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Extruder synthesis of a new class of polyurethanes: Polyacylurethanes based on poly(ε-caprolactone) oligomers

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Abstract

Using a micro-extruder a new class of polyurethanes, polyacylurethanes (PAUs), based on poly(ε-caprolactone) (PCL) oligomers and terephthaloyl diisocyanate was synthesized. These polymers are anticipated to have potential for biodegradable and/or biomedical applications. Therefore, PAUs were synthesized without the use of any, possibly toxic, catalysts.

PCL diols of different molecular mass were used, namely 750, 1000, 1250, 1500, 2000, 3000 and 4000 g/mol. These diols were synthesized by thermal polymerization at 150 °C without the use of any catalyst. The PAUs of terephthaloyl diisocyanate were synthesized by reactive extrusion using a micro-extruder of 5 cm^3 at 130 °C.

The PAUs obtained were characterized using DSC, GPC, DMTA, SAXS and tensile testing.

Surprisingly, PAUs based on PCL chains of 750, 1000, 1250 and 1500 g/mol were found to show microphase separation/micro crystallization as proven by SAXS data combined with DSC. This microphase separation creates elastomeric properties as is known from polyurethanes.

In the PAUs based on PCL chains of 2000, 3000 and 4000 g/mol part of the PCL was found to crystallize and no evidence of any phase separation of the acylurethane block was found.

Keywords: Polyurethane; Polyacylurethane; Acylisocyanate

1. Introduction

Segmented polyurethanes are widely used in medical, automotive and industrial applications [1–3]. This type of polymers usually consists of ‘soft’ and ‘hard’ segments in the polymer chain giving rise to a microphase-separated morphology, lending this type of polymer its specific properties. Microphase separation is caused by the physical incompatibility of both segments [4,5] and is thus a factor that influences the thermal and mechanical properties of the final polymer.

The combination of a relatively high biocompatibility and the wide variety of physical and chemical properties that can be achieved makes this class of polymers very interesting for the (bio)medical field.

Although these polymers are generally accepted to be biocompatible the use of potentially toxic catalysts during their synthesis leaves the majority of these materials not to be fully biocompatible [6]. As shown previously it is possible to synthesize polyurethanes without the use of any catalyst, but only with low reaction rates [7]. An additional disadvantage of polyurethanes applied as degradable material in the biomedical field is the slow degradation and resorption of the urethane groups in combination sometimes with the release of toxic aromatic diamines [8–10].

Diacylisocyanates might be a good substitute for regularly used diisocyanates. These kinds of compounds have activated isocyanate groups due to the neighboring carbonyl group, which makes these compounds much more reactive towards hydroxyl groups and thus very suitable for chain extension without catalyst [11]. Concerning the resulting polymers it is known that the acylurethane groups hydrolyze relatively fast [12] and are expected to release terephthalamide and/or terephthalic acid upon degradation, which are considered to be non-toxic [13]. Moreover, for the

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synthesis of acylisocyanates no phosgene is needed making the method less dangerous than regular isocyanate synthesis.

Several methods to synthesize mono acylisocyanates have been published [14–19]. The most straight forward method is based on the reaction of oxalyl chloride with primary amides [20,21]. Diacylisocyanates can be prepared in a similar way as shown by Tsuge [22] and Urano [23]. Polycondensations with these diacylisocyanates have been described in literature: poly(*N*-acylurethane)s [24], poly (*N*,*N*′-diacylurea)s [25] and poly(*N*-acylamide)s [26] have been prepared using diacylisocyanates in combination with diols, diamides and dicarboxylic acids, respectively. Polyacylurethanes have been prepared using propane diols and aroyl diisocyanates. Endo et al. mentioned the polycondensation of poly(tetramethylene oxide) with isophthaloyl diisocyanate forming the corresponding polyacylurethane [24].

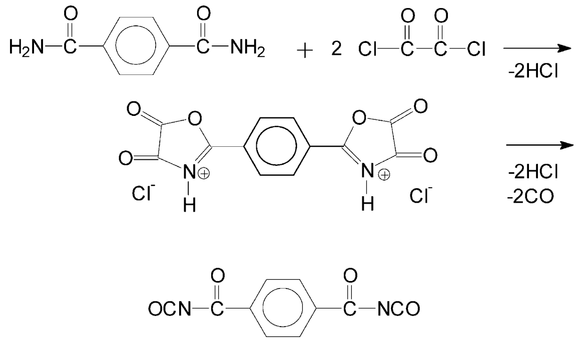
Despite the wide spectrum of experimental work that has been carried out with acylisocyanates, to the best of our knowledge polyesteracylurethanes have not been reported yet.

In this work the preparation of polyesteracylurethanes by chain extension of preformed poly(ε-caprolactone) diols in a micro-extruder is described. The thermal and mechanical properties of these polymers were evaluated using DSC, GPC, DMTA, SAXS and tensile testing.

2. Experimental

2.1. Materials and methods

Terephthalamide (TCI), oxalyl chloride (99%, Acros), acetone (PA, Merck), hexane (PA, Merck) and chloroform (HPLC, Merck) were used as received. 1,2-Dichloroethane (PA, Merck) was dried over 3 Å mol sieves. 1,4-Butanediol (Aldrich) and 1-butanol (Aldrich) were distilled from 3 Å mol sieves. 1-Butanol (Janssen Chimica) was dried with K_2CO_3 and subsequently distilled from sodium. ε-Caprolactone (Union Carbide) was distilled from CaH_2 under reduced pressure. 1,4-Dioxane (Merck) was distilled from sodium. Dimethylacetamide (DMAc, Acros), dimethylsulfoxide (DMSO, Acros) and *N*-methylpyrrolidone (NMP, Acros) were distilled from CaH_2 and subsequently distilled from methylene diphenyl diisocyanate (MDI). Before use the glassware was siliconized with a silicone solution from SERVA (Heidelberg, Germany) followed by drying at 130 °C. Poly(ε-caprolactone) with a molecular mass of 42.5×10^3 g/mol (Aldrich) was used as received.



Scheme 1. Reaction scheme for the synthesis of terephthaloyl diisocyanate with intermediate as proposed by Urano and Speziale [21,23].

^{1}NMR and ^{13}C NMR spectra were recorded using a 200 MHz Varian NMR apparatus. A Perkin–Elmer DSC-7 operating under nitrogen atmosphere at a scan speed of 10 °C/min was used for thermal analysis. For the quenching experiment the samples were kept for 5 min at 100 °C in a home built hot stage, whereupon the samples were cooled rapidly by immersion in liquid N_2. Infrared Spectroscopy (FTIR) was performed on a Mattson instruments 'Galaxy' 2001 equipped with a Golden Gate (Graseby Specac) ATR accessory. DMTA measurements were carried out with a Rheometrics RSA II at a frequency of 1 Hz. The films were cooled to −120 °C and subsequently heated at a rate of 2 °C/min. Small-angle X-ray scattering (SAXS) measurements were performed on an Bruker NanoSTAR, equipped with a Kristalloflex K760-8 3.0 kW X-ray generator with cross-coupled Göbel mirrors and Cu K_α-radiation ($\lambda=0.154$ nm) resulting in a parallel beam of about 0.05 mm^2 at the sample position (a Siemens multiwire type area detector was used). The sample-detector distance was 0.65 m. Measurement time was 1 h. GPC measurements were performed in THF on a Spectra Physics AS 1000 system using universal calibration with a Viscotek H-502 viscometer and a Shodex RI-71 refractive index detector. The columns were calibrated with polystyrene standards. Tensile tests were performed at 21 °C with a 100 N load cell at an extension rate of 10 mm/min with an Instron (4301) tensile tester using rectangularly ($40\times2.2\times0.1$ mm^3) shaped specimens cut from a solvent-cast film. The values obtained are averages of at least three samples.

The chain extensions were carried out using a 5 cm^3 micro-extruder (DSM research products B.V. serial nr. 96053, The Netherlands). The extruder operated with two co-rotating conical screws and was of the self-wiping type. The extruder was equipped with a loop extending the screw length and with a switch providing a choice between output of material and further extrusion. The revolutions of the screws were set at 92 rpm, the temperature at 130 °C. During operation, the pressure change caused by the increase of viscosity of the material was monitored by the force needed to turn the screws. Reactions were carried out in the extruder under a nitrogen blanket.

PAU films were cast at room temperature from chloroform. The films were allowed to dry overnight and dried further in a vacuum oven at 37 °C for 24 h.

2.2. Terephthaloyl diisocyanate (TPHDI)

Terephthaloyl diisocyanate was synthesized using a modified version of the method of Tsuge et al. [22] (Scheme 1). Oxalyl chloride (5.15 ml; 0.06 mol) was added to a suspension of terephthalamide (3.28 g; 0.02 mol) in dichloroethane (30 ml). The HCl produced was trapped with a gas trap. After refluxing the mixture for 3 h a clear, slightly yellow, solution was obtained. The remaining oxalyl chloride and solvent were removed using a Rotavap apparatus at 40 °C and 10 mbar. The acylisocyanate was collected using a short path distillation apparatus (Büchi GKR-50) ($T = 110–120$ °C; $p = 6 \times 10^{-2}$ mbar). The terephthaloyl diisocyanate formed transparent crystals with yields exceeding 98%. The acylisocyanate was stored under argon as it readily reacts with moisture from the air. Melting point: 117 °C.

^{1}NMR ($CDCl_3$ δ 7.26): δ 8.15 (s, 2H; ArH). ^{13}C NMR ($CDCl_3$ δ 77): δ 166 (CO), 135(*Ar*CO), 129 (NCO), 126 (Ar), FTIR (Golden Gate): 2240, 1779, 1704 cm^{-1}. Anal. Calcd for ($C_{10}H_4N_2O_4$): C 55.59, H 1.85, N 12.95. Found: C 55.56, H 1.83, N 12.83

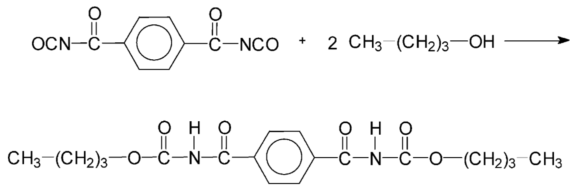
2.3. 1-Butanol adduct of TPHDI

A mixture of terephthaloyl diisocyanate (0.5 g; 2.31 mmol) and a large excess of butanol (5 ml; 0.06 mol) in 1,4-dioxane (10 ml; 0.11 mol) was reacted for 8 h at room temperature. During reaction a white solid, the product, precipitated and was collected by filtration. The product was washed with acetone and hexane and dried under reduced pressure at 40 °C. The reaction scheme is depicted in Scheme 2. Yield 100%

^{1}NMR (DMSO-d6 δ 2.5, 3.1): δ 11.1 (s, 1H; NH), 7.9 (s, 2H; ArH), 4.1 (t, 2H; $J = 7.2$ Hz, CH_2O), 1.6 (q, 2H; $J = 8.7$ Hz, $CH_2CH_2CH_2$), 1.4 (m, 2H; $J = 7.4$ Hz, $CH_3CH_2CH_2$), 0.9 (t, 3H; $J = 7.2$ Hz, CH_3), FTIR (Golden Gate): 3243, 2965, 1763, 1681 cm^{-1}.

2.4. Synthesis of poly(ε-caprolactone), a typical procedure

A mixture of ε-caprolactone (100.28 g; 0.88 mol) and the initiator 1,4-butanediol (4.73 g; 0.052 mol) were reacted at 150 °C for 7 days to yield a polyester with a molecular mass of 2000 g/mol. ^{1}H NMR spectroscopy was used to verify full conversion. Six different poly(ε-caprolactone) diols were synthesized: 750, 1000, 1500, 2000, 3000 and 4000 g/mol. The reaction scheme is depicted in Scheme 3.



Scheme 2. Reaction scheme for the synthesis of the 1-butanol/terephthaloyl diisocyanate adduct.

^{1}NMR ($CDCl_3$ δ 7.26): δ 4.10 (t; 2H; OCH_2), 3.65 (t; $HOCH_2$), 2.25 (t, 2H; CH_2CO), 1.6 (m, 2H; $OCH_2CH_2CH_2$, +2H; CH_2CH_2CO and some contribution of BDO), 1.40 (q, 2H; $OCH_2CH_2CH_2$), FTIR (Golden Gate): 2941, 1720, 1471 cm^{-1}.

2.5. Synthesis of the polyacylurethane, a typical procedure

The micro-extruder ($T = 130$ °C) was fed with a mixture of (5.13 g; 2.57 mmol) poly(ε-caprolactone) (2000 g/mol) and a slight excess of (0.5649 g; 2.61 mmol) terephthaloyl diisocyanate. The retention time until the pressure remained constant in the extruder was 4 min. The other polyacylurethanes containing poly(ε-caprolactones) of the above mentioned molecular masses were prepared with the same stoichiometric amounts. The reaction is depicted in Scheme 4. Prior to further use, the products were stored at −18 °C under a nitrogen atmosphere.

The polymers obtained were dissolved in chloroform (0.02 g/ml of chloroform) and cast at room temperature in a silanized petri dish. From here on the polymers will be abbreviated as PAU*x* with *x* as the molecular mass of the corresponding PCL.

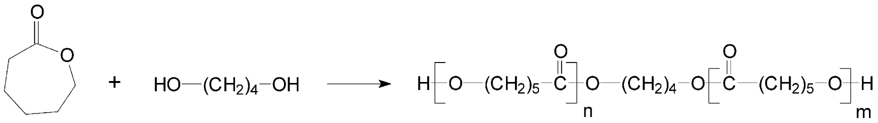
^{1}NMR (DMSO-d6 δ 2.5, 3.1): δ 11.5 (s, 1H; CONHCO), 7.9 (m, 2H; ArH), 4.10 (t, 2H; OCH_2), 2.25 (t, 2H; CH_2CO), 1.6 (m, 2H; $OCH_2CH_2CH_2$, +2H; CH_2CH_2CO with some contribution of BDO), 1.40 (m, 2H; $OCH_2CH_2CH_2$), FTIR (Golden Gate): 3261, 2944, 2866, 1760, 1727, 1683, 1497 cm^{-1}.

3. Results and discussion

3.1. Terephthaloyl diisocyanate

The synthesis of TPHDI was performed according to a slightly modified version of Tsuge et al. [22]. In contrast to Tsuge et al. who have been able to synthesize TPHDI with a yield of 79%, the method currently described had a yield of over 98%. This significant improvement of the yield is accompanied by a melting point increase of 15 °C (117 °C) compared to earlier reported values [27].

Solvents for chain extensions and condensations with acylisocyanates described in literature are DMSO, DMAc and NMP [24]. It is, however, also reported that acylisocyanates react with these solvents [28]. For this reason we determined the stability of TPHDI dissolved in these solvents at room temperature in concentrations of 1 mol/l. The stability is monitored with FTIR via the acylisocyanate peak present at 2240 cm^{-1}. The solution is kept under argon while at regular intervals a drop of solution is measured with an ATR-IR element. As an example, the presence of the isocyanate peak of TPHDI in DMSO and NMP as a function of time is shown in Fig. 1. Even though



Scheme 3. Synthesis of poly(ε-caprolactone).

the solutions remained clear, the figure shows the disappearance of TPHDI in DMSO and in NMP over time. DMSO showed the quickest decrease of the isocyanate peak, NMP the slowest. Chain extension in these solvents was deemed possible provided that the chain extension reaction takes place at a much faster rate than the side reactions. Chain extension in the bulk will prevent these side reactions.

Less reactive solvents like 1,2-dichlorobenzene, 1,4-dioxane, chloroform, ε-caprolactone, toluene and even 1,2-dichloroethane were not capable of (re)dissolving the TPHDI. In most cases the TPHDI seemed to dissolve, but after a few minutes a suspension was formed. This is another clear indication of reaction making these solvents unsuitable for chain extension.

Although the synthesis seems relatively simple it is not yet completely understood.

3.2. Poly(ε-caprolactone)

Poly(ε-caprolactone) was synthesized in bulk using 1,4-butanediol as an initiator, yielding a telechelic polyester with two hydroxyl end groups (Scheme 3) [7]. No catalyst or solvent was employed during the polymerization [29]. After 7 days, NMR analysis showed complete absence of monomer. The molecular mass was calculated based on the initial monomer-initiator ratio. The thus prepared polyols had molecular masses between 750 and 4000 g/mol.

3.3. Chain extension in bulk

The reactants were mixed in the extruder hopper and subsequently injected. After about 4 min of reaction time in the extruder the pressure, measured via the force needed to turn the screws in the extruder, remained constant, implying that the reaction had finished since maximum viscosity had been reached.

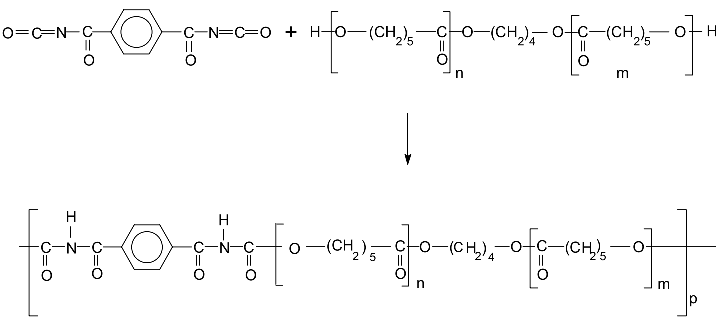
The products formed from the various PCLs were visually different from each other. PAU2000, 3000, 4000 and 750 were white, while PAU1500, 1250 and 1000 were slightly transparent. All polymers were completely soluble in chloroform and films were prepared by solvent casting. From solutions of 20 g/l films of about 0.1 mm thickness were prepared for tensile and DMTA testing as well as for DSC and characterization by SAXS and FTIR. The cast films had the same appearance as the material obtained from the extruder.

To confirm the molecular structure of the PAUs, the 1-butanol adduct of TPHDI was synthesized as a model compound. NMR and IR spectra showed comparable peaks for the 1-butanol adduct and the PAUs. It was also shown that the ratio of the peaks originating from the acylurethane and the ester moiety changed according to the lengths of the PCL parts.

In Table 1 the molecular masses of the polyacylurethanes as determined by GPC are presented. It can be seen that even though stoichiometric addition of the reactants is very difficult with a micro-extruder the molecular masses obtained are still reasonably high, varying from 5.6×10^3 to 3.4×10^4 g/mol.

3.4. Thermal properties

Comparison of the melting points (T_m, DSC), glass transitions (T_g, DSC and T_g, DMTA) and the flow points (T_{fl}, DMTA) provides useful information about a possible microphase-separated structure. The polyesters used are relatively short polymers, so quenching was needed to reveal the T_g of the unextended polyols as it is generally known that PCL crystallizes very fast and has a high degree of crystallinity. The T_g of the PAUs were determined using the offset of E' as obtained by DMTA and the onset of the glass transition temperature as determined by DSC. The T_gs



Scheme 4. Chain extension of PCL with TPHDI.

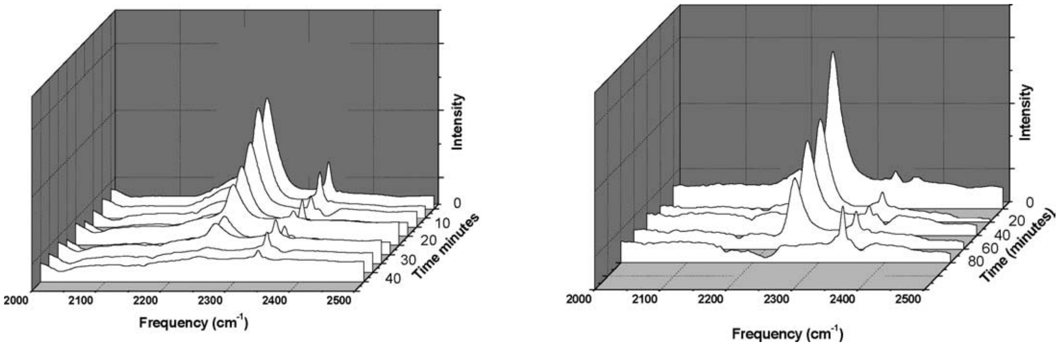


Fig. 1. Decrease of the acylisocyanate peak at 2242 cm^{-1} of TPHDI dissolved in DMSO (left) and NMP (right) followed in time with FTIR. The FTIR spectra were taken at regular time intervals of 5 min for DMSO and 20 min for NMP.

and T_m's of the polyesters and PAUs are presented as a function of hard segment content in Fig. 2 and Table 2.

As expected, a slight decrease in T_g of the polyol is found with shorter chain length due to the increased concentration of end groups. The difference in T_g of the PAUs compared to the T_gs of the polyols before chain extension is due to a certain degree of phase mixing in combination with an increase in physical crosslinks, which also increases the T_g [30].

For T_m it is found that polyesters with molecular masses of at least 2000 g/mol and their PAU counterparts show a similar T_m. The shorter polyesters and corresponding PAUs show a huge difference, however. As expected for the polyesters, T_m decreases with decreasing polyester length due to an increase in end group concentration. However, T_m of the PAUs increases with decreasing polyester length. These higher T_ms cannot be attributed to the melting of the PCL part of the polymer since the T_m for the homopolymer of PCL is 70 °C. It can, therefore, be concluded that these PAUs show some degree of microphase separation due to their increasing urethane content and that their urethane part is crystalline. The PAUs based on polyesters with a molecular mass of 2000, 3000 and 4000 g/mol have a T_m similar to the melting point of the corresponding polyesters. For this reason hardly any or no microphase separation occurs in these polymers.

This difference in melting temperature is supported by the melting point depression theory for copolymers of Flory [31]:

$$\frac{1}{T_m} - \frac{1}{T_m^*} = -\left(\frac{R}{\Delta H_f}\right) \ln X_a$$

Here T_m is the observed copolymer melting temperature and T_m^* is the observed melting temperature of the homopolymer A. X_A is the mole fraction of A-units in the copolymer, ΔH_f is the latent heat of fusion of A-units of homopolymer A and R is the gas constant.

Table 1
GPC data of the synthesized polyacylurethanes

PCL	Polyacylurethanes GPC-data			
M_n (g/mol)	PAU code[a]	M_n (g/mol)	M_w (g/mol)	M_w/M_n
750	PAU750	5.6×10^3	1.1×10^4	2.0
1000	PAU1000	1.5×10^4	3.2×10^4	2.1
1250	PAU1250	3.4×10^4	6.2×10^4	1.8
1500	PAU1500	1.7×10^4	3.4×10^4	2.0
2000	PAU2000	1.9×10^4	3.7×10^4	2.0
3000	PAU3000	1.0×10^4	2.0×10^4	2.0
4000	PAU4000	1.4×10^4	2.6×10^4	1.9

The PAUs were completely soluble in DMSO, DMAc, DMF, THF, chloroform, 1,4-dioxane and 1,2-dichlorobenzene.

[a] PAU*x* with *x* representing the molecular mass PCL used.

Table 2
Thermal transitions of the PAUs and the corresponding polyesters as determined by DSC

PAU			Polyol before chain extension	
PAU code	$T_{g,DSC}$ (°C)	T_m (°C)	T_g (°C)	T_m (°C)
PAU750	−54	114	−80	23
PAU1000	−55	100	−78	29
PAU1500	−62	83	−75	42
PAU2000	n.d.	43	−76	42
PAU3000	−58	53	−73	47
PAU4000	−64	56	−73	50
PCL			−70	70

n.d., not detected with DSC.

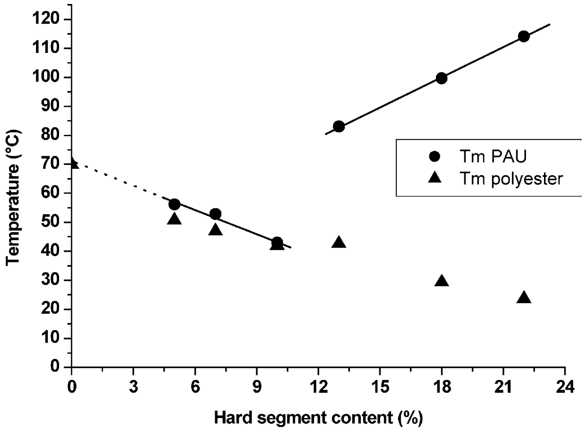


Fig. 2. Melting point of the PAUs and the corresponding polyesters plotted as function of the hard segment content.

Although the theory is originally based on random copolymers it has also been applied for segmented copolymers [32,33].

According to the theory of Flory, the molar volumes of the crystallizable and non-crystallizable units should be equal and since the exact molar volume of the hard segment relative to a PCL repeating unit is not known the ratio between the molecular mass of the hard segment and a repeating unit of soft segment is used in order to estimate the amount of soft segment units that the hard segments represent. This yields a value of 1.90 based on molecular masses of 216.44 and 114.14 g/mol for, respectively, TPHDI and a ε-caprolactone monomer. X_A was then calculated with the following equation:

$$X_A = \frac{1.90}{1.90 + (\mathrm{PCL}/114.14)}$$

with PCL as the molecular mass of the soft segment used and 114.14 g/mol as the molecular mass of an ε-caprolactone unit.

By plotting $1/T_m$ (Table 2) as a function of $-\ln X_A$ two linear relationships are obtained, (Fig. 3) that can only be explained by the presence of two different crystalline types of material: Acylurethane and PCL in this case. If PCL is taken as A, extrapolating to a polymer consisting for 100% out of PCL the T_m of pure poly(ε-caprolactone) should be obtained (Fig. 4). The value obtained in this case is 72 °C, which corresponds neatly to its literature value [34]. The same extrapolation can be carried out for the T_m of pure polyacylurethane, yielding a temperature of 229 °C. Regrettably this compound could not be checked against the melting point of the 1-butanol adduct since this degraded before a melting point was reached.

In Fig. 5 the E-moduli of the synthesized polymers as obtained by DMTA are plotted and in Table 3 the thermal transitions are presented, which confirm the transitions found with DSC. PAU4000 is only recorded to a temperature of −10 °C since the material did not possess sufficient mechanical properties to withstand a complete heating scan. The rubber plateaus of PAU750, 1000 and 1500 are temperature independent. This confirms that these polyacylurethanes have a well-separated phase structure like polyurethanes and that the chain extender has a uniform length. Sharp flow transitions are very typical for a uniform hard segment [35].

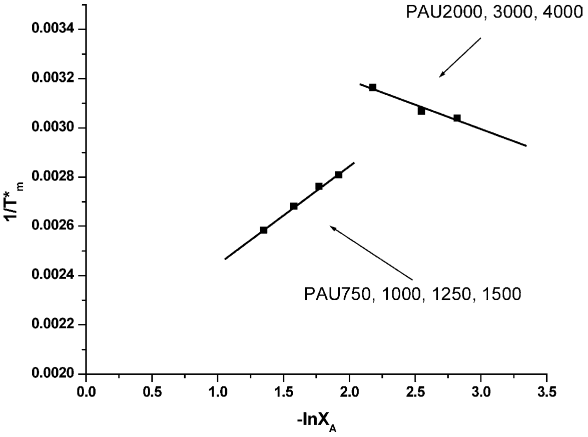


Fig. 3. Reciprocal of the melting temperature as a function of the molar fraction of hard segment in the polyacylurethane system.

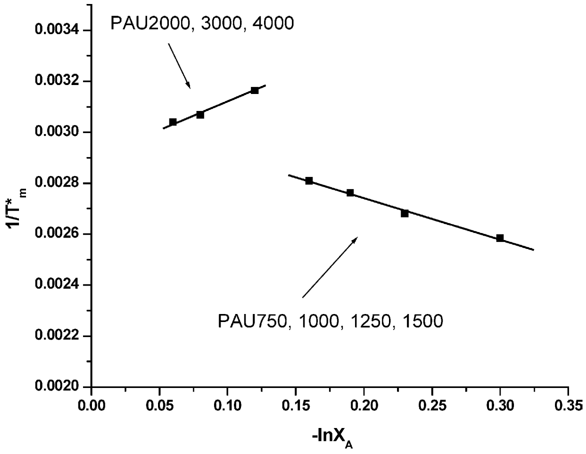


Fig. 4. Reciprocal of the melting temperature as a function of the molar fraction of ε-caprolactone segments in the polyacylurethane system.

Table 3
Thermal transitions of the PAUs and the corresponding polyesters determined with DMTA

PAU code	T_{fl} (°C)	$T_{g,DMTA}$ (°C)
PAU750	117	−53
PAU1000	105	−52
PAU1500	81	−59
PAU2000	42	−55
PAU3000	51	−62
PAU4000	–	−61

The E' value of the rubber plateau changes with changing concentrations of hard segment. The polymers with a low content of hard segment consist largely of crystalline PCL, which gives a high E'. If the amount of chain extender increases, a decrease in E' is visible with PAU1500 as minimum. If the hard segment content is increased further,

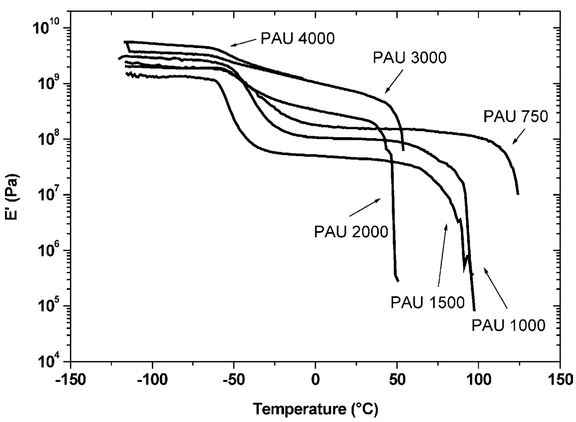


Fig. 5. Storage modulus (E') versus temperature for the different PAUs.

the E' increases again since an increased amount of crystalline material originating from hard segment will give a higher E'.

3.5. SAXS

According to DSC and DMTA data a phase-separated structure exists for the PAUs with soft segment molecular masses of 750, 1000, 1250 and 1500 g/mol. The scattering curves of these materials are presented in Fig. 6 with the scattering intensity plotted against the *q*-vector (nm^{-1}). For all PAUs measured a single broad peak is found indicating a certain degree of ordering [36]. Using the *q*-value at maximum scattering intensity (q_{max}) the inter-domain spacing (*D*) is calculated and listed in Table 4.

As can be seen from Table 4, for all these PAUs the inter-domain spacing decreases with increasing hard segment concentration indicating a decreasing length of soft segment in between the hard domains. The scattering peak of PAU2000, however, also shows some periodicity although no multiple domain morphology in the sense of hard and soft domains has been observed by DSC. Therefore, its periodicity can only be caused by crystalline PCL. The scattering curves of PAU1500 measured at different temperatures are shown in Fig. 7.

Fig. 7 demonstrates that heating of this material results in larger distances between the domains at higher temperatures. Above its T_{fl} at 100 °C a complete loss of ordering occurs, which is an indication that no microphase-separated structure is present in the melt [37]. The other PAUs show the same behavior. This suggests that the microphase separation is due to micro crystallization of the acylurethane segment. The inter-domain spacings as a function of temperature for the PAUs are listed in Table 5.

To see if the polyacylurethanes show a reversible phase separation, PAU1500 was heated for 1 h to a temperature well above the T_m observed with DSC, and after it was allowed to cool for 30 min, remeasured. The scattering curves are presented in Fig. 8. This shows that the morphology is reversible.

Table 4
Calculated inter-domain spacing of the PAUs

PAU code	q_{max} (nm^{-1})	*D* (nm)
PAU2000	0.38	16.5
PAU1500	0.79	8.0
PAU1000	1.00	6.3
PAU750	1.23	5.1

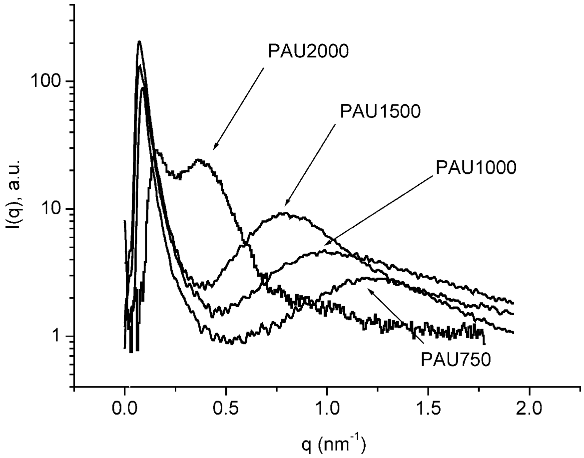


Fig. 6. SAXS scattering curves of PAU750, 1000, 1500 and 2000.

3.6. Tensile properties

The large variety in molecular masses of the hard and soft segments yields the possibility to tailor mechanical properties. As can be seen in Table 6, polymers with a low content of hard segment, namely PAU2000, 3000 and 4000, have a high Young's modulus due to the high amount of crystalline PCL present. Upon increasing the hard segment concentration, the polyester chain length will become shorter thereby reducing the fraction of crystalline PCL and thus decreasing the modulus of the polymer. For PAU1500 and lower, however, the increase of hard segment concentration will enable hard segments to phase separate, which leads to an increase in modulus.

Another clear difference between the polymers is the variation in breaking strain. PAU3000, 4000 and PCL itself show a low breaking strain. This is not caused by the high crystallinity of the materials, but probably by the low molecular mass of these particular polymers, as high molecular weight PCL has a breaking strain of more than 500% [38]. The four samples that did show a high strain at break, PAU1000, 1250, 1500 and 2000, are shown in Fig. 9. PAU1000 and 2000 are similar, after the initial modulus, both show a yield point followed by a plateau. The presence of a yield point implies that both polymers have some form of crystallinity/physical crosslinks in a continuous phase. In the case of PAU1000 this is crystalline hard segment, whereas in the case of PAU2000 this is crystalline PCL. PAU1250 and 1500 show typical elastomeric behavior.

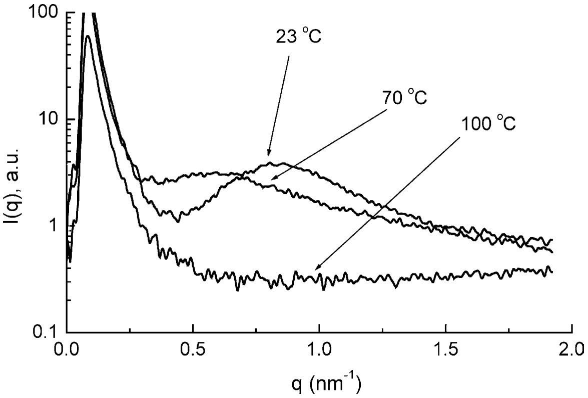


Fig. 7. SAXS measurements of PAU1500 at different temperatures.

Table 5
Calculated inter domain spacings as a function of temperature

PAU code	*T* (°C)	*D* (nm)	*T* (°C)	*D* (nm)	*T* (°C)	*D* (nm)
PAU1500	23	7.5	70	11.1	100	–
PAU1000	23	6.2	70	7.6	100	–
PAU750	20	5.1	70	5.6	130	–

Both have a low initial modulus followed by a sigmoidal curve and a very high breaking strain (more than 1100%). In addition PAU1250 has a very high upturn, which can be explained by strain-induced crystallization. Because of the similarity in structure, this upturn was also expected for PAU1500, but was not found. This might be due to differences in soft segment polydispersity between the different PAUs.

A polyurethane based on a hard segment of 1,4-butanediisocyanate and 1,4-butanediol and a PCL length of 1600 g/mol is included in Fig. 9 and Table 6 for comparison [7]. This shows that it is possible to obtain comparable tensile properties to the PAUs.

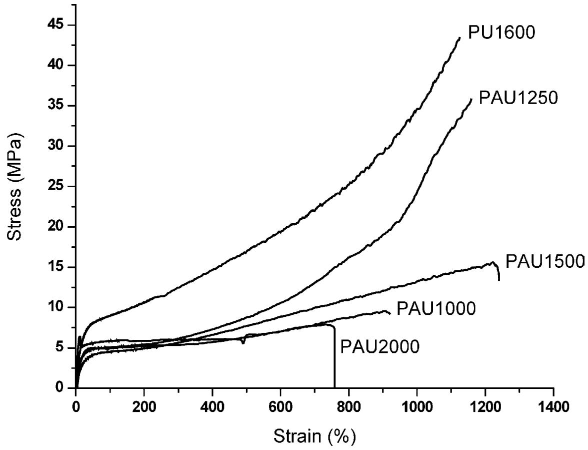


Fig. 9. Stress–strain curves of PAU1000, 1250, 1500, 2000 and PU1600.

4. Conclusions

Diacylisocyanates based on terephthalamide were synthesized using oxalyl chloride. Solvents like 1,2-dichlorobenzene, 1,4-dioxane, 1,2-dichloroethane, chloroform, ε-caprolactone and toluene were found to be unsuitable because of side reactions. Moreover, it was also found that TPHDI reacts with polar solvents like DMSO, NMP and DMAc, which makes chain extension without these solvents preferable. The synthesis of the corresponding polyurethane of the acylisocyanates was carried out successfully without the use of any toxic catalyst using a micro-extruder. Within 4 min at 130 °C the chain extension reaction with TPHDI reached a constant viscosity indicating maximum conversion.

Even though the hard segments of the polyacylurethanes described in this manuscript were very small and not very likely to cause microphase separation [39], analysis with DSC, DMTA, SAXS and tensile testing showed a multiple domain morphology for the polymers based on PCL with a molecular mass of 750, 1000, 1250 and 1500. They also showed a very flat rubber plateau in DMTA indicating a very uniform hard segment. The polymers based on PCL chains with a molecular mass of 2000, 3000 and 4000 only showed crystalline PCL and did not feature microphase separation.

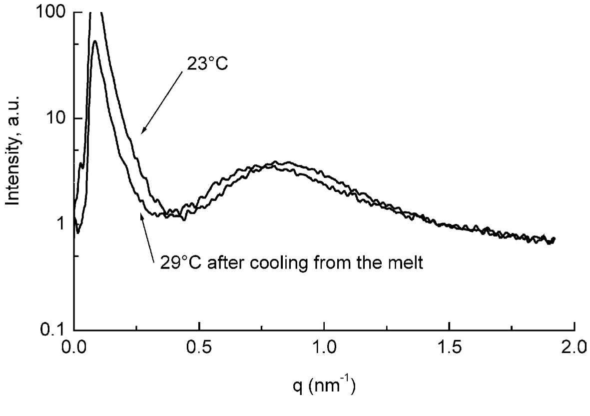


Fig. 8. Thermally reversible morphology of PAU1500.

A variety of mechanical properties was obtained for the various PAUs. Depending on hard segment content, tensile testing yielded from low to relatively high values for breaking strain, tensile strength and Young's modulus. Values between 8.1 and 1125%, 8 up to 32.2 MPa and 93.6 up to 328 MPa were found for these properties, respectively. The polymers PAU1250 and 1500 showed elastomeric properties.

The very fast polymerization of elastomeric polyacylurethanes using a micro-extruder without the use of any

Table 6
Tensile properties of PAUs with different PCL lengths

Sample	Young's modulus (MPa)	Strain at break (%)	Tensile strength (MPa)
PAU750	96.1	13.5	8.0
PAU1000	51.6	833.0	7.4
PAU1250	26.5	1117.0	32.2
PAU1500	33.4	1125.0	13.9
PAU2000	155.8	626.5	9.1
PAU3000	333.7	5.2	10.0
PAU4000	342.8	8.1	16.1
PCL	344.0	12.2	15.1
PU1600	50.4	1081.0	43.7

The values are averages of at least three measurements.

(possibly toxic) catalysts produced soluble linear polymers in high yields and thus might be the route to a new class of biomedical polyurethanes.

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