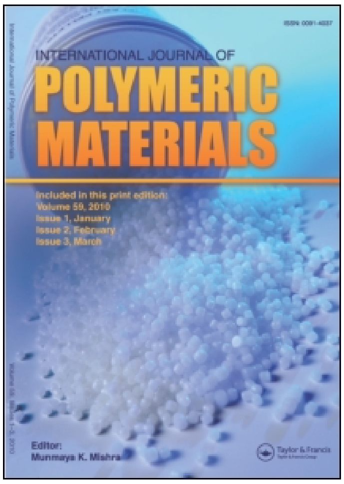

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# Thermoplastic Elastomers 4. Poly(ether-ester-imide)s Derived from Trimellitic Anhydride, 1,6-Diaminohexane, 1,4-Dihydroxybutane and Poly(ethylene oxide)

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Four thermoplastic elastomers having the structure of poly(ether-ester-imide)s, PEEIs, were prepared and characterized. The hard segments were synthesized from 1,4-dihydroxybutane and from an imide dicarboxylic acid based on 1,6-diaminohexane and trimellitic anhydride. Poly(tetramethylene oxide)-1000, poly(ethylene oxide)-1000 or mixtures of both oligoethers served as soft segments. The PEEI based on neat PEO-1000 was also modified by a solid state post-condensation which raised the $\eta_{rel}$ value by a factor three. All PEEIs were characterized by $^1$H NMR spectroscopy, inherent viscosity and DSC measurements, and stress-strain measurements. The PEEIs based on neat PEO-1000 were also characterized by dynamic thermal mechanical analysis, by hysteresis measurements and by melt rheology.

*Keywords*: Thermoplastic elastomers; Poly(ethylene oxide); Polycondensation; Trimellitic anhydride; 1,6-Diaminohexane

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## INTRODUCTION

In previous parts of this series [1, 2] we have described thermoplastic elastomers prepared by transesterification polycondensation of imide monomer **1a** with various poly(tetramethylene oxide) diols (PTMOs) and with poly(ethylene oxide) diols (PEOs). Furthermore, we have reported [3] on thermoplastic elastomers derived from imide monomer **1b** and three different PTMOs. A couple of these poly(ether-ester-imide)s, PEEIs, had good mechanical properties. However, when PTMO-2000 (number average molar mass ($M_n$ = 2000Da)) was used macrophase separation was observed during the polycondensation and even for PTMO-1000 partial macrophase separation was found at the end of the polycondensation process. Furthermore, the rate of crystallization was slower than expected in view of the higher flexibility of imide monomer **1b** relative to imide monomer **1a**. Therefore, we have continued our study of elastomeric PEEIs in this work, using neat PEO-1000 or a combination of PEO-1000 and PTMO-1000, hoping to improve the properties of PEEIs exclusively derived from PTMOs. Finally, the mechanical properties of the best PEEI of this work should be compared to those of the poly(ether-ester) **6**, which was prepared under similar conditions [1] and serves as a model for commercial thermoplastic elastomers [4–6].

## EXPERIMENTAL

### Materials

Titanium tetrabutoxide, 1,6-diaminohexane, 1,4-dihydroxybutane and poly(ethylene oxide) diol (PEO-1000, having a number average molecular weight of 1000 Da) were purchased from Aldrich Co. (Milwaukee, WI, USA). The diols were azeotropically dried with toluene. Trimellitic anhydride was a gift of Dr. Becks AG (Hamburg) and was used as received. The poly(tetramethylene oxide), diol PTMO-1000, was a gift of DSM Research (Geleen, NL) and was azeotropically dried with toluene.

The antioxidant Irganox 1330® and titanium tetrabutoxide were also gifts of DSM Research and were used as received.

## Polycondensations

### *PEEI 5b*

The imide diethyl ester **1b** (262 mmol), 1,4-dihydroxybutane (392 mmol) and poly(ethylene oxide) diol-1000 (92.4 mmol) were weighed into a cyclindrical Büchi® steel reactor equipped with stirrer, distillation head and gas-inlet plus gas-outlet tubes. The antioxidant Irganox-1330 (1.1 g) and 2.75 g of a solution containing 4.0 g $Ti(OBu)_4$ in 1 L of 1,4-dihydroxybutane were added. The reaction mixture was heated in an atmosphere of nitrogen to 200°C over a period of 1h. The temperature was then raised to 225°C and a vacuum of 15–20 mbar was applied for 40 min. Afterwards the temperature was raised to 240°C and maintained for 130 min, whereby a vacuum of 1,5 mbar was applied. The hot melt was finally extruded under pressure into cold water and dried at 60°C *in vacuo*. PEEI **2** was prepared as described previously.

### *PEEI 4*

The imide diethyl ester **1b** (9.53 mmol), 1,4-dihydroxybutane (14.3 mmol), PTMO-2000 (1.68 mmol) and PEO-1000 (1.68 mmol) were weighed into a cylindrical glass reactor equipped with stirrer, gas-inlet and outlet tubes. The antioxidant Irganox-1330® (0.2 g) and a 0.9 g of solution containing 4.0 g $Ti(OBu)_4$ in 1 L of 1,4-dihydroxybutane were added. The reaction mixture was heated in an atmosphere of nitrogen to 200°C over a period of 1h. The polycondensation was conducted as described above for PEEI **5b**.

## Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 25°C. Solutions containing 1 g PEEI in 1 L of azeotropically dried m-cresol were applied.

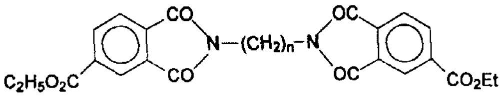
The DSC measurements were performed on a PERKIN Elmer DSC-7 in aluminum pans under nitrogen with a heating rate of 20°C/min. The m.p. of the monomer was determined at a heating rate of 3°C/min.

The IR spectra were recorded with KBr pellets on a Nicolet Md "Impact 410" FT IR-spectrometer.

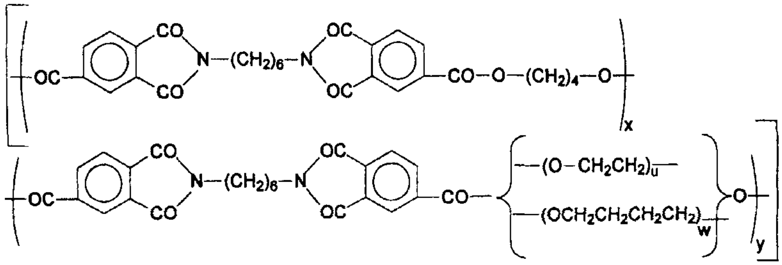
The $^1H$ NMR spectra were recorded with a Bruker AMX 400 FT NMR spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ or a mixture of $CDCl_3$ and trifluoroacetic acid (volume ratio 4 : 1) containing TMS as internal shift reference served as solvent.

The wide angle X-ray measurements were conducted with a Siemens D-500 diffractometer using Ni-filtered $CuK_\alpha$ radiation at 25°C. Films having a thickness of 0.5 mm were melt-pressed and annealed for this purpose.

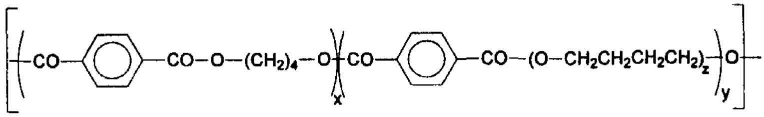
The DMTA measurements were performed on a Rheometrics RSA-II apparatus using annealed melt-pressed films. A frequency of 1 Hz and a heating rate of 3°C/min (starting at −130°C) were used for all measurements.



**1a** n = 4
**1b** n = 6



**2**: PEO/PTMO = 0/100
**3**: PEO/PTMO = 10/90
**4**: PEO/PTMO = 50/50
**5**: PEO/PTMO = 100/O



**6**

For the stress-strain measurements S3A tensile specimens (DIN 53544) were prepared from films having a thickness of 0.5 mm. The measurements were conducted at a constant draw rate of 50 mm/min on a Zwick Md 1445 apparatus and evaluated with the Zwick software 7005. Each value represents the average of 5 measurements. For the hysteresis measurements the same apparatus in combination with the 7007 software was used. The measurements were conducted at 20°C with 10 cycles applying an elongation of 100 or 500% and a draw ratio of 10 mm/min. Each value represents an average of 3 measurements.

## RESULTS AND DISCUSSION

### Syntheses

All polycondensations of this work were conducted with the imide monomer **1b**, the synthesis of which was described in the preceeding part of this series [3]. 1,4-Dihydroxybutane was selected as reaction partner for the formation of the hard segment, because this diol is a standard hard segment component in numerous commercial TPEs, and because it was used in all previous publications of this series [1 – 3]. Poly(tetramethylene oxide) diol and poly(ethylene oxide) diol, having number average molecular weights of 1000 Da, were used as soft segments. The feed ratio of these reaction partners were calculated in such a way that all PEEIs of this work had a hard segment content of 40 weight%. Two PEEIs containing neat PTMO-1000 or neat PEO-1000, and two copolymers containing mixtures of both soft segments were prepared. Their structures are presented in the formulas **2**–**5**. It was observed that during the syntheses of the co-PEEIs **3** and **4** the reaction mixture turned turbid due to partial macrophase separation. In contrast, clear melts were obtained throughout the syntheses of PEEIs **2** and **5**. This trend is surprising and suggests that soft segments (including imide units) based on PEO and soft segments derived from PTMO are not completely miscible.

As a consequence of this observation it was concluded that the PEEI **5** might have more interesting properties than the co-PEEIs **3** and **4**, and thus, a larger quantity of PEEI **5** was synthesized and labeled **5b**. A part of **5b** was subjected to a post-condensation in the solid state and

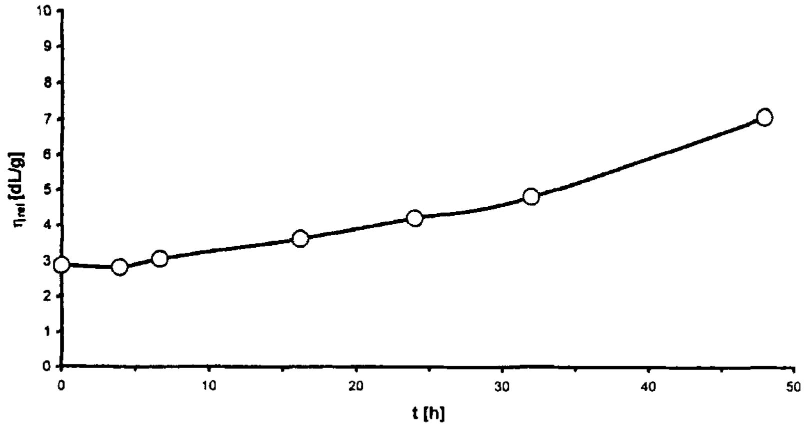


FIGURE 1 Influence of the solid state post-condensation on the solution viscosity of PEEI **5b**.

the resulting PEEI was labeled **5c**. The success of this post-condensation is illustrated by Figure 1, showing the steady increase of the solution viscosity with time. The chemical structure and composition of all PEEIs were checked by $^1H$ NMR spectroscopy (as demonstrated by Fig. 2) and satisfactory agreement between the NMR spectra and expected structures was found in all cases (the spectrum of PEEI **2** was published in the preceeding part [3]. Furthermore, IR spectra were recorded from KBr pellets and found again to agree with the expected structure. These IR-spectra were quite analogous to those displayed and discussed in the 2nd part of this series.

Finally, it should be mentioned that the inherent viscosities of all PEEIs were high enough to allow for representative measurements of physical and mechanical properties and for comparison with the poly(ether-ester) **6**. This poly(ether-ester) served as reference and model of commercial TPEs, such as the Arnitel® series of the DSM company. Synthesis and properties of poly(ether-ester) **6** were published in the first part of this series of papers [1].

## Physical Properties

In order to demonstrate the crystallinity of the hard segments of the new PEEIs and to enable a comparison of the crystal structure, WAXS

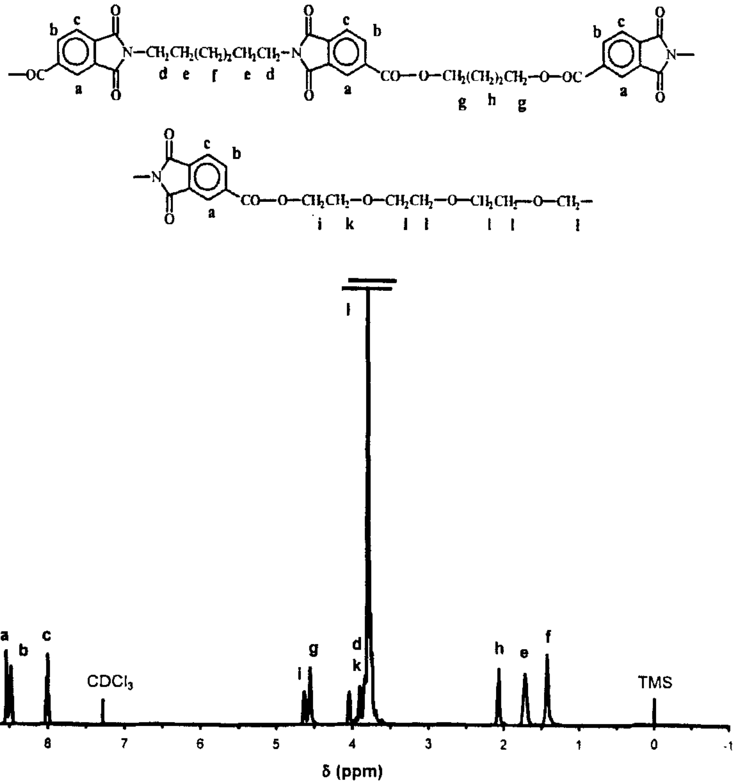


FIGURE 2 400 MHz $^1$H NMR spectrum of PEEI **5b**.

powder patterns were recorded. The WAXS powder patterns of PEEI **5a** (or **5b** and **5c**) displayed in Figure 3 suggests the existence of orthorhombic or monoclinic chain-packing. A comparison with the previously published [3] powder pattern of PEEI **2** indicates that all reflections above $2\vartheta = 10°$ were identical, whereas a difference was found at lower scattering angles. Two weak reflections are detectable at 7.0 and 9.0 Å (calculated as first order reflections *via* the Bragg equation), whereas only one reflection at 8.7 Å was found in the case of PEEI **2**. However, a detailed analysis of this phenomenon was not intended in this work.

The DSC measurements, conducted with a standard heating and cooling rate of 20°C/min, revealed for all PEEs a melting endotherm in the temperature range of 190–202°C in the first heating curve and

TABLE I Physical properties of the poly(ether-ester-imide)s prepared in this work from imide monomer **1b**

| *PEEI* | *PEO* *PTMO* | $\eta_{inh}$[a] *(dL/g)* | $T_m$[b] *(1. heat)* *(°C)* | $T_m$[b] *(2. heat)* *(°C)* | *Tensile stress at 100% longation (MPa)* | *Tensile stress at break (MPa)* | *Elongation at break (%)* |
|---|---|---|---|---|---|---|---|
| **2** | 0/100 | 1.10 | 197 | 199 | 14.2 | 34.5 | 615 |
| **3** | 10/90 | 1.22 | 202 | 198 | 12.3 | 32.9 | 617 |
| **4** | 50/50 | 1.36 | 190 | 188 | 11.3 | 34.9 | 666 |
| **5a** | 100/0 | 1.19 | 196 | 192 | – | – | – |
| **5b**[c] | 100/0 | 1.38 | 196 | 193 | 12.9 | 28.0 | 573 |
| **5c**[d] | 100/0 | – | – | – | 9.7 | 53.0 | 783 |

[a] Measured at 25°C with c = 1g/L in m-cresol.

[b] From DSC measurements with a heating rate of 20°C/min.

[c] Upscaling of the synthesis of **5a**.

[d] Obtained by post-condensation of **5b** at 175°C.48 h, $\eta_{rel}$ had increased from 2.7 dl/g to 7.1 dL/g.

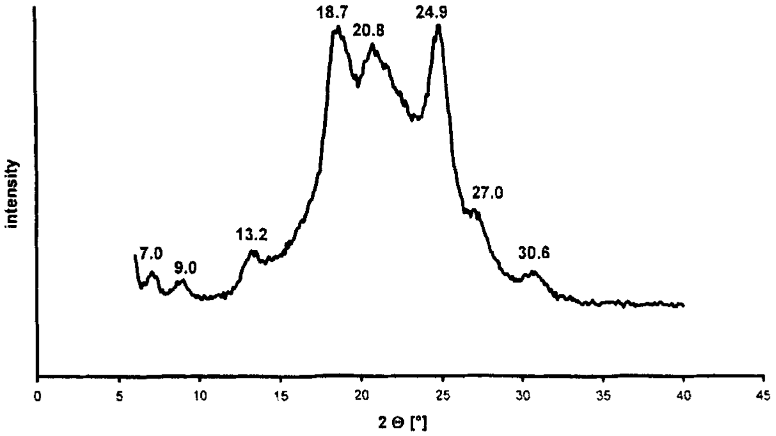


FIGURE 3 WAXS powder pattern of PEEI **5a**.

nearly the same values in the second heating trace. Interestingly a minimum of the melting temperature ($T_m$) was found for the 50/50 co-PEEI **4**. A similar minimum was observed for analogous co-PEEIs of the imide monomer **1a**, and thus, must be considered as a reproducible structure-property relationship. However, it is difficult to understand why the mixture of the soft segments reduces size or perfection of the crystallites of hard segments. The macrophase separation in the polycondensation process of **3** and **4** should have favored the formation of longer hard segments, and thus, higher $T_m$s. However, the more important result is the absence of a well defined crystallization exotherm in the cooling trace. Furthermore, a recrystallization exotherm was found in the second (and third) heating curve, proving a relatively slow crystallization when compared to the PEE **6**. Therefore, it may be concluded on the basis of DSC measurements that the PEEIs based on PEO segments and those derived from PTMO show similar rates of crystallization.

Dynamic mechanical thermoanalysis (DMTA) of the PEEIs **2** and **5b** gave the following information. In the case of **5b**, storage modulus E', loss modulus E" and tan $\delta$ are typical for a mainly two-phasic system, and thus, analogous to the DMTA patterns of PEEI **2** and PEE **6** (Fig. 4). This point needs to be emphasized, because the PEEIs derived from imide monomer **1a** showed a more complex phase behavior [1]. In the case of **5b** an E' value of 139 MPa was found at

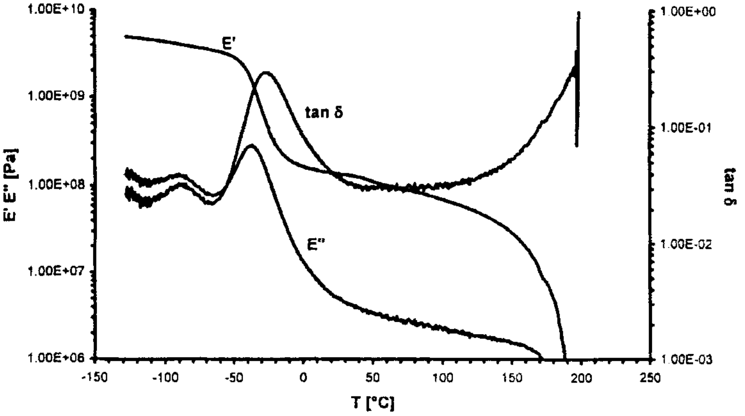


FIGURE 4 Dynamic mechanical thermoanalysis of PEEI **5b**.

+20°C and a maximum of $\tan\delta$ at −27°C, quite similar to the values of **2**. However the E” maximum of **5** appeared at −37°C maximum but at −59°C in the case of **2**. The reason for this apparent contradiction is the fact that the phase transitions were rather flat in the case of **2** and sharp for PEEI **5**. The DMTA values of PEE **6** show: E' = 159 MPa at 20°C, $\tan\delta_{max} = -51°C$ and $E''_{max} = -67°C$. Hence, it is clear that all PEEIs derived from imide monomer **1b** possess higher glass-transitions than PEE **6** due to the presence of the less mobile imide units (compared to terephthalic acid) in the amorphous phase.

The stress-strain measurements of the PEEIs **2**–**5b** are displayed in Figure 5 and revealed little differences. PEEI **2** shows a slightly better performance in terms of tensile stress than the PEO containing TPEs. However, the most interesting comparison concerns the PEEIs **5b** and **5c**. As demonstrated in Figure 6, the elongation at break of **5c** is considerably higher due to the higher molecular weight. The initial tensile stress of **5c** is lower than that of **5b**, but increases more rapidly and finally reaches the double value of **5b**.

This trend may be explained by an initially less perfect crystallization of **5c** which is typical for polymers having higher molecular weights. However increasing elongation favors stress-induced crystallization with the consequence of higher tensile stress values. The mechanical properties of the PEEIs **5b** and **5c** were also compared by

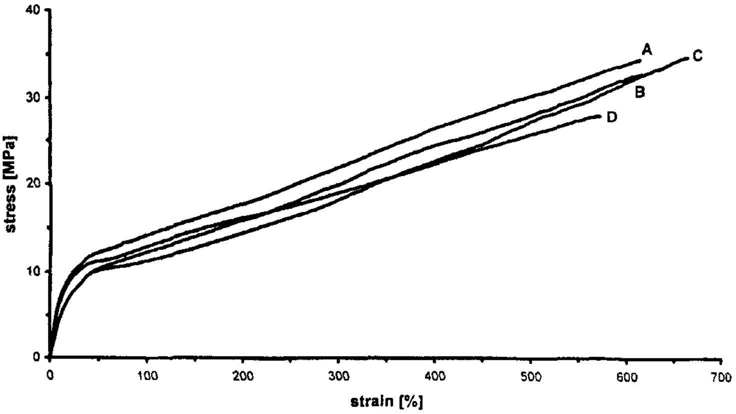


FIGURE 5 Stress-strain measurements of: A) PEEI **2**, B) PEEI **3**, C) PEEI **4**, D) PEEI **5b**.

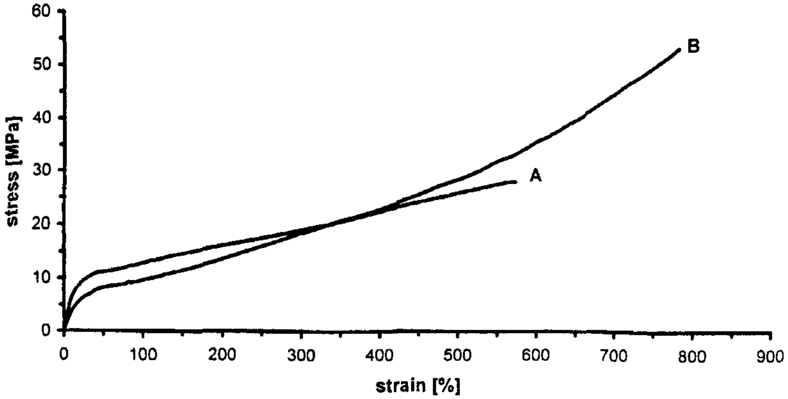


FIGURE 6 Stress-strain measurements of: A) PEEI **5b**, B) PEEI **5c**.

hysteresis measurements at an elongation of 500%. As illustrated in Figures 7A and 7B the elongation (strain) of **5c** begins at slightly lower stress values (approx. 8 instead of 10 MPa) but ends at a value of 30 MPa, whereas **5b** reaches the maximum around 25 MPa. In contrast, the elastic recovery (permanent set) of **5c** goes down to a region of 230–270% elongation, whereas the elastic recovery of **5b** stops in the region of 260 to 300°C. In other words the post-condensation had indeed the consequence of a better mechanical performance although the difference is not really significant.

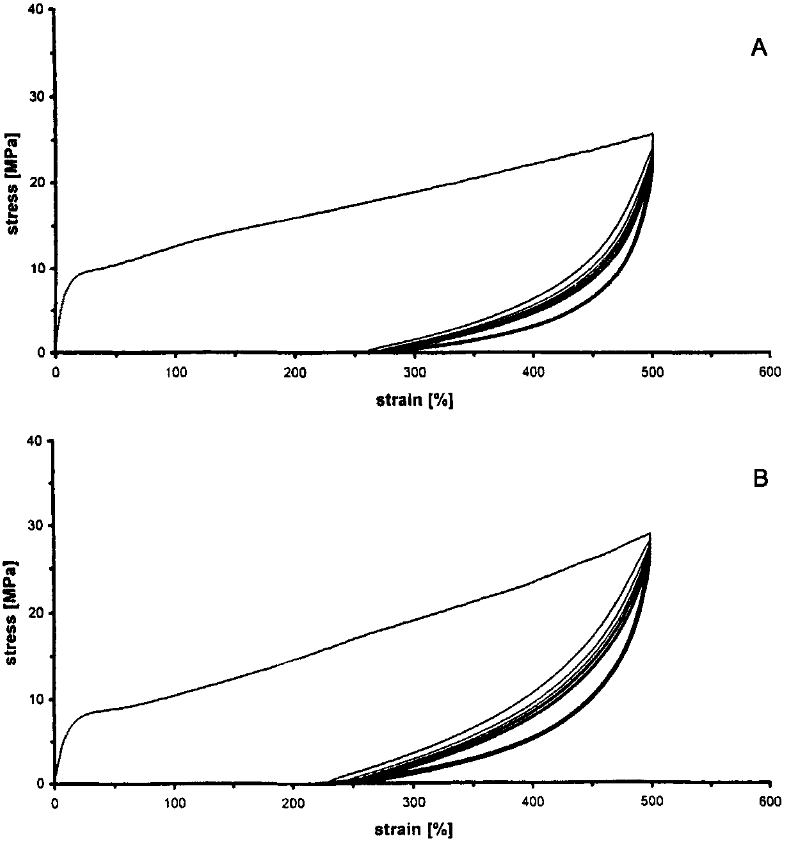


FIGURE 7 Hysteresis measurements at 500% elongation: A) PEEI **5b**, B) PEEI **5c**.

Furthermore, it is noteworthy that the mechanical properties of **5c** even surpass those of PEE **6**. For this poly(ether ester) the tensile stress at 500% elongation was found around 24 MPa (29 MPa for **5c**) and the permanent set was in the range of 370–390% elongation. A deeper understanding of these mechanical properties and the differences between the TPEs **5b**, **5c** and PEE **6** requires a detailed analysis of their morphologies which was beyond the scope of this study.

Finally the properties of molten PEEI **5b** were characterized by dynamic rheological measurements (Fig. 8). These measurements were conducted at 240°C under nitrogen with a frequency sweep from

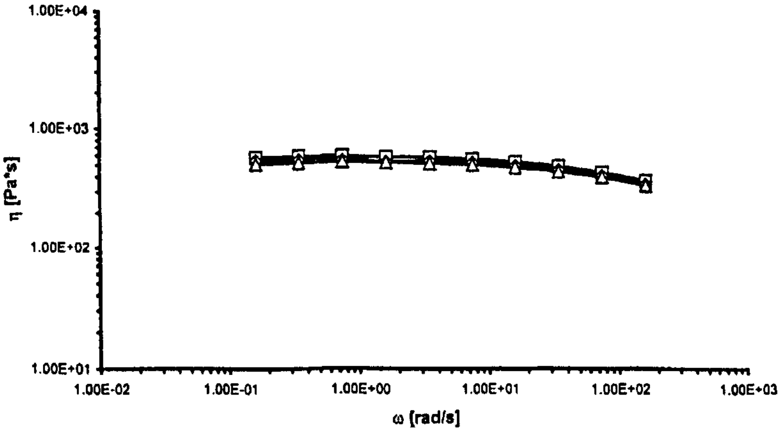


FIGURE 8 Dynamical rheological measurements of PEEI **5b** in the melt at 240°C after preheating of 5 (Δ), 10 (□) and 15 min (o).

$10^{-1}$ (rad/s) to $2 \times 10^2$ (rad/s). The time of the preheating was varied from 5 to 10 and 15 min. The melt viscosity decreased from 576 Pas to 543 and finally to 511 Pas with longer preheating times. These values indicate a slow but steady degradation of this TPE, but nearly identical values were found for PEE **6**.

## CONCLUSION

The results presented in this paper allow the following conclusion. When in PEEIs of structure **2** the PTMO-1000 soft segment is gradually replaced by PEO-1000 the mechanical properties slightly decrease and macrophase separation occurs during the synthesis with mixtures of the two soft segments. The best results were obtained for PEEIs exclusively containing PEO-1000 soft segments and in this case a solid state post-condensation proved to favor better mechanical properties. The higher molecular weight obtained by the post-condensation resulted in a higher elongation at break in a higher tensile stress at break and in a better performance in the hysteresis measurements (*i.e.*, better elastic recovery). The performance of **5c** in these mechanical tests was also superior to that of the standard TPE **6**. Furthermore, it may be an advantage that the polar PEO segments are oil repellent. On the other hand, it is obvious that the PEO segments favor an uptake of water compared to less polar PTMO containing chains.

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