Direct Synthesis of (Meth-)acrylate Poly(ε-caprolactone) Macromonomers

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The microwave assisted ring-opening polymerization of ε-caprolactone (ε-CL) in the presence of methacrylic acid (MA) or acrylic acid (A) yields radical polymerizable polyester macromonomers. In this paper we show a fast access to defined unsaturated macromonomers from unpurified educts. The process has the advantage of requiring only one step and provides high functionality. The investigation of the thermal properties shows that the melting point of the macromonomers is adjustable in a range between 46 and 51°C.

Introduction

Interest in Microwave accelerated organic synthesis is rapidly increasing in this decade. The advantage of microwave assisted reaction processes in polymer chemistry has also become a versatile field of investigation (1a–e). The benefit of microwave assisted ring-opening polymerization of ε-caprolactone, consisting of a significant increase in reaction rate under microwave conditions, is well known in the literature (2a–e).

Polyester macromonomers are required to prepare polyester brushes by the "grafting through" approach (3). They can principally be prepared by two procedures: End-capping of polylactones with vinylic derivatives (4a, b) or by initiation of the lactone polymerization by a vinylic derivative with a suitable initiation group (5). Both methods require mostly two steps and often the addition of activation reagents. In contrast to the common syntheses, this work describes a fast access (one step with a reaction time of 90 min) to polyester macromonomers with a high degree of functionalization and defined chain length. We used microwave irradiation as a powerful energy source for the ring-opening polymerization and functionalization with (meth-)acrylic end groups of the obtained polyester in a single step (Scheme 1). Due to the rapid noncontact heating under microwave conditions, a fast optimization of the synthesis applying a
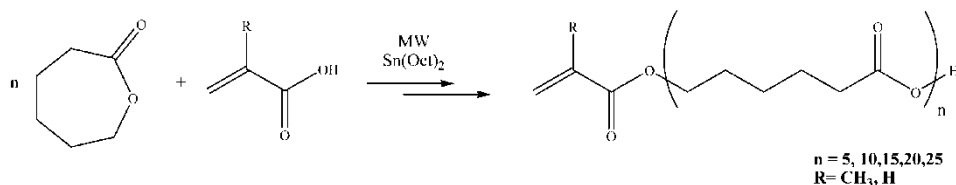
Scheme 1. Preparation of macromonomers.

short reaction sequences was possible. However, a comparison with classical thermal activation showed no significant acceleration effect under microwave conditions.

Among common biodegradable synthetic polymers, poly(ε-caprolactone) attracts much interest because of its thermal properties. In fact, the high decomposition temperature of about 350°C and low melting point of about 55°C provide a wide range of applications (6a, b). By investigating the melting points of the obtained macromonomers, we show that a range of different melting points is accessible by adjusting the molar ratio between ε-caprolactone and (meth-)acrylic acid.

Experimental

Materials

ε-Caprolactone (Fluka), acrylic acid (Merck), methacrylic acid (Aldrich) and tin(II) 2-ethylhexanoate (Aldrich) were used without purification. All experiments were carried out in sealed vessels under air.

Measurements

The structures of the synthesized polymers were proven by ^{1}H-NMR spectroscopy using a Bruker Avance DRX 500 spectrometer at 500.13 MHz, using CDCl3 as solvent. The δ-scale was calibrated to TMS. Thermal properties were determined using a Mettler Toledo DSC822e Controller apparatus in a temperature range between -10 and 100°C at a heating rate of 10°C per minute. The melting point values are reported as the average of the peak maxima of the second and the third measurements. Gel permeation chromatography (GPC) was performed on a Waters system equipped with a set of three 300×8 mm 2 MZ Gel SD plus columns (with 10^4, 10^3 and 10^2 Å porosity) in THF relative to poly(styrene) standards. The results were corrected by applying the Mark-Houwink relationship (7). Matrix-assisted laser desorption-ionization time of flight spectrometry (MALDI-TOF) was performed on a Bruker Ultraflex TOF mass spectrometer using the reflector mode and a 337 nm nitrogen laser. The samples were dissolved in chloroform and mixed with a dithranol solution. Microwave assisted experiments were carried out in a mono-mode microwave (CEM-Discover) equipped with a fiber-optic temperature device operating at a maximum power of 300 W.

Synthesis of the Macromonomer

1.86 ml (2.00 g, 17.5 mmol) of ε-caprolactone were mixed with 4 mol% of tin 2-ethylhexanoate and different molar ratios of methacrylic or acrylic acid (Table 1) in a 10 ml vial sealed with a septum. The mixture was irradiated to a constant temperature of 180°C, resulting from a regulated power of maximum 50 W. Cooled down to room

Table 1
Characterization of (meth-)acrylate macromonomers

Entry	Ratio of [acid]^a to [ε-CL]	M_n^b/g·mol^{-1}	PD^b	DPn^b	Conversion^c of acid^a/%	T_m^d/°C
PCLMA 5	1:5	1392	1.9	12	39	49.0
PCLMA 10	1:10	1664	2.1	15	53	49.4
PCLMA 15	1:15	1784	2.1	16	61	49.7
PCLMA 20	1:20	2248	2.1	20	64	51.0
PCLMA 25	1:25	2907	1.8	26	71	51.0
PCLA 5	1:5	1277	1.7	11	61	45.8
PCLA 10	1:10	1281	1.9	11	72	47.7
PCLA 15	1:15	1749	2.0	15	e	49.9
PCLA 20	1:20	2015	2.0	18	e	50.0
PCLA 25	1:25	2291	2.1	20	e	50.6

^{a}Methacrylic acid and acrylic, respectively.
^{b}GPC with polystyrene calibration and corrected by applying the Mark-Houwink relationship (7).
^{c}^{1}H-NMR.
^{d}DSC.
^{e}Not detectable.

temperature, the reaction mixture was diluted with 5 ml of chloroform and poured into 250 ml of a mixture of cold hexane/diethylether (1/1). The precipitated macromonomer was isolated by filtration and dried under vacuum.

^{1}H-NMR (CDCl$_3$): For sample PCLMA5 $\delta = 6.09$ (s, 1H, **H**H′C=C), 5.55 (s, 1H, H**H**′C=C), 4.06 (t, $^3J_{HH} = 6.8$ Hz, 2H, OC**H**$_2$), 2.30 (t, $^3J_{HH} = 7.4$ Hz, 2H, C**H**$_2$COO), 1.94 (s, 3H, C=CC**H**$_3$), 1.3–1.8 (m, 6H, C**H**$_2$(C**H**$_2$)$_3$C**H**$_2$) ppm. For sample PCLA5 $\delta = 6.40$ (d, $^3J_{HH} = 17.3$ Hz, 1H, **H**H'C=), 6.12 (dd, $^3J_{HH} = 17.2$ Hz, $^3J_{HH} = 10.3$ Hz, 1H, C=C**H**COO), 5.82 (d, $^3J_{HH} = 17.3$ Hz, 1H, H**H**′C=) 4.06 (t, $^3J_{HH} = 6.8$ Hz, 2H, OC**H**$_2$), 2.31 (t, $^3J_{HH} = 7.5$ Hz, 2H, C**H**$_2$COO), 1.3–1.8 (m, 6H, C**H**$_2$(C**H**$_2$)$_3$C**H**$_2$) ppm.

Results and Discussion

The synthesis of the polyester macromonomers was performed by ring opening polymerization as shown in Scheme 1. Tin octoate is known as a suitable transesterification catalyst for the ring-opening polymerization of ε-CL and was therefore used for acceleration of this reaction (8). All reactions were carried out in a mono-mode microwave at constant temperature of 180°C with a reaction time of 90 min from unpurified educts in bulk under air. It is interesting to note that even at such high temperatures the spontaneous free radical polymerization of the (meth-)acrylic derivates can be prevented. We polymerized different molar ratios of ε-caprolactone and (meth-)acrylic acid to yield macromonomers with accordant chain length. The conversion of (meth-)acrylic acid was estimated from the relative ratio between the intensity of the hydrogen atoms of the double bond in the free (meth-)acrylic acid (for MA: singlet at 6.22 and 5.66 ppm; A: doublet at 6.53 and 5.97 ppm) and the hydrogen atoms of the esterified (meth-)acrylic acid (for MA: singlet at 6.09 and 5.55 ppm; A: doublet at 6.40 and 5.82) ppm and is presented in Table 1. In the case of lower acrylic acid concentrations (entry PCLA 15, 20 and 25),
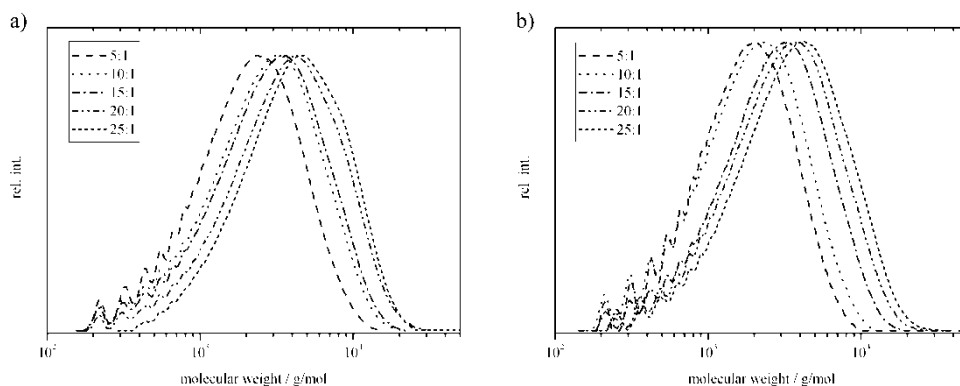
a)

b)

Figure 1. Molecular weight distribution (GPC with polystyrene calibration and corrected by applying the Mark-Houwink relationship (7)) of a) polyester methacrylates polymerized with different ratios of [MA]:[ε-CL], reaction time 90 min at 180°C and b) polyester acrylates polymerized with different ratios of [A]:[ε-CL], reaction time 90 min at 180°C.

it was not possible to separate the signals. Moreover, the GPC results of the different macromonomers are shown in Table 1 respectively.

It is clearly possible to conclude that the molecular weight of the macromonomers can be controlled by the ratio of (meth-)acrylic acid to ε-caprolactone (Figure 1 and 2). At the lower ratios the detected molecular weights are higher than the calculated values, which is attributable to the lower conversions of the (meth-)acrylic acid in this experiment.
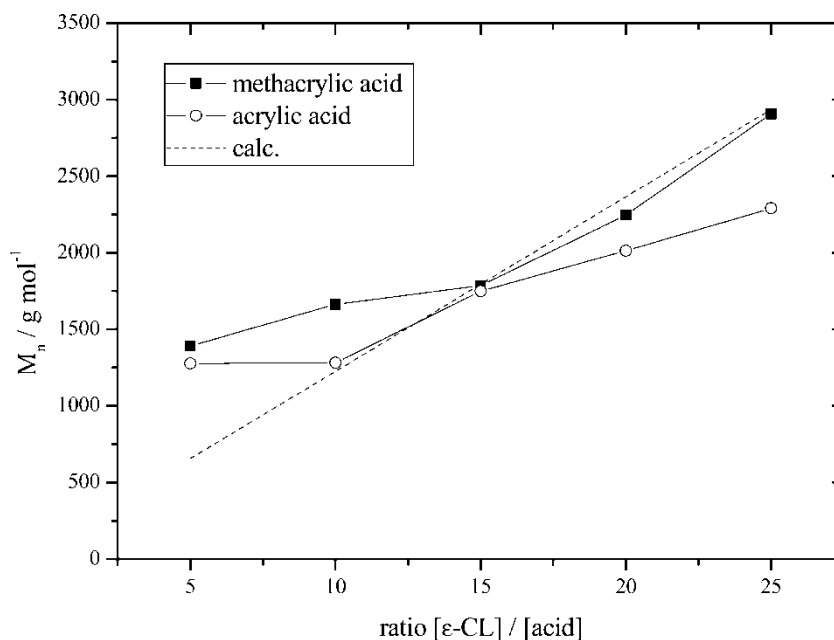

Figure 2. Number-average of the molecular weights (GPC with polystyrene calibration and corrected by applying the Mark-Houwink relationship (7)) of (meth-)acrylate macromonomers vs. molar ratio of [ε-CL]/[MA] (■) and [ε-CL]/[A] (○) respectively.
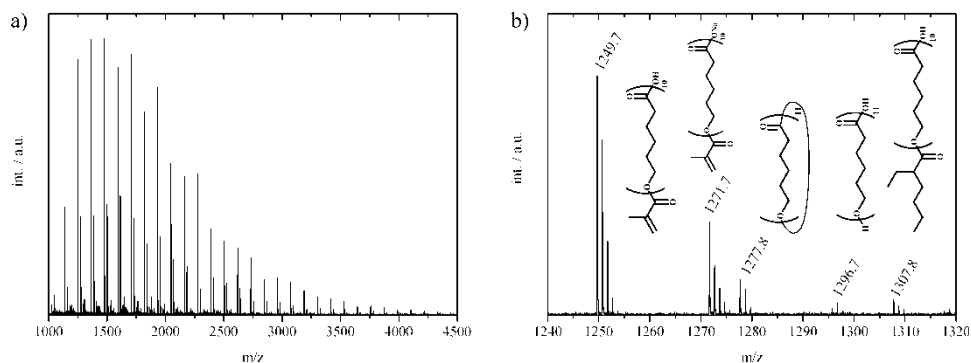
Figure 3. MALDI-TOF mass spectrum (reflector mode) of the reprecipitated poly(ε-caprolactone) methacrylate polymerized with a molar ratio of [ε-CL]/[MA] = 5/1, reaction time 90 min at 180°C; a) full spectrum, b) 1240-1320 m/z fragment (corresponding macromolecules cationized with Na⁺).

Figure 3 shows a fragment of a MALDI-TOF mass spectrum of a poly(ε-caprolactone) methacrylate macromonomer prepared by a molar ratio of ε-CL/ MA = 5/1 as a typical example. The signals correspond to macromolecules cationized with Na⁺. It is possible to assign all signals (Table 2). The proportion of the polyester with a methacrylate end group move approaches 8% measured on the relative intensities. Side products are cyclic polyester (8%), unfunctionalized polyester (2%) and polyester with octylate end group (4%). This distribution of the products is nearly constant over the entire range of molecular weights.

Many publications deal with the mechanism of the ring-opening polymerization of ε-caprolactone. For example, L. J. Liu et al. allege a kind of microwave assisted acid-initiated ring-opening polymerization of ε-caprolactone (9a−e). In this publication, the incorporation of various carboxylic acids is explained by an initiation mechanism. We somewhat hypothesize a two step mechanism. In the first step, the polymerization is initiated by traces of water. The incorporation of the (meth-)acrylic acid proceeds slower through an esterification mechanism (Scheme 2). If the carboxylic acid acted as an initiator, it should have been incorporated as an end group quantitative. This is in contrast to our results, showing clearly that (meth-)acrylic acid is incorporated only in a range between 39 and 72%. This is definitely not in accordance with the above mentioned initiation mechanism. GPC and ¹H-NMR analyses allowed us to plot the dependence of conversion of methacrylic acid and ε-caprolactone and number-average of the molecular weights against reaction time (Figure 4). The conversion of ε-caprolactone is quantitative after

Table 2
Identified PCL macromolecules

m/z	Corresponding molecule + Na⁺	Calc. mass	Rel. int./a.u.
1249.7	MA[O(CH$_2$)$_5$CO]$_{10}$OH	1249.7	60
1271.7	MA[O(CH$_2$)$_5$CO]$_{10}$ONa	1271.7	26
1277.8	−[O(CH2)$_5$CO]$_{11}$−(cyclic)	1277.8	8
1296.7	H[O(CH$_2$)$_5$CO]$_{11}$OH	1295.8	2
1307.8	Oct[O(CH2)5CO]$_{10}$OH	1307.8	4
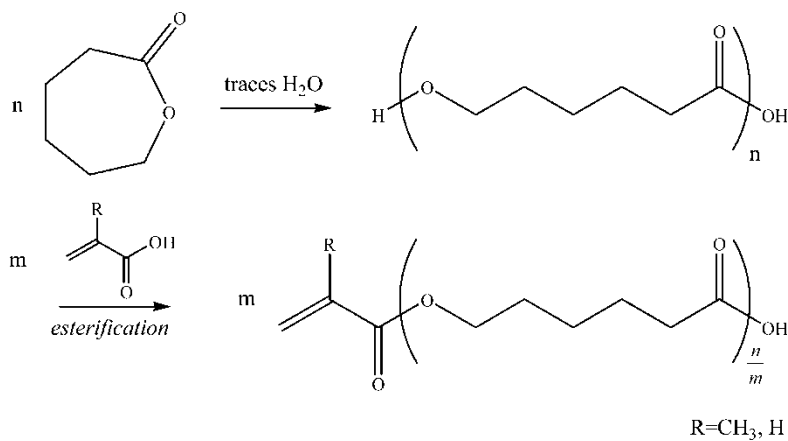
Scheme 2. Hypothetical mechanism of one-pot synthesis of poly(ε-caprolactone) (meth-)acrylates.

about 15 min, whereas the esterification with methacrylic acid is only 63% after 90 min. The number-average of the molecular weights strongly increases at the beginning of the reaction. It reaches a maximum after approximately 5 min at 3900 g/mol, and then decreases to be nearly constant at 1700 g/mol. An ongoing conversion of methacrylic acid in the absence of free ε-caprolactone and a decreasing number-average of the molecular weights correspond further to the postulated two-step mechanism.

It was expected that the incorporation of (meth-)acryl esters as end groups at a crystal-lizable polyester chain has a influence on the melting point of the material. Sanchez and Eby described the thermal behavior for copolymers with Equation 1 (10). For low fractions
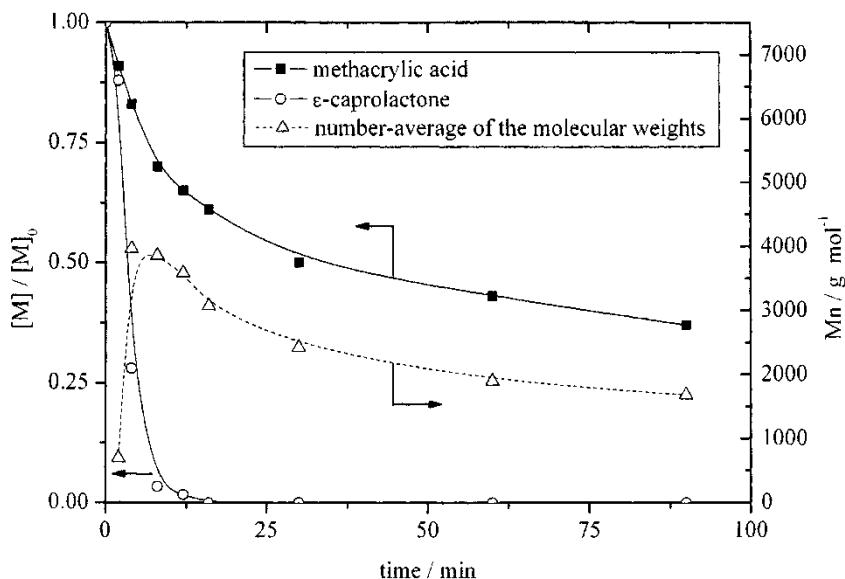

Figure 4. Dependence of the conversion of methacrylic acid (■) and ε-caprolactone (○) and number-average of the molecular weights (△) on reaction time. Samples from a microwave assisted polymerization of ε-caprolactone in presence of methacrylic acid (15 : 1) at 180°C.
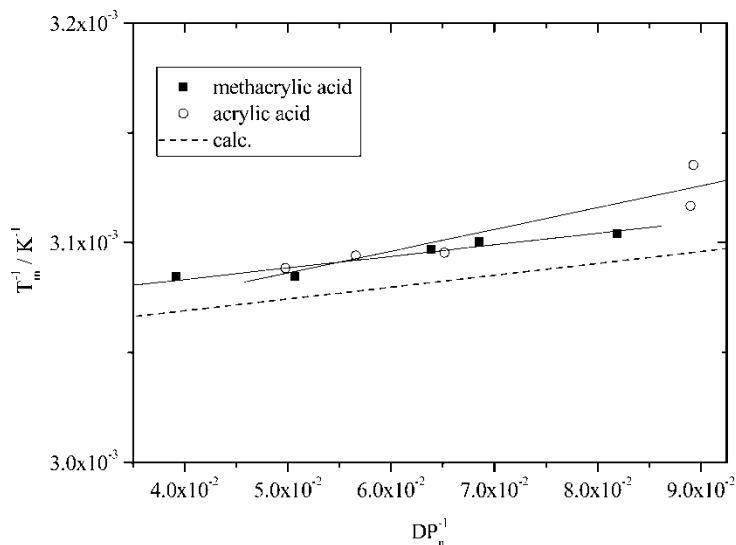
Figure 5. Dependence of the reciprocal melting points on the reciprocal degree of polymerization of the methacrylate (■) and acrylate (○) polyester.

of a non-crystallizable component, e.g. end group effects, the logarithmic term can be approximated using, $\ln(a) = \ln(X_{cry}) = \ln(1 - X_{noncry}) = -X_{noncry} = -\overline{DP}_n^{-1}$, where $\overline{DP}_n$ is the degree of polymerization.

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_m} \ln(a) \qquad (1)$$

In Figure 5, the dependence of the reciprocal melting point on the reciprocal degree of polymerization of the methacrylate and acrylate polyester is presented. Additionally, we show a straight line calculated from $\Delta H_m = 15.4\,kJ/mol$ and $T_m^0 = 55°C$ (11). The observed melting points are in good correlation to the theory (Equation 1). However, the influences of the side products such as unfunctionalized polyester and cyclic polyester to the melting points are not considered.

Conclusions

It can be confirmed from the above described results that the microwave assisted direct conversion of ε-caprolactone with (meth-)acrylic acid shows fast access to polyester macromonomers. The melting points of the macromonomers show the expected dependence on the molecular weight, which is easily adjustable by the ratio between (meth-)acrylic acid and ε-caprolactone.

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