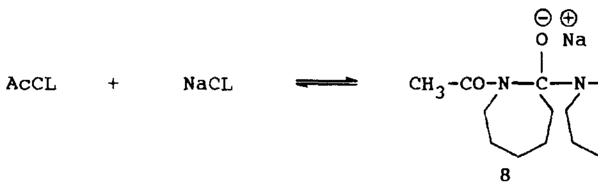
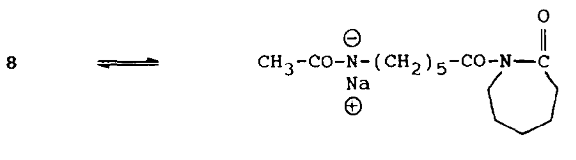


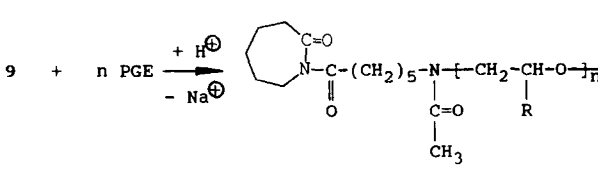
Figure 3 H.p.l.c. of products at 140°C according to *Figure 1*



(2)



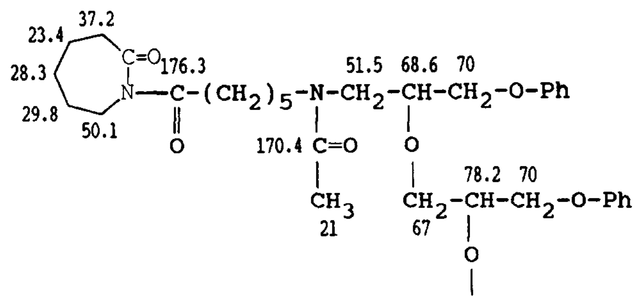
(3)



(4)

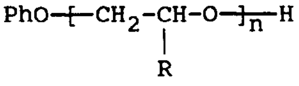
M.s. measurements of peak 4 (*Figure 2*) gave the following fragments: $m/z = 362, 245, 150, 133, 113, 94, 85, 57, 41$.

The main structure of peak 10 was established by ^{13}C n.m.r. spectroscopy:



11

At a temperature of 140°C, the chain length of oligomers $CL(PGE)_n$ (**7**) decreases to $n = 4$ and oligomers of the structures **1** and **12** were additionally found (*Figure 3*, *Table 1*). For structural identification see 'Experimental' section.



$$PhO\text{-}[\text{-}CH_2\text{-}\underset{R}{CH}\text{-}O\text{-}]_n\text{-}H$$

12

Owing to the mechanism of anionic polymerization the degree of polymerization can be increased by reducing the concentration of the initiator. In further experiments only 0.4 mol% of NaCL and AcCL were used. Consequently, the reaction rates decreased and the conversion of PGE reached 33% in 7 h at 100°C. The product distribution shifts to higher molar masses. At 100°C, the number of repeat units of the last separated peak for oligomers **7** was $n = 10$. The number of oligomeric by-products increased at 140°C and it can be concluded that the last unsolved peak group includes oligomers **7** with $n = 18$ (*Figure 4*). It can be assumed that further oligomeric by-products result from the 'anomalous' ring-opening reaction which is preferred at higher temperatures.

Table 1 Structure of products according to the chromatogram in *Figure 3*

Peak	Structure	Peak	Structure
1	**7** ($n = 1$)	11	**1** ($n = 3$)
2	PGE	12	**12** ($n = 4$)
3	**7** ($n = 2$)	13	**1** ($n = 4$)
4	**12** ($n = 1$)	14	**12** ($n = 6$)
5	**1** ($n = 1$)	15	**1** ($n = 5$)
6	**7** ($n = 3$)	16	**12** ($n = 6$)
7	**12** ($n = 2$)	17	**1** ($n = 6$)
8	**1** ($n = 2$)	18	**12** ($n = 7$)
9	**7** ($n = 4$)	19	**1** ($n = 7$)
10	**12** ($n = 3$)		

Table 2 Structure of products according to the chromatogram in *Figure 6*

Peak	Structure	Peak	Structure
1	PGE	6	**7** ($n = 9$)
2	**7** ($n = 3$)	7	**7** ($n = 10$)
3	**7** ($n = 6$)	8	**7** ($n = 11$)
4	**7** ($n = 7$)	9	**7** ($n = 12$)
5	**7** ($n = 8$)	10	**7** ($n = 13$)

Reaction of PGE with catalytic amounts of sodium caprolactam (NaCL)

Figure 5 shows the relation between the degree of conversion and the polymerization time for PGE at various temperatures and at a concentration of NaCL of 1 mol%. The initial reaction rates are lower than those in *Figure 1*. An induction period can be observed at lower temperatures (80 and 100°C). Consequently, there should be different reaction mechanisms if NaCL/AcCL or NaCL initiating agents are used.

Investigations by h.p.l.c. showed products **7** ($CL(PGE)_n$) only, regardless of the concentration of the initiator and the temperature (80 to 120°C). The number of repeat units reaches $n = 13$ at 80°C (*Figure 6*, *Table 2*) and $n = 9$ at 120°C. Oligomers of structures **1** and **12** were additionally found at 140°C.

Kinetic evaluations of the reactions performed showed no significant order at temperatures below 100°C. A kinetic order of unity for PGE was found for reactions at 120°C and 140°C. These results correspond to kinetic data published[41,42].

Reaction of PGE with catalytic amounts of sodium caprolactam (NaCL) and N*-acetyl imidazole (AcIMI)*

As mentioned above, the polymerization of PGE can also be initiated by tertiary amines. Thus, it was of interest to compare the initiation steps for the NaCL-initiated polymerization with the initiation step induced by a tertiary amine. For this purpose, NaCL and *N*-acetyl imidazole (AcIMI) were used in a molar ratio of 1 : 1.

At temperatures between 100 and 140°C only products of structure **12** were found. They indicated the preferred reaction mechanism of the reaction induced by the tertiary

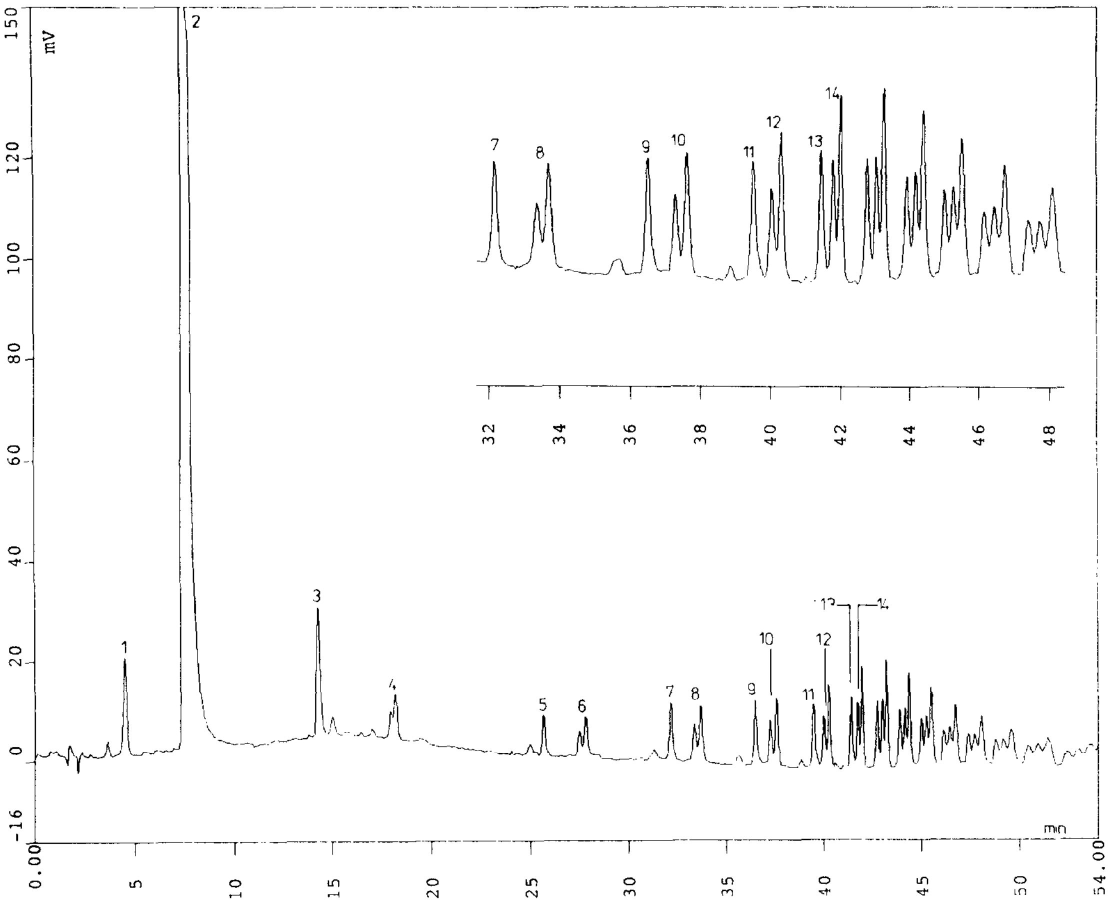


Figure 4 H.p.l.c. of products from PGE at 140°C, initiated with 0.4 mol% NaCl and 0.4 mol% AcCL

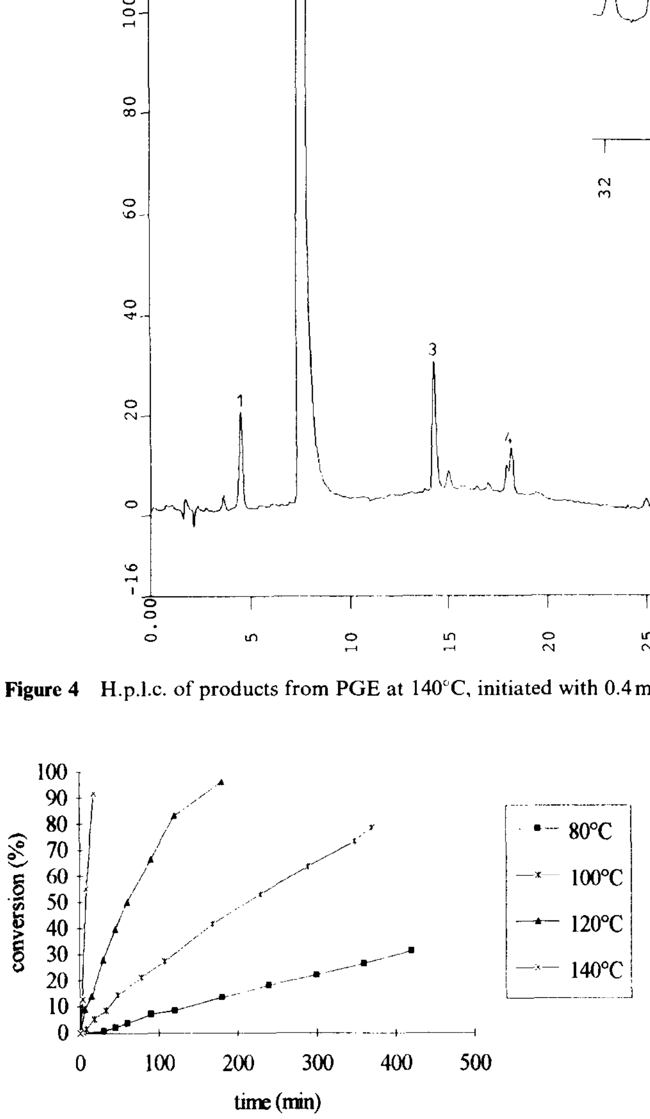
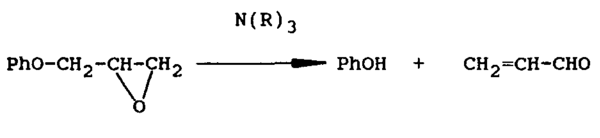
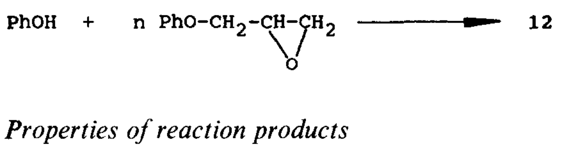


Figure 5 Conversion of PGE as a function of the reaction time at different reaction temperatures. Molar ratio of PGE : NaCL = 1 : 0.01

amine (equations (5) and (6)):



$$\mathrm{PhO{-}CH_2{-}CH{-}CH_2 \ (epoxide)} \xrightarrow{\mathrm{N(R)_3}} \mathrm{PhOH} + \mathrm{CH_2{=}CH{-}CHO} \quad (5)$$



$$\mathrm{PhOH} + n\,\mathrm{PhO{-}CH_2{-}CH{-}CH_2 \ (epoxide)} \longrightarrow \mathbf{12} \quad (6)$$

Properties of reaction products

The reaction products are partially soluble in cold acetone, acetic acid and acetonitrile. They are completely soluble in tetrahydrofuran (THF), chloroform and toluene.

Several products were dissolved in hot acetone and they precipitated by cooling. From these products melting ranges and molar masses were determined by v.p.o. (*Table 3*).

It is evident that the highest molar masses were obtained at 120°C. There is no significant difference in the molar masses of products from reactions with 0.4 mol% and 1 mol% concentrations of the initiator. The conversion of epoxide at 100°C is very low. This

Table 3 Melting ranges of reaction products depending on the type and concentration of the catalytic system and the reaction temperature

Initiating system	Reaction temp. (°C)	Melting range (°C)	Molar masses ($\mathrm{g\,mol^{-1}}$)
NaCL : AcCL = 1 : 1 (1 mol% each)	100	100–104	2717
	120	107–111	3996
	140	114–118	1510
NaCL : AcCL = 1 : 1 (0.4 mol% each)	100	85–87	341
	120	78–80	3722
	140	95–98	2363
NaCL (1 mol%)	100	74–78	2227
	120	78–83	2891
	140	72–76	2979
NaCL (0.4 mol%)	100	85–90	979
	120	92–95	1615
	140	84–88	1314
NaCL : AcIMI = 1 : 1 (1 mol% each)	100	107–112	–
	140	116–120	–
NaCL : AcIMI = 1 : 1 (0.4 mol% each)	140	96–100	–

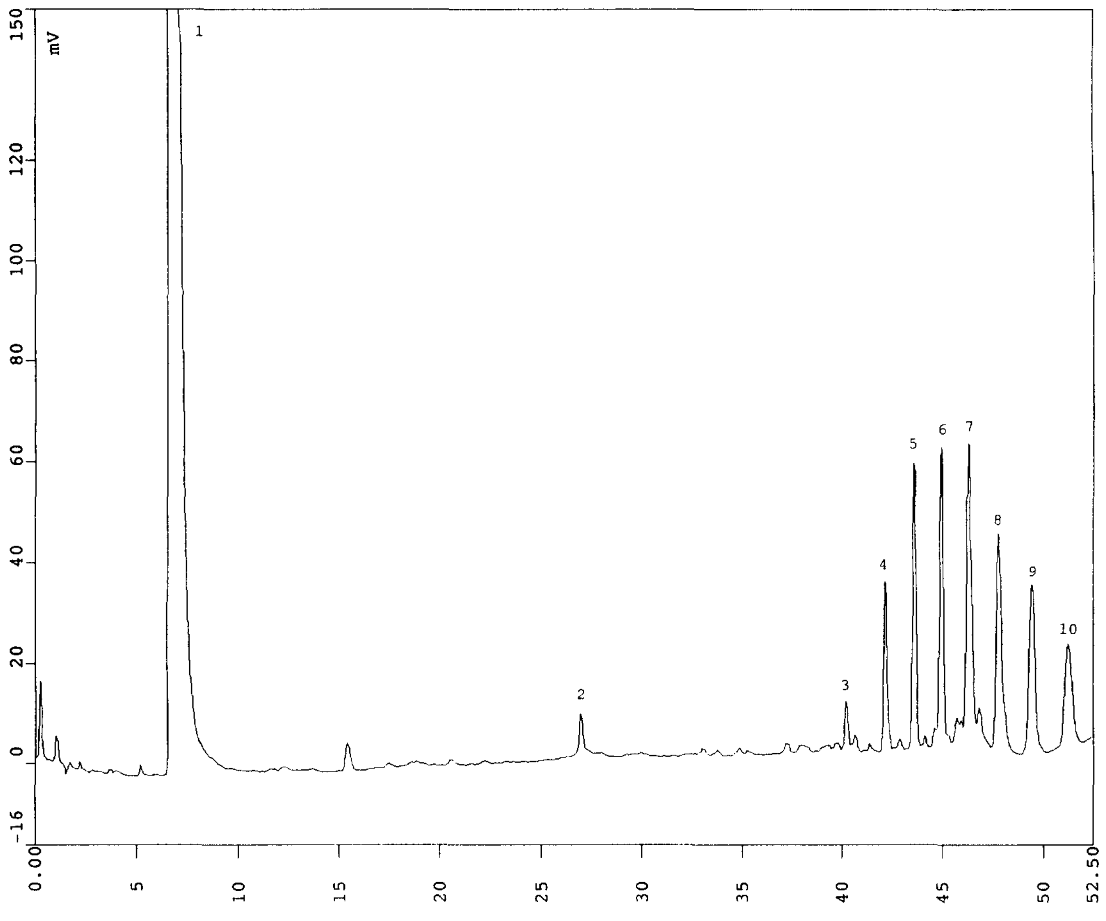


Figure 6 H.p.l.c. of products from PGE at 80°C, initiated with 1 mol% NaCL

results in a considerable deviation of the expected molar masses.

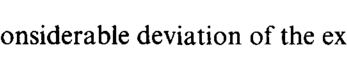
EXPERIMENTAL

Chemicals

2,3-Epoxypropyl phenyl ether (phenyl glycidyl ether, PGE) from Fluka was distilled before use (b.p. = 120°C at 1.974 kPa). Sodium caprolactam (NaCL) was synthesized as well as *N*-acetyl caprolactam (AcCL) according to the literature[43,44]. Oligomers of structures **1** and **12** were synthesized as described elsewhere[2,45]:

oligomers **1**	PGE : *N*, *N*-dimethylbenzylamine = 1 : 0.15 (moles); T = 70°C; t = 8 h
oligomers **12**	PGE : 1-methylimidazole = 1 : 0.25 (moles); T = 70°C; t = 4 h

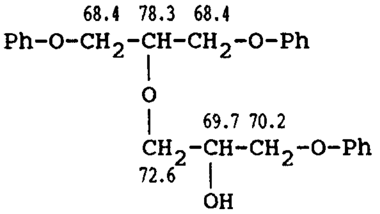
The oligomer mixtures were separated by means of preparative h.p.l.c. Isolated compounds were identified by using ^{13}C n.m.r. spectroscopy and mass spectrometry. By way of example, the following compounds were found from an oligomer distribution according to oligomers **12** (^{13}C n.m.r. signals in ppm[46]):



$$\overset{69.9}{\mathrm{Ph{-}O{-}CH_2}}{-}\underset{\mathrm{OH}}{\underset{|}{\overset{69.0}{\mathrm{CH}}}}{-}\overset{69.9}{\mathrm{CH_2{-}O{-}Ph}}$$

$$M_{calc} = 244 \text{ g mol}^{-1}$$

Mass spectrum: m/z = 244 (M^+), 150, 137, 133, 94.
Mass spectrum: m/z = 394 (M^+), 300, 244, 287.



$$\overset{68.4}{\mathrm{Ph{-}O{-}CH_2}}{-}\underset{\substack{|\\ \mathrm{O}\\ |\\ \underset{72.6}{\mathrm{CH_2}}{-}\underset{\substack{|\\ \mathrm{OH}}}{\overset{69.7}{\mathrm{CH}}}{-}\overset{70.2}{\mathrm{CH_2}}{-}\mathrm{O{-}Ph}}}{\overset{78.3}{\mathrm{CH}}}{-}\overset{68.4}{\mathrm{CH_2{-}O{-}Ph}}$$

$$M_{calc} = 394 \text{ g mol}^{-1}$$

The same measurements were performed for compounds that were obtained from the oligomer **1** distribution.

Reactions

PGE was kept under dry argon and then poured into a thermoregulated glass reactor (100 ml) equipped with magnetic stirrer and thermometer. PGE was preheated up to the desired temperature and the initiator was then introduced from a separate flask. During the reaction, a continuous flow of dry argon was allowed to pass through the reactor. At various time intervals aliquots were removed for analytical procedures. The composition of the reaction mixtures (moles) and the temperatures are reported in the text. No solvent was used.

Measurements

The epoxy content was determined by titration with perchloric acid in acetic acid/tetraethylammonium bromide (TEAB); the indicator was crystal violet[47]:

150–200 mg of the given sample was dissolved in 10 ml acetone. After adding 10 ml of a solution of TEAB in acetic acid (20 g TEAB in 100 ml acetic acid) and 2 or 3 drops of a solution of crystal violet in acetic acid (1%), the sample was titrated with 0.1 N perchloric acid in acetic acid (violet → green). Then

$$\text{epoxy content (mmol g}^{-1}) = \frac{(V - V_0) \times c(\mathrm{HClO_4}) \times f(\mathrm{HClO_4})}{E}$$

where E (g) = sample weight; $c(\mathrm{HClO_4})$ (mmol ml^{-1}) = concentration of perchloric acid; $f(\mathrm{HClO_4})$ = factor of perchloric acid; V (ml) = consumption of perchloric acid; and V_0 (ml) = blank value.

H.p.l.c. was carried out with an apparatus from Knauer Wissenschaftliche Geräte KG (Germany): column, 250 × 3 mm, Ultrasep ES 100 RP18 (6 μm); solvent gradient from 40 to 99% CH_3CN in water in 40 min; flow = 0.7 ml min^{-1}; u.v. detection, λ = 254 nm. Identification of oligomeric products—separation by means of preparative h.p.l.c.: column, 250 × 32 mm, Nucleosil C 18 (7 μm); solvent gradient from 40 to 99% CH_3CN in water in 40 min; flow = 20 ml min^{-1}; u.v. detection, λ = 254 nm. N.m.r. spectra were measured using a Gemini 300 n.m.r. spectrometer (Varian): solvent, deuterated chloroform; standard, hexamethylene disiloxane; resonance frequency, 75.423 MHz. Mass spectra were measured by using an AMD 402 mass spectrometer (AMD Intectra GmbH): electron excitation at 70 eV. Molar masses were determined by means of a v.p.o. apparatus from Knauer Wissenschaftliche Geräte KG (Germany): calibration substance, benzil (10 to 40 g kg^{-1} in toluene); solvent, toluene; temperature, 50°C.

CONCLUSIONS

Phenyl glycidyl ether (PGE) reacts with a catalytic system of sodium caprolactam (NaCL) and sodium caprolactam/*N*-acetyl caprolactam (NaCL/AcCL) to form oligomeric products that depend on the reaction temperature. At 80°C, the main products result from the initiation of the ϵ-caprolactam anion. At increased temperatures (140°C) further initiation steps predominate. This results in the formation of products without CL units but with aliphatic double bonds (**1**) and phenoxy terminal groups (**12**). The highest molar masses are obtained at 120°C and they decrease at elevated temperatures.

ACKNOWLEDGEMENT

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