Poly(ether ester)s from Pivalolactone, Alkanediols, and Dimethyl Terephthalate. 2.† Synthesis and Characterization

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Received June 14, 1993; Revised Manuscript Received September 13, 1993•

ABSTRACT: Thermal properties of poly(ether ester)s prepared from pivalolactone (PVL), a homologous series of alkanediols (*n*G), and dimethyl terephthalate *via* a two-stage melt process were studied. Both the melting and crystallization temperatures of the poly(ether ester)s decreased with increasing length of the alkanediol used. An odd/even effect was observed, which was explained by assuming a planar zigzag structure. Furthermore, it was shown that the structure of the poly(ether ester)s could be described as consisting of crystalline alkylene terephthalate sequences, responsible for the melting behavior, and amorphous *n*G–PVL units. A Mark–Houwink equation was determined from viscometric data and from the molecular weights of the poly(ether ester)s. It was found that copolymers with molecular weights $M_n \geq 10\,000$ can be prepared by performing the polycondensation step at 275 °C for 2.5 h or by applying a postcondensation. Furthermore, upscaling of the process could be carried out from 25 to 1000 g. The poly(ether ester)s were thermally stable up to 280 °C and showed a melting behavior dependent upon the alkylene terephthalate block length.

Introduction

Poly(α,α-dialkyl-β-propiolactone)s exhibit a wide variety of physical properties with degrees of crystallinity ranging from 10 to 85% and melting temperatures varying from 25 to 240 °C, depending upon the substituents. Polypivalolactone (PPVL), i.e. poly(α,α-dimethyl-β-propiolactone), has a high degree of crystallinity (up to 80%), which made PPVL attractive as a candidate for applications such as in fibers[1] and in converting elastomeric polymers into thermoplastic elastomers.[2,3] Fibers spun from PPVL have shown good elastic properties, color stability, and a better resistance to chemicals as compared with Nylon-6 and poly(ethylene terephthalate).[1,4,5]

Several types of segmented poly(ether ester)s based on the pivalolactone (PVL) unit have been synthesized, showing promise as engineering polymers due to the high tendency to crystallize, the solvent resistance, and the narrow molecular weight distribution of the PVL blocks. Polymerization of PVL using polytetrahydrofuran (poly(THF)) as an initiator was carried out by Yamashita et al., resulting in the formation of poly(PVL-*block*-THF-*block*-PVL).[6] More recently, PVL-grafted copolymers were prepared by grafting PVL onto carboxylated poly(phenylene oxide).[7] The result was an amorphous backbone with crystallizable grafted PPVL segments, which formed thermally reversible cross-linked domains. Wagener et al. investigated the synthesis of poly(PVL-*block*-oxyethylene)[8] and studied the effect of the length of both segments on the phase separation behavior of these poly(ether ester)s.[9,10]

As part of our study on the synthesis of copolymers containing PVL units, introduction of other groups in PPVL by means of interchange reactions was investigated.[11,12] Random copolymers with high thermal stability were obtained *via* interchange reactions of PPVL with Bisphenol A polycarbonate and dimethyl terephthalate (DMT).[12]

As mentioned above, poly(ether ester) block and graft copolymers containing PPVL have been synthesized by copolymerization of PVL with preformed polyethers. In our previous paper we reported on the synthesis of PVL-based poly(ether ester)s by applying condensation and ring-opening reactions simultaneously.[13] *Via* a two-stage melt process poly(ether ester)s were prepared by starting with mixtures of PVL, alkanediols, and DMT (see Scheme I). Apart from the presence of ether bonds, the copolymers contained no or only small amounts of sequences of PVL units. In order to investigate the properties of these *n*GT–*n*G–PVL-based copolymers (see Scheme I), especially in relation to their composition, the two-stage melt process was studied in more detail with a homologous series of alkanediols, ranging from 1,2-ethanediol (2G) to 1,10-decanediol (10G). In this paper results are presented on the relationship between the composition of these copolymers and their thermal properties. (The mechanical properties of the poly(ether ester)s will be discussed in a forthcoming paper.[14])

Furthermore, attempts have been made to increase the molecular weight of the poly(ether ester)s. Low molecular weight prepolymers were prepared by the reaction of PVL and bis(hydroxybutyl) terephthalate, and by subsequent condensation in the melt the effect on the molecular weight was studied. In addition, the influence of the polycondensation temperature and reaction time on the synthesis of poly(ether ester)s from PVL, DMT, and 1,4-butanediol (4G) was investigated. In order to relate results from viscometric measurements to molecular weights, the Mark–Houwink constants were determined from size exclusion chromatography and viscometric measurements.

Experimental Section

Materials. Pivalolactone (PVL) was purified by distilling over calcium hydride and was stored under nitrogen at −30 °C. Dimethyl terephthalate (DMT), 1,2-ethanediol (2G), 1,3-propanediol (3G), 1,4-butanediol (4G), 1,5-pentanediol (5G), 1,6-hexanediol (6G), and 1,8-octanediol (8G) were obtained from Merck and were used as received. The other alkanediols used were purchased from Aldrich and were used without further purification. Tetrabutylorthotitanate (TnBT, Merck) used as a

† Part 1: cf. ref 13.

• Abstract published in *Advance ACS Abstracts*, November 1, 1993.

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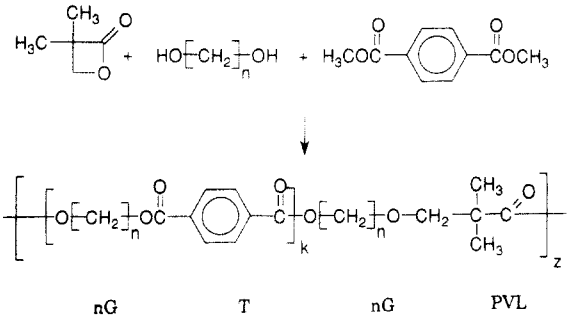
Scheme I. Poly(ether ester)s from PVL, Alkanediols, and DMT



catalyst in the polymerization procedures, was added as a solution in dry toluene or as a solution in 4G (large-scale polymerization). Triphenyl phosphite used in the prolonged condensation step was obtained from Aldrich. Bis(hydroxybutyl) terephthalate (BHBT), mp 72 °C, was synthesized from DMT and a 20-fold excess of 4G.[15]

Trifluoroacetic acid (TFA, Janssen Chimica) and chloroform (Merck) were used without further purification. Ethanol and methanol used for precipitation were of technical grade.

Synthesis of Copolymers. Small-scale polymerizations (up to 25 g of polymer) were carried out in a 50-mL reaction vessel as described in our previous paper.[13] Analogously, copolymers were prepared on a medium scale in a 250-mL reaction vessel, equipped with a stainless steel stirrer with a provision for measuring the torque of the stirrer.

In a typical medium-scale polymerization procedure, PVL (15.0 g, 0.15 mol), DMT (67.9 g, 0.35 mol), 4G (63.0 g, 0.70 mol), and TnBT (0.1 wt %) were placed in the reaction vessel (Table III, exp no. P4GT-70/09). The reaction vessel was evacuated and flushed with nitrogen three times and inserted into a fluidized sand bath kept at 200 °C. After 10 min the first methanol appeared in the receiver, and while the contents were stirred (100 rpm) under nitrogen for 2 h, the methanol formed was distilled out. The temperature was raised to 250 °C over a period of 30 min and was kept at 250 °C for another 30 min. In the second stage of the reaction a vacuum (30 mbar) was applied for 30 min and the polymerization was completed by stirring (60 rpm) at 250 °C and 0.3–0.6 mbar for 5 h. During this stage, the torque measured increased slowly until a constant value was reached. The clear viscous melt was cooled to room temperature, and after purification by dissolving in chloroform, followed by precipitation in methanol, 93.2 g of a white fiber-forming polymer was obtained ($[\eta]$ = 0.37 dL/g in chloroform).

Analogously, a large-scale polymerization was carried out in a stainless steel batch reactor (up to 1000 g of polymer) of a general type used for poly(alkylene terephthalate) synthesis. PVL (70.0 g, 0.70 mol), DMT (316.9 g, 1.63 mol), 4G (294 g, 3.27 mol), and TnBT (0.1 wt %) were placed in the reactor (Table III, exp no. P4GT-70/10). After 2 h at 200 °C, during which the methanol formed was distilled out, the temperature was raised to 250 °C. In the second stage of the reaction a vacuum (15 mbar) was applied for 30 min and the polymerization was completed by heating at 250 °C and 0.8 mbar for 2.5 h, during which the torque measured increased from 0.1 to 0.6 N m. Next, the clear viscous melt was removed from the reactor by pressing it through a bottom valve using a small overpressure. The clear polymer fiber was cooled in a water bath and wound upon a spool. After chipping and drying, about 400 g of a polymer was obtained ($[\eta]$ = 0.39 dL/g in chloroform).

Model System. A prepolymer of BHBT and PVL was prepared as reported previously.[13] Samples of the prepolymer obtained after 360 min of reaction at 200 °C, with η_{inh} = 0.08 dL/g in chloroform, together with 0.1 wt % TnBT were placed in 10-mL polymerization tubes equipped with a provision for applying a vacuum or keeping a nitrogen atmosphere. After evacuating and flushing with nitrogen three times, the tubes were inserted into a salt bath kept at 200 °C. A vacuum of 0.06 mbar was applied, and after various reaction times, the tubes were removed from the temperature-controlled bath and the products dissolved in chloroform, precipitated in ethanol, and filtered.

Viscometry. Viscometric measurements were carried out with solutions of 0.050 g of polymer in 10 mL of chloroform, using an Ubbelohde viscometer thermostated at 25 °C. In the case of polymers which were not soluble in chloroform, trifluoroacetic acid was used (c = 0.25 g/dL). In this study, limiting viscosity numbers $[\eta]$ were determined at one concentration using an equation derived by Raju et al.,[16]

$$\log[\eta] = \log\{(\eta_{rel} - 1)/c\} - K(\eta_{rel} - 1) \quad (1)$$

Equation 1 was reported by Raju et al. to have a good fit when K = 0.14 for $\eta_{rel} - 1 < 0.3$ and K = 0.12 for $0.3 < \eta_{rel} - 1 < 0.8$. The applicability of this method for our study was tested by comparison with $[\eta]$ values obtained by extrapolation to zero concentration. In all cases the differences between the results remained within the experimental error.

Size Exclusion Chromatography. Size exclusion chromatography (SEC) was performed on a Hewlett Packard chromatograph (HP 1090) equipped with an UV diode array detector and a refractive index (RI) detector (HP 1073A). Five Ultrastyragel columns with pore sizes of 10^5, 10^4, 10^3, 5×10^2, and 10^2 Å were applied. Methylene chloride was used as solvent and eluent at room temperature, while a sample concentration of ~0.2 wt % was used. The injection volume was 240 μL. Calibration was performed using polystyrene standards having narrow molecular weight distributions and known molar masses from 0.226 to 2000 kg/mol. All data were processed using a HP 300 computer equipped with a HP software package.

Measurements. NMR spectra were recorded on a Bruker AC 250F using a deuterated solvent; chemical shifts are in parts per million downfield from TMS. Thermal analyses were carried out at a heating/cooling rate of 20 °C/min using a Perkin-Elmer DSC 7. Gallium and indium were used for calibration; all DSC runs were carried out under a nitrogen atmosphere. TGA measurements were carried out under a helium atmosphere at a heating rate of 20 °C/min using a Perkin-Elmer TGA 7.

Results and Discussion

Copolymer Synthesis from Pivalolactone, Alkanediols, and Dimethyl Terephthalate. As was found previously using 1,3-propanediol (3G) and 1,4-butanediol (4G),[13] poly(ether ester)s were also obtained by a two-stage melt process from pivalolactone (PVL), dimethyl terephthalate (DMT), and a homologous series of alkanediols (nG) in the presence of tetrabutylorthotitanate (TnBT). Two series of copolymers were prepared, in which the initial compositions in mol % were PVL/nG/DMT = 25/50/25 (PnGT-50) and PVL/nG/DMT = 13/58/29 (PnGT-70), respectively. Most of the copolymers were soluble in chloroform, and their ^{1}H NMR spectra showed the same characteristics as the ones studied previously;[13] i.e. a significant amount of ether bonds and only isolated PVL units were present in these copolymers. From the ^{1}H NMR spectra the composition was calculated, and it can be seen from Figure 1 that the amount of PVL units slowly decreased with increasing n, whereas an increase was found for the number of nG and terephthalate (T) units. The decrease in the amounts of PVL units with n reflected the decreasing reactivity of the higher diols with respect to ring-opening of a cyclic ester.

The compositional data in Figure 1 also show that in the copolymers the nG/T ratio was larger than 1 irrespective the type of nG used, thus showing that part of the excess alkanediol in the initial reaction mixture was incorporated as alkylene units in the copolymers. The deviation of the nG/T ratio from 1 was in contrast with the value obtained for poly(alkylene terephthalate)s and for copolymers based on higher lactones[13,17] and was caused by the occurrence of other types of condensation reactions in the case of β-lactones.[13]

In Figure 2 thermal properties of the poly(ether ester)s are shown. Since two copolymers of the first series did not show a melting temperature; i.e. for n = 5 and 7 (Figure

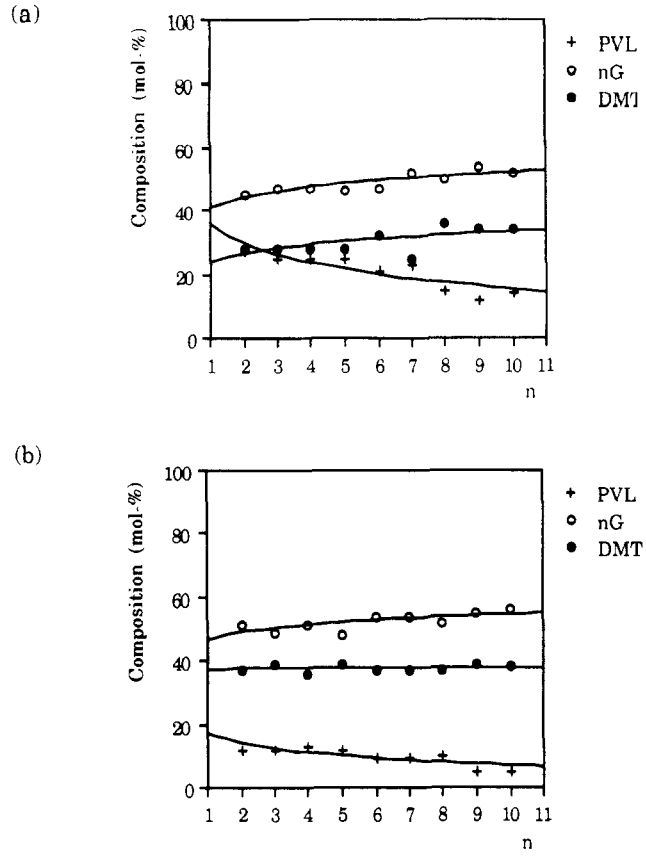


Figure 1. Composition of poly(ether ester)s from PVL, alkanediols, and DMT as a function of the number of methylene units n (initial composition in mol % PVL/nG/DMT = (a) 25/50/25 and (b) 13/58/29).

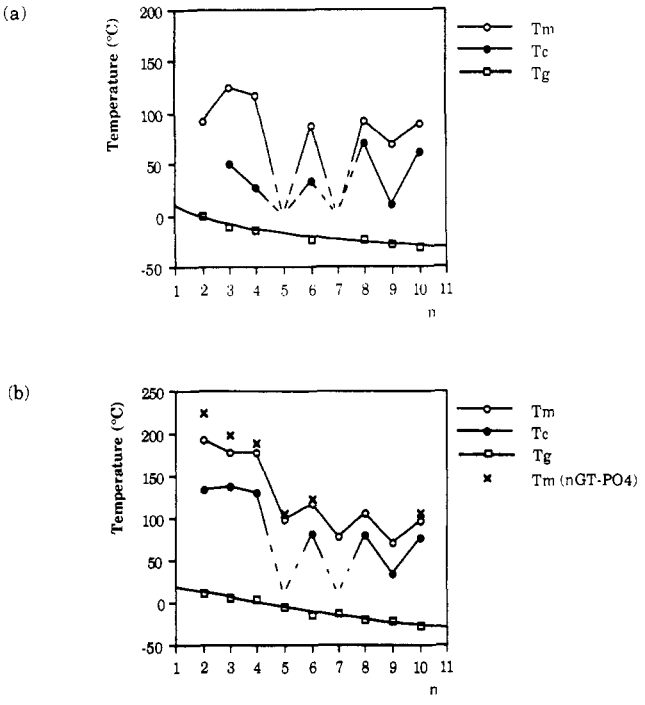


Figure 2. Thermal properties of poly(ether ester)s versus the number of methylene units n of the alkanediol: (a) PVL-based copolymers (initial composition in mol % PVL/nG/DMT = 25/50/25); (b) PVL-based copolymers (PVL/nG/DMT = 13/58/29) and nGT–PO4-based copolymers (PO4/nG/DMT = 33/33/33).[27]

2a), a second series of copolymers was studied containing a larger amount of alkylene terephthalate units. All copolymers of this series demonstrated melting temperatures as shown in Figure 2b. Although the initial compositions were the same within one series, the composition of the copolymers differed (as illustrated by Figure 1), which might have an effect on the thermal properties. Overall, the glass transition temperature T_g as well as the melting temperature T_m and the crystallization temperature T_c decreased with the increasing number of methylene units n of the nG used. The latter transition temperatures alternated between even- and odd-membered alkylene units. The members with n = 3, 4, 6, 8 or higher membered alkylene units crystallized rapidly from the melt, whereas for n = 5 and 7 crystallization appeared to be slow. Comparable behavior with respect to crystallization has been observed for a homologous series of poly(alkylene terephthalate)s.[18]

The odd/even effect for the melting temperature curve of a homologous series of polymers was already reported earlier for various polyesters and polyurethanes,[19] and also for polymers of terephthalic acid and a series of nG ranging from 2G to 10G.[18,20,21] It was concluded that this phenomenon was related to the planar zigzag structure of these polymers, and an explanation was offered on the basis of different crystal packings observed.[19] More recently, several liquid crystalline polymers with flexible spacers were synthesized, which showed the same type of odd/even effect.[22-26] This effect for the melting temperatures of poly(ester imide)s prepared by Kricheldorf et al. was explained by the type of chain packing. The smaller tilt angle in the odd-membered polymers resulted in a less stable crystal lattice, and thus lower melting points were observed.[26]

Wolfe prepared a series of poly(ether ester)s based on alkylene terephthalate (nGT) and poly(tetramethylene oxide) (PO4), in which nG was varied.[27] The melting temperatures of these copolymers containing 50 mol % nGT are plotted in Figure 2b along with data for the PVL-based copolymers with a comparable amount of nGT units. From Figure 2b it can be seen that the nGT–nG–PVL-(Scheme I) and the nGT–PO4-based copolymers were remarkably alike, both showing an odd/even effect and comparable melting temperatures.

As far as the PVL-based poly(ether ester)s are concerned, it is assumed that the sensitivity of the thermal properties to the number of methylene units, odd or even, was related to an alternation of the crystal structure as depicted in Figure 3. Assuming a planar zigzag structure for these copolymers, different crystal packings can be present for an odd (n = 3) or an even (n = 4) number of methylene units. The fact that lower melting temperatures were observed for the copolymers with an odd number of methylene units indicated that the chain packing of these copolymers, as presented by structure a in Figure 3, was thermodynamically less stable.

Apart from the effect of the type of alkanediol on the properties, also the influence of the composition of the PVL-based poly(ether ester)s on their properties was studied. By varying the composition of the initial reaction mixtures, a broad range of copolymers was synthesized from PVL, DMT, and 3G or 4G.[13] In Figure 4 thermal properties of the copolymers are plotted as a function of the amount of PVL units in the copolymers. Both the melting temperature T_m and the crystallization temperature T_c decreased continuously with increasing amounts of PVL in the copolymers. The decrease in T_m can be related to the decreasing fraction of nGT units. Incorporation of large amounts of PVL resulted in products which were highly viscous liquids. The limits of PVL units incorporated for copolymers with a melting temperature above room temperature were 40 and 30 mol % for copolymers prepared from 3G and 4G, respectively. By comparing T_m and T_c a measure for the rate of crystallization can be obtained. For the copolymers prepared from PVL, 4G, and DMT the supercooling was about 40

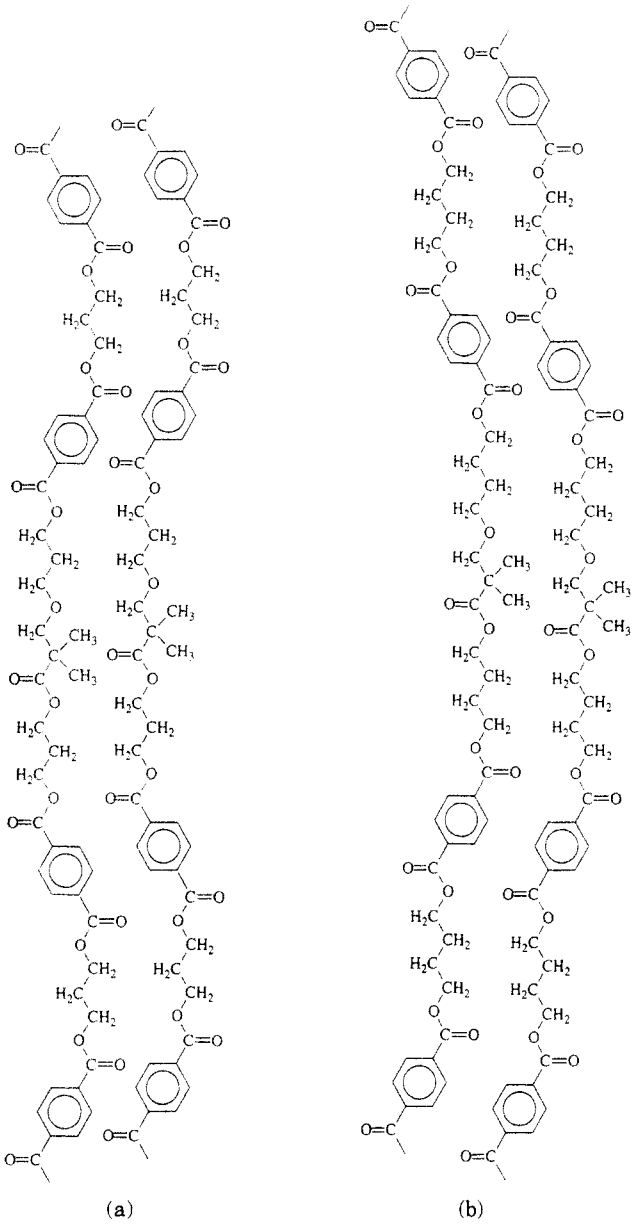
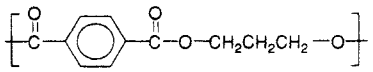


Figure 3. Possible chain packings of poly(ether ester)s from PVL, DMT, and (a) 3G and (b) 4G.

°C (at a heating/cooling rate of 20 °C/min), which appeared comparable with other poly(ether ester)s.

Considering the T_m's of both homopolymers, i.e. of polypivalolactone (T_m = 228 °C) and of poly(propylene terephthalate) (T_m = 218 °C), it is obvious that the melting behavior of the 3G–PVL-based poly(ether ester)s deviated from the expected behavior of random copolyesters of PVL and propylene terephthalate. Therefore, attempts were made to find a relationship between the melting behavior of the 3G–PVL-based poly(ether ester)s and the morphology of the copolymers. The chemical structure of the 3G–PVL-based copolymers was elucidated in our previous paper[13] and it appeared that in the chains of these poly(ether ester)s mainly two units were present, i.e.



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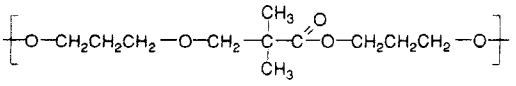


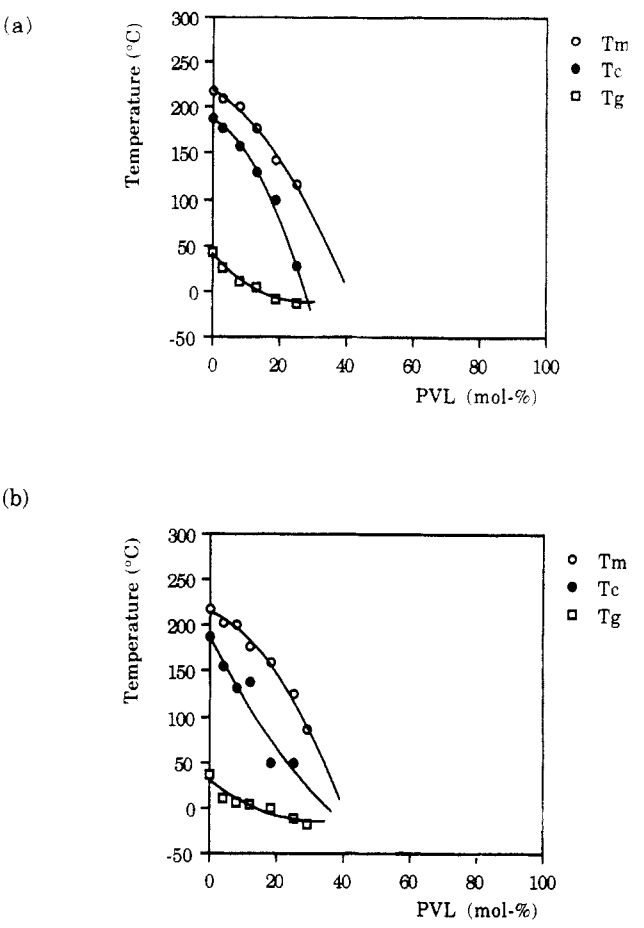


Figure 4. Thermal properties of poly(ether ester)s from PVL, DMT, and (a) 3G and (b) 4G as a function of the mol % PVL in the poly(ether ester)s.

It was also concluded that in the poly(ether ester)s only isolated PVL units were present.[13] Therefore, it was suggested that the crystalline behavior of these copolymers is due to the presence of crystalline 3GT sequences. Assuming a planar zigzag structure, a chain packing of the poly(ether ester)s may be presented as shown in Figure 3a. The melting behavior of the poly(ether ester)s might therefore be described using the following equation,[28]

$$1/T_m - 1/T_m^\circ = -(R/\Delta H_u) \ln p \qquad (2)$$

in which T_m is the melting temperature of the copolymer, T_m° is the melting temperature of the crystallizable homopolymer, R is the gas constant and ΔH_u is the enthalpy of fusion per repeating unit; p is defined as the sequence propagation probability. For a random copolymer p equals the mole fraction of crystalline units X_a,[28] thus converting eq 2 into

$$1/T_m - 1/T_m^\circ = -(R/\Delta H_u) \ln X_a \qquad (3)$$

As was shown in our previous paper,[13] the amount of 3GT units could be determined directly from the ^{1}H NMR spectra of the poly(ether ester)s. Plotting $1/T_m$ versus $-\ln X_a$ yielded a linear relation for the copolymers (Figure 5). The deviation from linearity for the copolymer with the lowest amount of 3GT units was probably caused by the presence of crystalline PVL sequences (4 mol %) in this copolymer. From Figure 5 ΔH_u was determined as ΔH_u = 24.7 kJ/mol repeating unit, whereas the calculated value, based on group contributions,[29] was 29 kJ/mol. The fact that the value of ΔH_u determined using eq 3 was less than the calculated value is due to the absence of very long 3GT sequences in the copolymers, which are required from a theoretical point of view.[28] Considering the relatively good fit of the experimental values to the straight

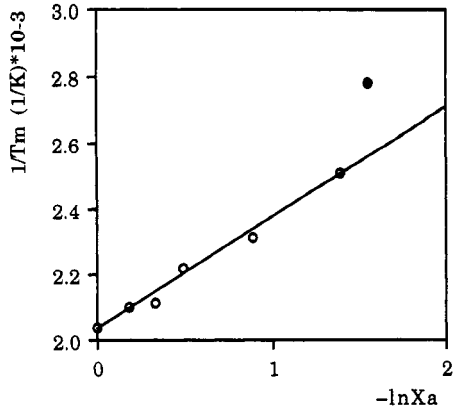


Figure 5. Plot of $1/T_m$ versus $-\ln X_a$ for poly(ether ester)s from PVL, 3G, and DMT.

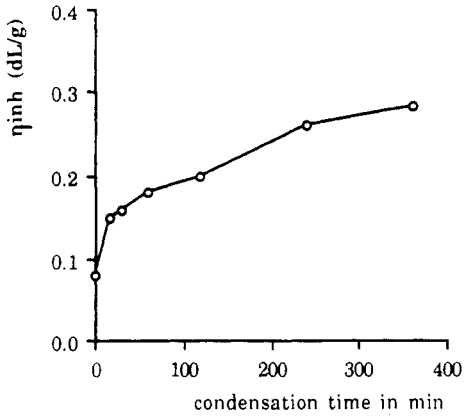


Figure 6. Logarithmic viscosity numbers (chloroform, 25 °C) of poly(ether ester)s prepared from equimolar amounts of PVL and BHBT versus the polycondensation time (TnBT; 200 °C; 0.06 mbar).

line of Figure 5 (regression coefficient $R = 0.99$), it can be concluded that the 3G–PVL-based poly(ether ester)s may be described as consisting of crystalline 3GT sequences and amorphous 3G–PVL units. By assuming this morphology, the melting behavior of these poly(ether ester)s, as shown in Figure 4a, in particular the presence of a limit of PVL units incorporated for copolymers with a melting temperature above room temperature, can be explained.

Due to the peak overlap in the ^{1}H NMR spectra of the copolymers based on PVL, DMT, and 4G, the number of 4GT units could not be determined accurately. Although no direct evidence was available, the similar melting behavior of these copolymers as was observed for the 3G–PVL-based poly(ether ester)s (see Figure 4) indicates a structure consisting of crystalline 4GT sequences and amorphous 4G–PVL units.

Effect of Reaction Conditions on the Molecular Weight. In order to study the influence of reaction conditions on the molecular weight of the PVL-based poly(ether ester)s, several reaction variables were varied. It was shown in our previous paper that with TnBT as a catalyst the best results were obtained.[13] Therefore, all polymer syntheses were performed using TnBT as a catalyst. The second stage of the two-stage melt process during which polycondensation takes place, was first studied using a model system.[13] Prepolymers of PVL and bis(hydroxybutyl) terephthalate (BHBT) were heated at 200 °C under vacuum, and results are shown in Figure 6. In Figure 6 η_{inh} of the poly(ether ester)s is plotted versus the polycondensation time and it can be seen that η_{inh} increased until after 360 min a value of 0.28 dL/g was reached. From the ^{1}H NMR spectra of the polymers obtained after various condensation times it appeared that

Table I. Effect of Condensation Temperature and Time on the Synthesis of Poly(ether ester)s from PVL, DMT, and 4G (TnBT; 0.1 mbar)

exp no.[a]	temp (°C)	time (min)	η_{inh}[b] (dL/g)
P4GT-60/22	200	150	0.10
23	225	150	0.15
24	250	150	0.14
25–2	275	150	0.30
26	300	150	0.13
25–1	275	90	0.25
25–2	275	150	0.30
25–3	275	210	0.35

[a] Composition of the copolymers (in mol %) after condensation: PVL/4G/DMG ≈ 19/49/32. [b] Determined from viscometric measurements in chloroform at 25 °C (c = 0.50 g/dL).

Table II. Effect of Postcondensation (200 °C; 0.1 mbar) on the Value of η_{inh} of Preformed 4G–PVL-Based Poly(ether ester)s

exp no.	catalyst[a]	time (h)	η_{inh}[b] (dL/g)	$\Delta\eta_{inh}$ (%)
P4GT-60/07[c]		0	0.24	
	A	1	0.30	24
	A	2	0.34	38
	A	4	0.34	38
	A	6	0.38	55
	B	24	0.73	201
P4GT-70/08[d]		0	0.46	
	A	1	0.53	15
	A	2	0.53	15
	A	4	0.56	23
	A	6	0.57	25
	B	24	0.67	47

[a] A = 1.0 wt % triphenyl phosphite; B = without catalyst. [b] Determined from viscometric measurements in chloroform at 25 °C (c = 0.50 g/dL). [c] Initial composition (in mol %): PVL/4G/DMT ≈ 19/49/32. [d] Initial composition (in mol %): PVL/4G/DMT ≈ 13/51/36.

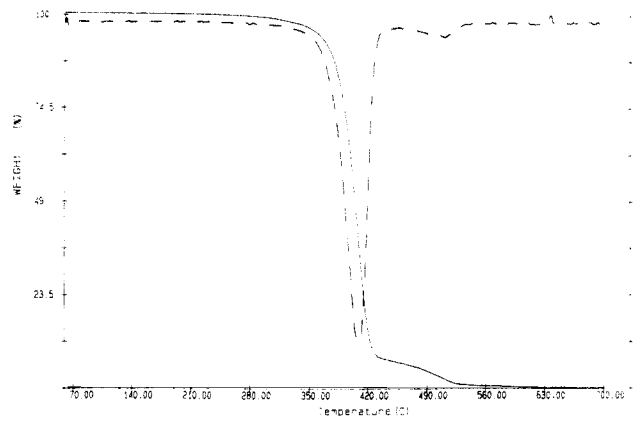
the amount of PVL units remained constant with respect to the number of aromatic units, whereas the 4G/T ratio showed a small decrease from 1.7 to 1.5.

Because in the model system the molecular weight of the copolymers still seemed to increase after 360 min at 200 °C, the second stage of the synthesis of poly(ether ester)s from PVL, DMT, and 4G was performed at various conditions in the presence of TnBT. From Table I it can be seen that copolymers obtained by applying condensation temperatures between 200 and 250 °C had significantly lower η_{inh} values than the copolymers obtained at a polycondensation temperature of 275 °C, whereas a further increase to 300 °C resulted in lower η_{inh} values. This decay in η_{inh} was probably caused by side reactions.

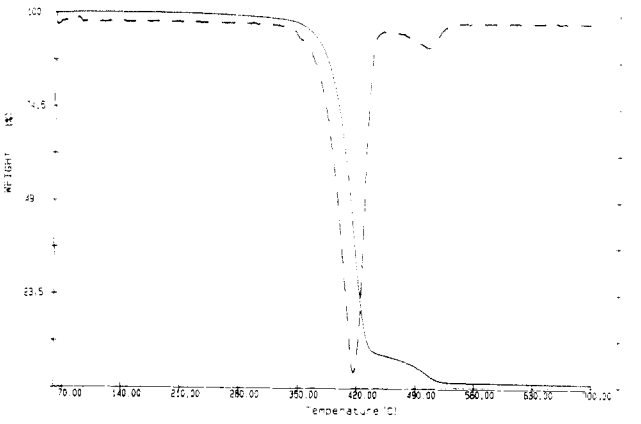
Apart from the effect of the polycondensation temperature also the influence of the polycondensation time was studied. From the experiments at 275 °C (Table I) it can be seen that η_{inh} increased steadily with the reaction time.

In order to obtain higher molecular weight poly(ether ester)s also prolonged condensations in the melt were carried out at 200 °C under reduced pressure (0.1 mbar), starting from two preformed copolymers with various η_{inh} values and compositions. The 4G–PVL-based poly(ether ester)s were prepared from PVL, 4G, and DMT by the general procedure[13] and were used after purification by the usual procedure. Results of the prolonged polycondensation with these copolymers are presented in Table II. An increase in η_{inh} was observed after condensation for a few hours in the presence of triphenyl phosphite as a chain extender.[30] Since the use of a catalyst may not only increase the rate of condensation reactions but also affect the structure of the poly(ether ester)s, due to randomization *via* interchange reactions, the prolonged polycondensation was also performed without adding a

(a) PVL/4G/DMT = 8/52/41



(b) PVL/4G/DMT = 13/51/36



(c) PVL/4G/DMT = 19/49/32

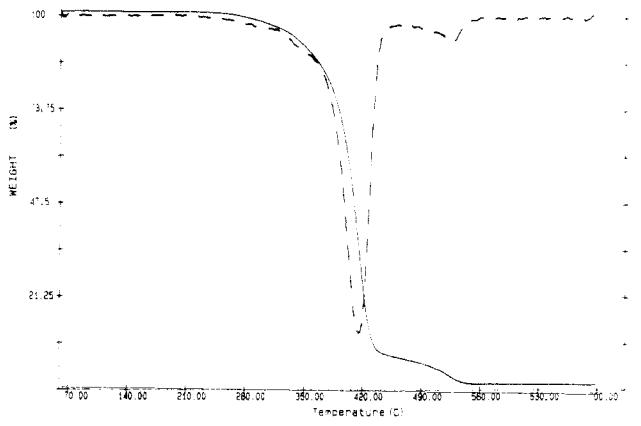


Figure 7. TGA curves of 4GPVL-based poly(ether ester)s with various compositions (mol %).

catalyst. It appeared that heating in the melt without a catalyst for a period of 24 h also resulted in a clear increase of η_{inh}.

Attempts to increase η_{inh} by solid-state polycondensation at 120–140 °C were not successful, probably due to the relatively low reaction temperatures, i.e. below the melting temperature of the copolymers applied.

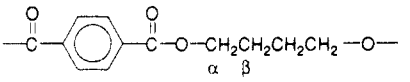
Thermal Stability of the Poly(ether ester)s. In order to study the thermal stability of the poly(ether ester)s, TGA measurements were carried out with the 4G–PVL-based copolymers. In Figure 7 TGA curves are shown of three poly(ether ester)s with various compositions. The TGA curves show that the temperature of the maximum polymer degradation rate was about 410 °C, irrespective of the amount of PVL units present in the copolymers. From the TGA curve of the copolymer shown in Figure 7c, it can be seen that this copolymer started to show weight loss at 280 °C. This result is in accordance with the decrease in molecular weight observed when the polycondensation was performed at 300 °C with a copolymer with the same composition (Table I).

Table III. Molecular Weights and Viscometric Data for *n*G–PVL-Based Poly(ether ester)s

exp no.[a]	$10^{-3}M_n$	$10^{-3}M_w$	$[\eta]^b$ (dL/g)	comments[c]
P3GT-50/01	8.6	14	0.19	
60/01	11	28	0.33	
60/02	2.3	3.3	0.08	no catalyst
60/03	6.7	13	0.19	SnOct as a catalyst
60/09	41	120	0.83	postcondensation
P4GT-50/05	16	37	0.38	
50/13	27	85	0.62	from PVL and BHBT
60/01	16	37	0.42	P_{cond} = 0.06 mbar
60/16-24	43	130	0.79	postcondensation
60/17-24	19	43	0.41	postcondensation
60/25-3.5	11	35	0.36	T_{cond} = 275 °C
60/28	10	24	0.28	
70/07-6	30	67	0.60	postcondensation
70/09	11	40	0.37	medium-scale
70/10	14	75	0.39	large-scale

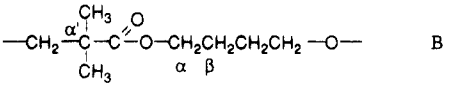
[a] Composition of copolymers (PVL/*n*G/DMT, in mol %): P*n*GT-50 ≈ 25/47/28, P*n*GT-60 ≈ 19/49/32, and P*n*GT-70 ≈ 13/51/36. [b] Determined from viscometric measurements in chloroform at 25 °C. [c] Unless otherwise noted, polymers were prepared in a small-scale reaction vessel using standard conditions in the presence of TnBT (3 h, 200–250 °C, N_2; 2 h, 250 °C, 0.1 mbar).

In general it is known that the rate of thermal chain-scission reactions and the mechanism by which these occur during polyester synthesis depends on the chemical structure of the polyester.[31] Two types of ester bonds are predominantly present in the 4G–PVL-based poly(ether ester)s,[13] i.e.



A

and



B

The main scission reaction for structure A, i.e. for poly(alkylene terephthalate)s, is abstraction of β-hydrogen atoms, resulting in the formation of a carboxylic acid and a vinyl end group.[31] Furthermore, β-hydrogen abstraction can also occur for structure B, but this type of reaction is less important for polyesters with aliphatic structures.[32] The most favored reaction for aliphatic ester structures is the cleavage of the acyl–oxygen bond, followed by the abstraction of a hydrogen atom from the α′-position.[32] However, in structure B no α′-hydrogens are present, due to the dimethyl substituted α′-carbon of the PVL unit. Also thermal degradation of PVL sequences by reverse polymerization,[33] or by random scission followed by unzipping,[34] could be excluded because the PVL-based copolymers did not contain PVL sequences.[13] Thus, probably the main reaction responsible for the thermal degradation of 4G–PVL-based poly(ether ester)s at temperatures above 280 °C is abstraction of β-hydrogen atoms from structure A.

SEC Measurements. SEC experiments were carried out in methylene chloride in order to relate the viscometric results to molecular weights of the PVL-based poly(ether ester)s. The synthesis of poly(ether ester)s from PVL, alkanediols, and DMT resulted in copolymers with a broad range of molecular weights (Table III). From the viscometric results single-point $[\eta]$ values were determined according to the method developed by Raju et al.[16] A

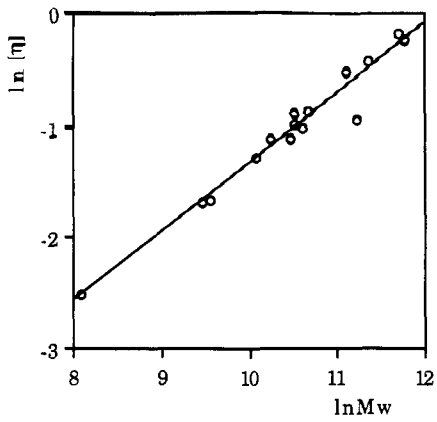


Figure 8. Mark–Houwink plot of ln [η] versus ln M_w for nG–PVL-based poly(ether ester)s (Table III).

double logarithmic plot of these [η] values versus weight average molecular weights determined by SEC is shown in Figure 8. From this plot the Mark–Houwink constants could be calculated; the equation derived from viscometric measurements in chloroform at 25 °C can be written as follows:

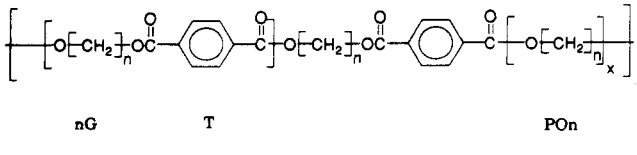
$$[\eta] = 5.2 \times 10^{-4} M_w^{0.62} \quad (4)$$

Equation 4 was determined using poly(ether ester)s with compositions (in mol %) ranging from PVL/nG/DMT = 25/47/28 to 13/51/36 when nG is 3G or 4G. Although copolymer composition and composition distribution may affect the [η] values, it is known that possible interactions between solvent molecules and one of the units are of more importance.[35] The fact that the Mark–Houwink plot had a relatively good fit (regression coefficient R = 0.96) indicated that chloroform is a good solvent for the poly(ether ester)s with the above-mentioned compositions.

Generally speaking, only polymers with molecular weights of 10 000 or more are of interest as far as thermal and mechanical properties are concerned. On the basis of the results shown in Table III and by using eq 4 it can be calculated that a copolymer with [η] = 0.31 dL/g has a M_n of 10 000 (assuming $M_w/M_n = 3$). Using eq 1, derived by Raju et al.,[16] the corresponding value for η_{inh} is 0.30 dL/g (with c = 0.50 g/dL).

The values of η_{inh} shown in Tables I and II indicate that molecular weights ≥10 000 can be achieved after polycondensation at 275 °C for 2.5 h or after a postcondensation. Furthermore, it appeared that upscaling from 25 to 100 g (medium scale) and 1000 g (large scale) could be carried out without major difficulties. Especially, the polymerization carried out in a reactor of a type also used for poly(alkylene terephthalate)s syntheses proved to be very efficient (Table III, exp no. P4GT-70/10). After 2.5 h of condensation at 250 °C already a polymer with M_n = 14 000 was obtained, indicating that poly(ether ester)s with sufficiently high molecular weights can be readily prepared *via* the two-stage melt process starting from PVL, DMT, and alkanediols.

Comparison with Other Poly(ether ester)s. Poly(ether ester)s are usually prepared by a two-stage process involving DMT, an alkanediol, and a poly(alkylene glycol ether) (POn). Using the general notation proposed by Perego et al.,[36]



nG T POn

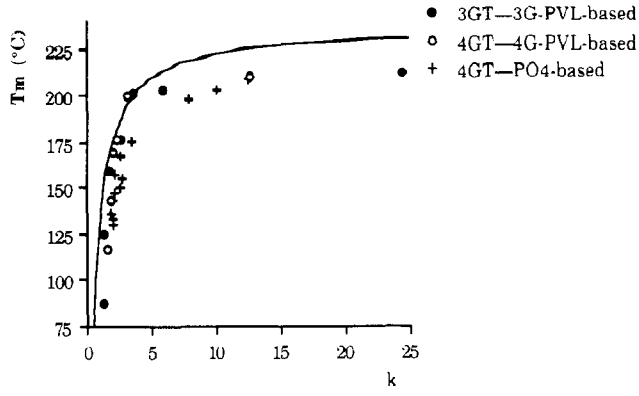


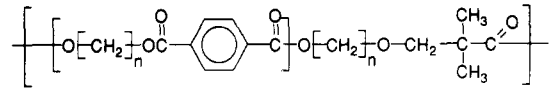
Figure 9. Melting temperature of three types of poly(ether ester)s versus the alkylene terephthalate block length k (T_m's of the 4GT–PO4-based copolymers from literature;[38] (—) according to Flory[39]).

the resulting poly(ether ester)s can be presented as

$$((nGT)_k\text{–POn})_z$$

in which k represents the number average nGT sequence length and POn denotes the poly(alkylene oxide) unit. Although a large variety of poly(ether ester)s have been prepared, the most important ones are based on ethylene terephthalate (2GT) or butylene terephthalate (4GT), whereas poly(alkylene glycol ether)s from ethylene oxide (PO2), propylene oxide (PO3), or tetramethylene oxide (PO4) are most frequently used.

In our previous paper the structure of the poly(ether ester)s prepared from PVL, DMT, and alkanediols was elucidated.[13] Using the above-mentioned general notation the structure can be indicated as follows,



nG T nG PVL

which can also be represented by

$$((nGT)_k\text{–}n\text{G–PVL})_z$$

in which k represents the number average nGT sequence length. For the nGT–PO4-based poly(ether ester)s a relationship has been reported between k and the mole fraction of nGT units.[37] As shown in Figure 9 T_m increases with increasing k for 4GT–PO4-based poly(ether ester)s.[38] A similar relationship was found for both 3GT–3G–PVL- and 4GT–4G–PVL-based poly(ether ester)s, thus indicating that the increase in T_m with increasing nGT fraction is related to the alkylene terephthalate block length. Figure 9 also shows the relationship between k and T_m using the equation from Flory's theory for extended chains,[39]

$$1/T_m = 1/T_m^\circ + (2R/\Delta H_m^\circ)/(Mk) \quad (5)$$

in which T_m° and ΔH_m° for poly(butylene terephthalate) (PBT) are 236 °C and 140 J/g, respectively, and M = 220 J/g, corresponding to the molar mass of a PBT chain segment. At higher values of k, the poly(ether ester)s have a lower T_m than predicted by theory, which may be due to folding of the chains.

The properties of the 4G–PVL-based copolymers, which are related to the alkylene terephthalate units (ease of processing, melting temperature, crystallization rate, and tensile strength), also show that these copolymers resemble the 4GT–PO4-based poly(ether ester)s, as will be presented in a forthcoming paper.[14] The properties of the 4G–PVL-based copolymers resulting from the nG–PVL segment

(glass temperature, chemical stability, and tear strength) indicate that these copolymers differ from the 4GT–PO4-based poly(ether ester)s,[14] probably because the *n*G–PVL parts of the PVL-based poly(ether ester)s are relatively short and contain both ether and ester bonds.

Conclusions

Poly(ether ester)s were prepared from PVL, DMT, and a homologous series of alkanediols *via* a two-stage melt process. The glass transition temperature of these poly(ether ester)s decreased with the increasing amount of methylene units n in the alkanediol used, whereas both the melting and the crystallization temperatures decreased with increasing n, while showing an odd/even effect. By assuming a planar zigzag structure for these PVL-based copolymers, different crystal packings were proposed for the odd- and even-membered polymers, of which the packing of the former was considered thermodynamically less stable.

The melting behavior of the poly(ether ester)s could be explained by assuming that these copolymers contain a fraction (X_a) of crystallizable alkylene terephthalate units. In accordance with theory, a linear relation was obtained by plotting $1/T_m$ versus $-\ln X_a$ for the 3G–PVL-based poly(ether ester)s, and the enthalpy of fusion was calculated as ΔH_u = 24.7 kJ/mol repeating unit. As expected from theory, this value appeared to be less than determined by other techniques.

In general, properties of polymers are not well developed until a molecular weight of 10 000 is reached. In order to prepare PVL-based copolymers with molecular weights $M_n \geq 10\,000$, several routes, including postcondensation, were studied. By conducting the condensation step at 275 °C for 2.5 h, copolymers with $M_n \geq 10\,000$ could be prepared. Poly(ether ester)s obtained by condensation at 300 °C were of lower molecular weight, which was attributed to the occurrence of side reactions and was confirmed by the results from TGA; i.e. weight loss started at 280 °C. When the polymerization was performed in a batch reactor of a type used in, e.g., PET synthesis, the synthesis of PVL-based poly(ether ester)s resulted in copolymers with $M_n \geq 10\,000$, thus indicating that the described process shows promise for developing new engineering polymers on an industrial scale.

Acknowledgment. The authors thank Mr. N. L. J. Meijerink and Mr. H. M. Schoffeleers (both from DSM Research) for the SEC analysis and for carrying out part of the viscometric measurements, respectively.

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