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### THERMOPLASTIC ELASTOMERS. II. POLY(ETHER-ESTER-IMIDE)S BASED ON 1,4-DIAMINO BUTANE, TRIMELLITIC ANHYDRIDE, 1,4-DIHYDROXYBUTANE, AND POLY(ETHYLENE OXIDE)S

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## THERMOPLASTIC ELASTOMERS. II. POLY(ETHER-ESTER-IMIDE)S BASED ON 1,4-DIAMINOBTUTANE, TRIMELLITIC ANHYDRIDE, 1,4-DIHYDROXYBUTANE, AND POLY(ETHYLENE OXIDE)S

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### ABSTRACT

A series of new poly(ether-ester-imide)s, PEEIs, was prepared from an imide dicarboxylic acid based on 1,4-diaminobutane and trimellitic anhydride. This imide dicarboxylic acid polycondensed with 1,4-dihydroxybutane formed the hard segments and poly(ethylene oxide), PEO-1000, or mixtures of PEO-1000 and poly(tetramethylene oxide), PTMO-1000, were used as soft segments. Whenever PTMO-1000 was used as comonomer, macrophase separation was observed at the end of the polycondensation. However, this macrophase separation had little influence on the mechanical properties. A poly(ether-ester-imide), PEEI, containing neat PEO-1000 was characterized by dynamic mechanical thermoanalysis, stress-strain and hysteresis measurements, and by melt rheology. The mechanical properties were compared with those of an analogous PEEI containing neat PTMO-1000 and with those of a poly(ether-

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ester), PEE, based on poly(butylene terephthalate) hard segments and PTMO-1000.

*Key Words:* Thermoplastic elastomers; Poly(ether imide)s; 1,4-Diaminobutane; Poly(ethylene oxide) diols; Trimellitic anhydride.

## INTRODUCTION

In the first part of this series [1], a new group of poly(ether-ester-imide)s, PEEIs, was prepared by polycondensation of the imide monomer 1 with 1,4-dihydroxybutane and poly(tetramethylene oxide)s. Depending on the length of the PTMO soft segment three classes of PEEIs (2–4) were obtained which were varied with respect to the hard segment/soft segment ratio. It was found that when PTMO-1000 and a hard segment content >30 wt% was used, macrophase separation set in at the end of the polycondensation process. The macrophase separation was much more pronounced and occurred much earlier in the polycondensation when PTMO-2000 was used. This macrophase separation is unfavorable for the mechanical properties, because it usually has the consequence that the coupling of hard and soft segments is incomplete.

In this connection, it was the purpose of this work to synthesize and characterize an analogous series of PEEIs containing PEO segments either alone or in combination with PTMO segments having the same number average molecular weight ( $M_n = 1000$  Da). It should be elucidated, if the admixture of the highly polar PEO-1000 to the less polar PTMO-1000 prevents the phase separation during the polycondensation process. Furthermore, the basic physical properties of these new PEEIs (**5b–e** and **6**) should be determined. Finally, the mechanical properties should be compared with those of a poly(ether-ester), PEE **7**, which served as a model of commercial thermoplastic elastomers (TPEs). Generally, commercial TPEs, having a poly(ether-ester) structure, are based on poly(butylene terephthalate) hard segments [2–8] due to their rapid crystallization and favorable melting temperature.

## EXPERIMENTAL

### Materials

Trimellitic anhydride was a gift of BASF AG (Ludwigshafen, Germany) and was used as received. 1,4-Diaminobutane, 1,4-dihydroxybutane, PTMO-1000 and PEO-1000 were purchased from Aldrich Co. (Milwaukee, Wisconsin). The glycols were dried by azeotropic distillation with toluene, and the 1,4-dihydroxybutane was distilled *in vacuo*. The imide monomer 1 was prepared from trimellitic anhydride and 1,4-diaminobutane as described in Part 1 of this series [1]. The antioxi-

dant Irganox 1330<sup>®</sup> and titanium tetrabutoxide were gifts from DSM Research (Geleen, The Netherlands) and were used as received.

### Polycondensations

#### PEEI 5d

Imid monomer 1 (9.95 mmol), 1,4-dihydroxybutane (14.9 mmol), PTMO-1000 (1.72 mmol), PEO-1000 (1.72 mmol), Irganox-1330<sup>®</sup> (40 mg), and a 40 mg/ml solution of Ti(OBu)<sub>4</sub> in 1,4-dihydroxybutane (250 mg) were weighed into a cylindrical glass reactor equipped with a mechanical stirrer and gas-inlet and gas-outlet tubes. The reactive mixture was rapidly heated to 195°C and stirred at this temperature for 1 hour. The polycondensation was then continued for 1 hour at 210°C and for another hour at 220°C. The liberated ethanol was removed with a slow stream of nitrogen. Finally, the melt was stirred at 250°C for 2.5 hour whereby a vacuum of 0.1 mbar was applied. The hot melt was mechanically removed from the reactor, cooled with cold water, and dried at 60°C *in vacuo*.

The PEEIs **5e** and **5e'** (the tenfold molar quantities were used) were prepared analogously. No PTMO-1000 was added, but PEO-1000 in a quantity of 3.43 mmol.

#### PEEI 6

The same procedure as for **5e** was used, but a PEO having a number average molecular weight of 1550 Da was added (3.44 mmol).

### 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.

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

The <sup>1</sup>H NMR spectra were recorded with a Bruker AMX 400 FT NMR spectrometer in 5 mm o.d. sample tubes. A mixture of CDCl<sub>3</sub> 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 Cu-K<sub>α</sub> radiation at 25°C. Films having a thickness of 0.5 mm were melt-pressed for this purpose and annealed.

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.

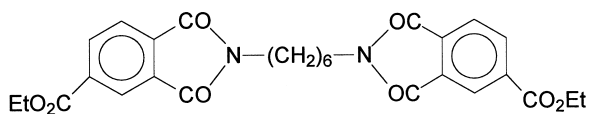
For the stress-strain measurements, S3A tensile specimens (DIN 53544) were prepared from films having a thickness of 0.5 mm. The measurements were conducted at a constant draw rate of 50 mm/min on a Zwick Md 1445 apparatus and evaluated with the Zwick software 7005. Each value represents the average of five measurements. For the hysteresis measurements the same apparatus in combination with the Zwick 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 three measurements.

The dynamic melt viscosity was studied by a Rheometrics RS 200 rheometer in a plate-plate configuration with a plate diameter of 25 mm and a gap of 1 mm. The rheological data were recorded with a Rheometrics Rhios 4.4.4 software as a function of frequency in the range of 10<sup>-1</sup> to 102 rad/s with a strain of 2% (in the linear viscoelastic regime). The experiments were performed at a temperature of 240°C under nitrogen.

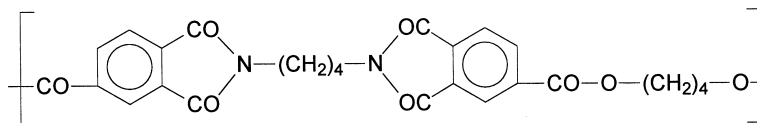
## RESULTS AND DISCUSSION

### Syntheses

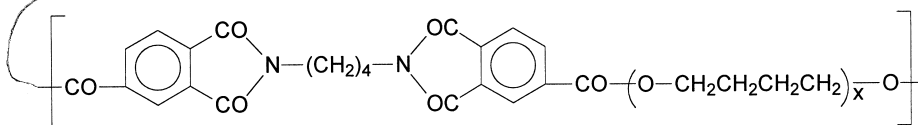
All syntheses were conducted in the same way, namely by transesterification and polycondensation of the imide diethyl ester **1** with 1,4-dihydroxybutane and PEO-1000 or mixtures of PEO-1000 and PTMO-1000. These polycondensations were catalyzed by titanium tetrabutoxide and an antioxidant was added to avoid O<sub>2</sub> initiated crosslinking. From all experiments, PEEIs having inherent viscosities around or above 1dL/g, were obtained which were high enough to allow for informative mechanical measurements. When neat PEO-1000 was used as a reaction partner of monomer **1**, the reaction mixture remained homogeneous over the whole course of the polycondensation (PEEI **5e**). In order to obtain a larger quantity for a more extensive characterization, the polycondensation was repeated with larger amounts of monomers and the resulting PEEI **5e'** had a higher molecular weight (Table 1). This is a typical consequence of upscaling polycondensation experiments which has mainly two reasons. First, the accuracy of weighing in larger quantities of starting materials is higher. Secondly, the surface/mass ratio of the reaction mixture is lower, and thus, a negative influence of different volatilities of monomers on the stoichiometry is reduced. Furthermore, a polycondensation was performed using a PEO-1550 (i.e., M<sub>n</sub>=1550 Da) to find out if the reactive mixture remains homogeneous and how the mechanical properties respond to a moderate increase of the PEO length (PEEI **6**). Again, a homogeneous reaction mixture was observed over the full course of the polycondensation.



1



hard segment

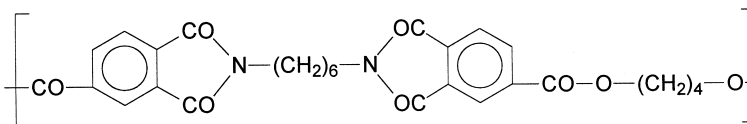


soft segment

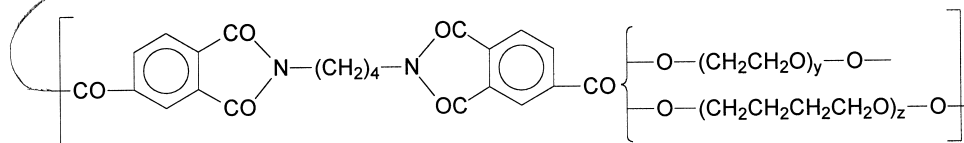
PEEI 2: x = PTMO-650

PEEI 3: x = PTMO-1000

PEEI 4: x = PTMO-2000



hard segment



soft segment

PEEI 5a: PEO/PTMO = 0/100

PEEI 5b: PEO/PTMO = 10/90

PEEI 5c: PEO/PTMO = 25/75

PEEI 5d: PEO/PTMO = 50/50

PEEI 5e: PEO/PTMO = 100/0

*Structure 1.*

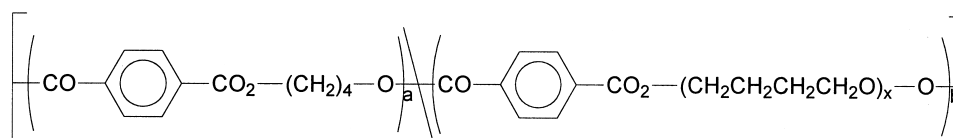
**Table 1.** Composition and Properties of Poly(Ether-ester-imide)s Containing Poly(Ethylene Oxide) and/or Poly(Tetramethylene Oxide) Soft Segments

Polymer	PEO-1000 PTMO-1000	Hard Segments [weight %] <sup>c)</sup>	Poly(alkylene oxide) [weight %] <sup>c)</sup>	$\eta_{inh}^a)$ [dL/g]	$T_m$ [°C] <sup>b)</sup> 1. heat	$T_m$ [°C] <sup>b)</sup> 2. heat
PEEI <b>5a</b>	0/100	40	42.8	1.25	209	207
PEEI <b>5b</b>	10/90	40	42.8	1.31	209	209
PEEI <b>5c</b>	25/75	40	42.8	1.39	201	205
PEEI <b>5d</b>	50/50	40	42.8	1.30	196	196
PEEI <b>5e</b>	100/0	40	42.8	100	212	213
PEEI <b>5e'</b>	100/0	40	42.8	1.30	207	209
PEEI <b>6</b>	PEO-1550	40	47.6	1.30	222	223
PEEI <b>7</b>	0/100	52.4	42.0	1.40	194	196

<sup>a)</sup> measured at 25°C with  $c=lg/L$  in m-cresol

<sup>b)</sup> from DSC measurements with a heating rate of 20°C/min

<sup>c)</sup> the difference to 100% represents imides units being part of soft segments



Structure 2.

In contrast to these results obtained with neat PEOs, all polycondensations performed with mixtures of PEO-1000 and PTMO-1000 showed a macrophase separation in the latest stage of the reaction process. The demixing began earlier when neat PTMO was used (PEEI 5a) and the addition of PEO delayed the demixing.

All PEEIs were characterized by IR and  $^1\text{H}$  NMR spectra. Whereas, the IR spectrum of a PEEI exclusively containing PTMO soft segments was published in the first part of this series [1], the spectra of the 50:50 copolymer PEEI 5d and the spectrum of the “PEO homopolymer” PEEI 5e' are presented in this work (Figures 1A and 1B). Characteristic for all PEEIs are three “CO-bands” around 1730–1770  $\text{cm}^{-1}$  (imide rings), 1690–1720  $\text{cm}^{-1}$  and around 1640  $\text{cm}^{-1}$ . Conspicuous differences are observable in the range of 1000–1300  $\text{cm}^{-1}$ , where the PEO segments display a particularly strong CO stretch vibration at 1250  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum of PEEI 5e' displayed in Figure 2 illustrates exemplarily the good agreement between the  $^1\text{H}$  NMR spectra and the expected structures.

### Physical Properties

The crystallinity of the hard segments was checked by wide-angle X-ray scattering (WAXS) measurements. These powder patterns (exemplarily exhibited for PEEI 5e' in Figure 3) proved to be in agreement with our previous study [1] that the hard segments adopt an orthorhombic or monoclinic chain packing and not a hexagonal one. Interestingly, the WAXS patterns of the PEO containing PEEIs 5e and 6 were somewhat different from those of PTMO containing PEEIs such as 5a, although the crystallites of the hard segments should be identical. However, a detailed study of this point was not intended in this work.

The DSC measurements confirmed the crystallization of all PEEIs. Quite analogous to the PTMO containing PEEIs described previously all PEO containing PEEIs crystallized slowly, but in two cases a broad, flat exotherm was detectable in the cooling curve at a cooling rate of  $-20^\circ\text{C}/\text{min}$ . Possibly the PEO segments act as a kind of plasticizer for the hard segments accelerating their crystallization. In contrast, no crystallization exotherm was observed in the cooling trace of PEEIs exclusively containing PTMO [1]. However, all PEEIs of this and our previous work exhibited a crystallization exotherm in the second heating curve. For the melting temperatures ( $T_m$ s) a clear trend was observable. The lowest value was determined for the 50:50 “copolymer” 5d (Table 1). The homopolymers 5a and 5e or 6 had higher  $T_m$ s and the highest one was found for PEEI 6. These higher  $T_m$ s may be attributed to a more perfect microphase separation in the



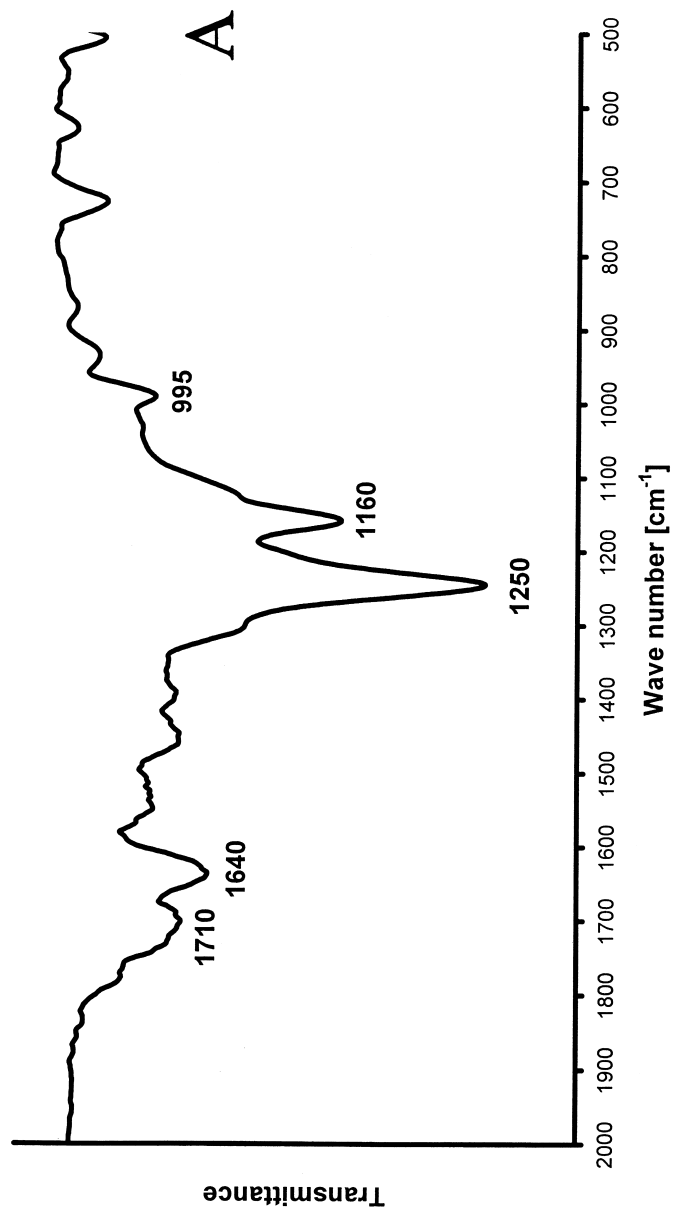


Figure 1. IR spectra (KBr pellets): (A) of PEEI 5d, (B) of PEEI 5e'.

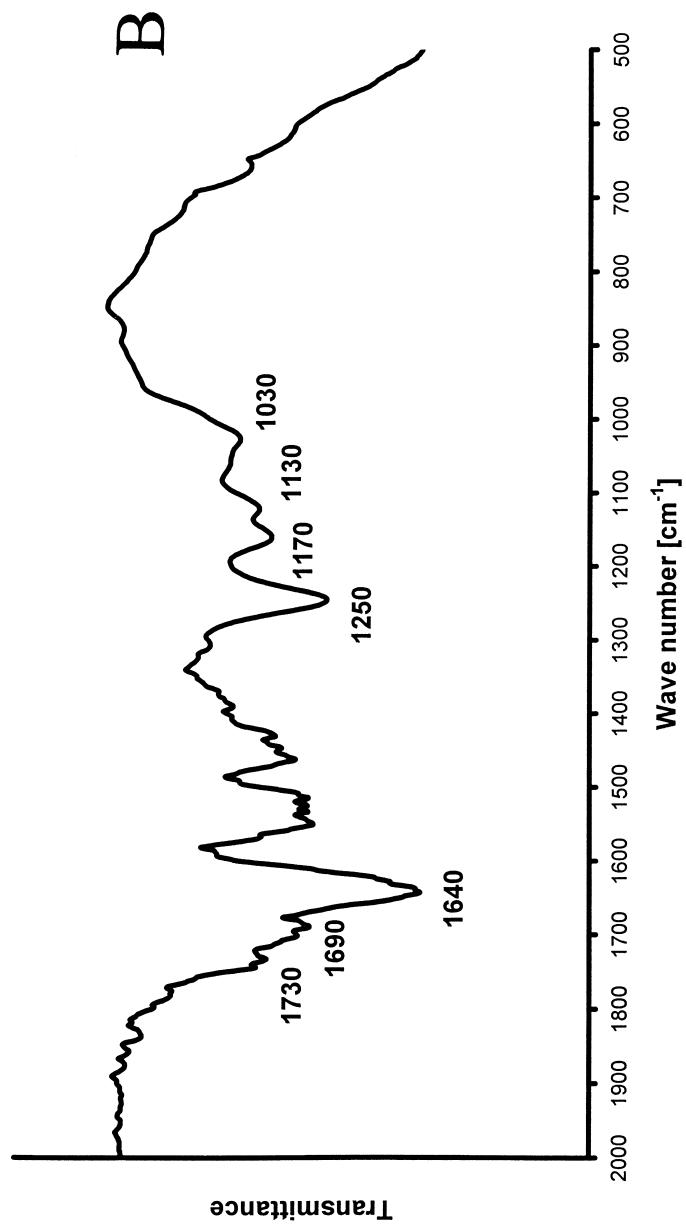


Figure 1. Continued

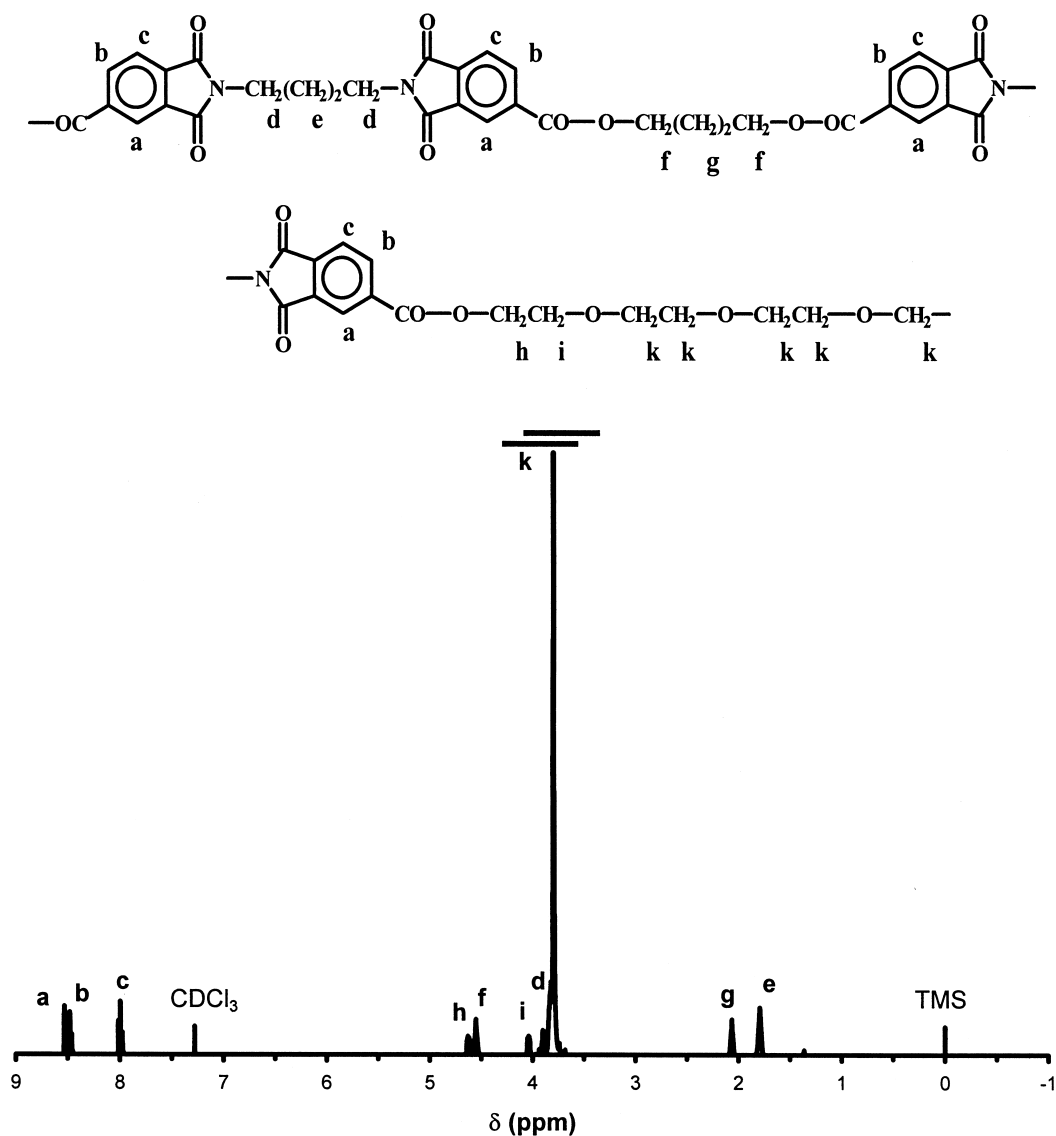


Figure 2. 400 MHz <sup>1</sup>H NMR spectrum of PEEI 5e'.

solid state when compared to the PEEI **5d**. However, PEEI **6** has longer hard segments than the PEEIs **5a–e** and this structural property makes certainly a major contribution to its relatively high  $T_m$ .

The stress-strain measurements of **5a–5d** did not reveal a clear trend. The curves displayed in Figure 4 and the data collected in Table 2 indicate that the highest elongation at break was found for **5a**, but the highest tensile stress values (at 100% elongation) were detected for **5b**. The tensile stress values of **5b** were even higher than those of **5a** up to an elongation of 400%, and thus, also this com-

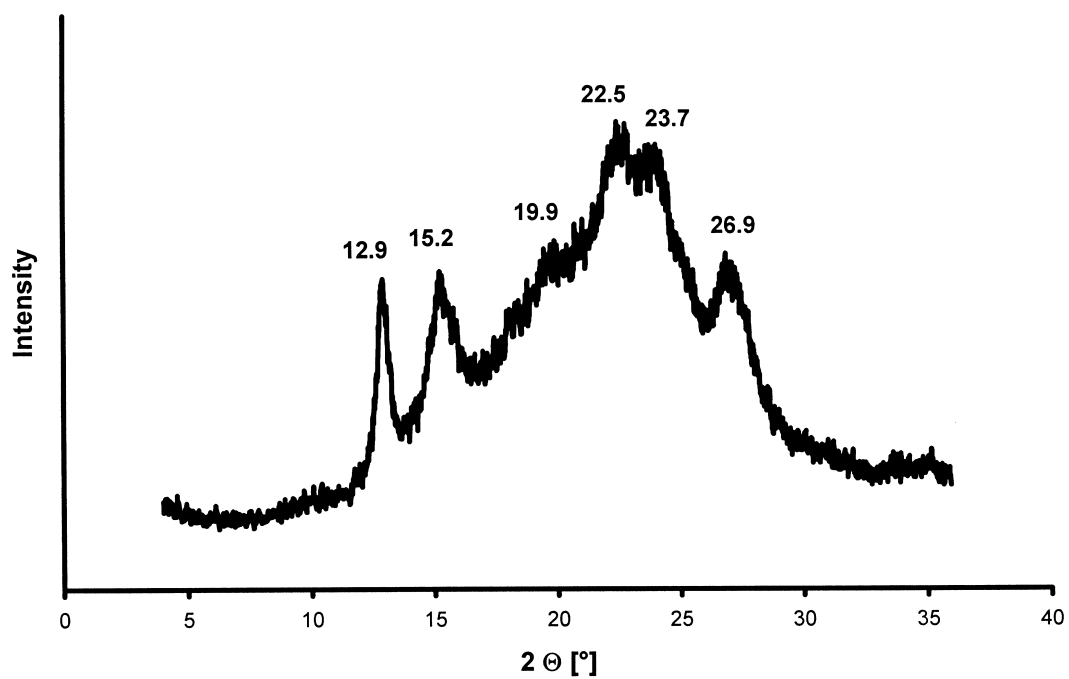


Figure 3. WAXS powder pattern of PEEI 5e'.

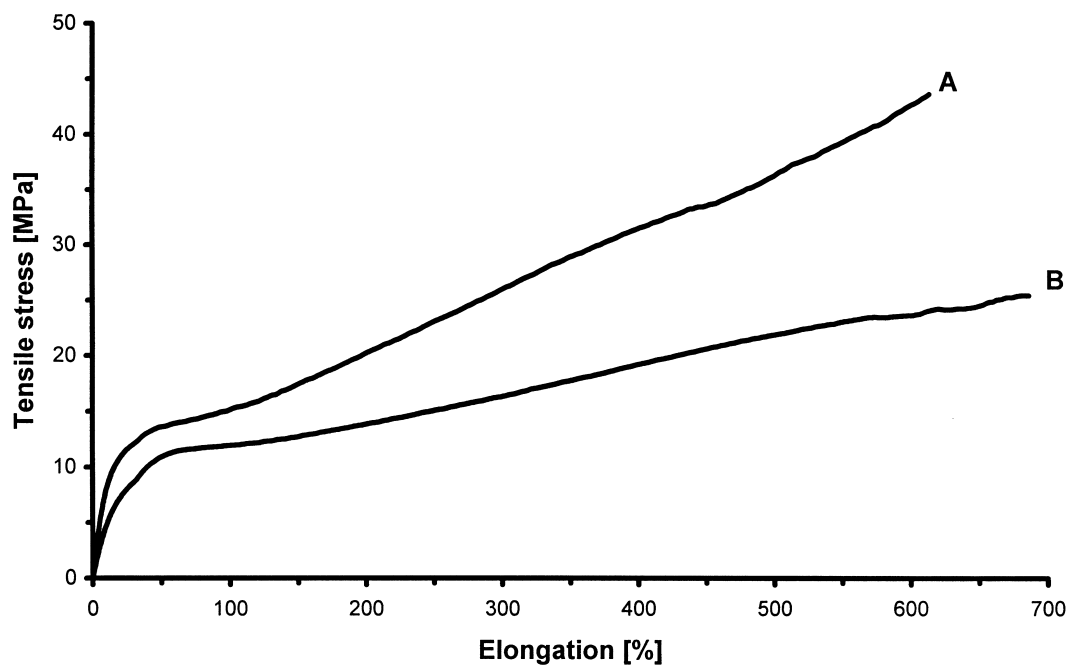


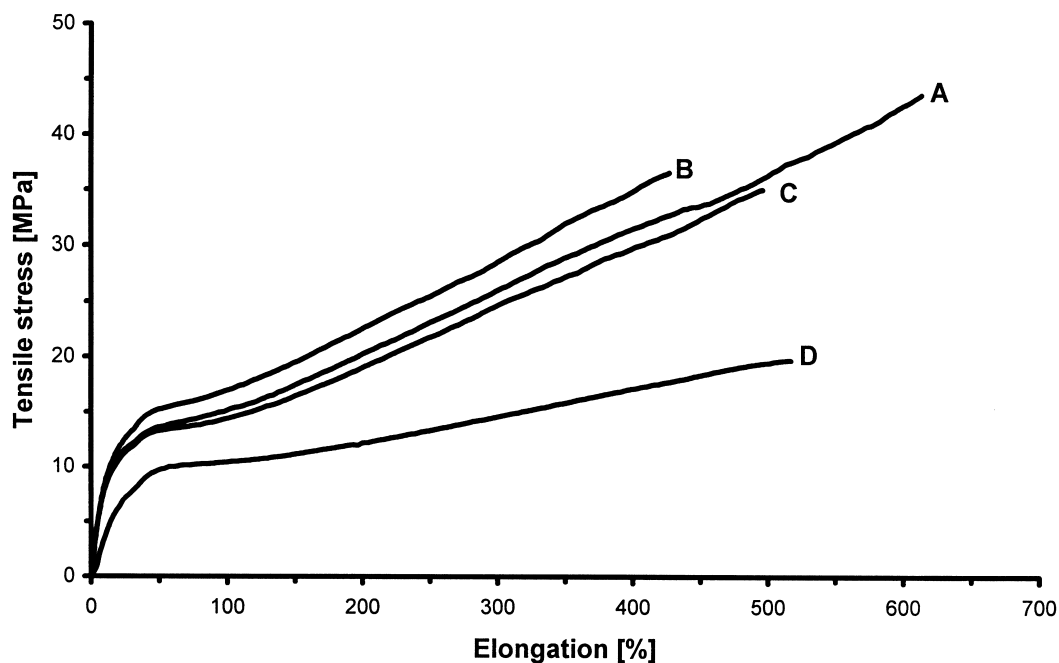
Figure 4. Stress-strain measurements of: PEEI 5a, b.

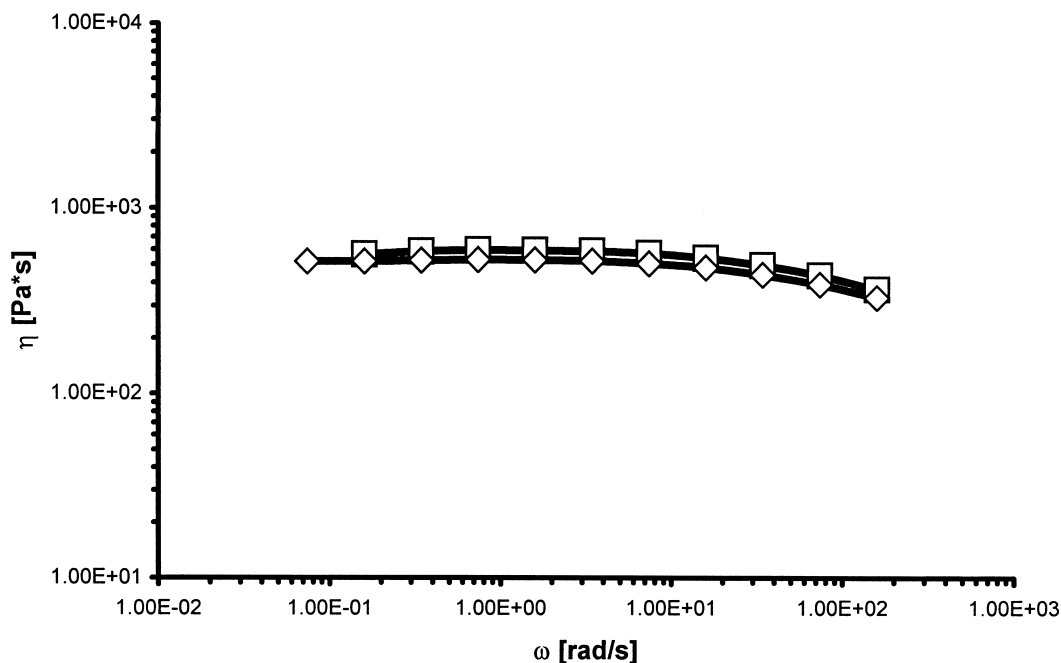
**Table 2.** Mechanical Properties of the PEEI **5a-e'**, **6**, and PEE **7**

Polymer	Tensile Stress at 100% Elongation [Mpa]	Tensile Stress at Break [Mpa]	Elongation at Break [%]
PEEI <b>5a</b>	15.0	43.5	615
PEEI <b>5b</b>	17.0	36.5	430
PEEI <b>5c</b>	14.5	35.0	495
PEEI <b>5d</b>	10.5	20.0	520
PEEI <b>5e'</b>	13.5	27.0	625
PEEI <b>6</b>	12.0	22.5	685
PEE <b>7</b>	14.0	35.5	735

parison denies any simple trend. The most conspicuous result of these measurements is finding that partial macrophase separation during the polycondensation of **5b–5c** does not have negative consequences for the mechanical properties when compared to the PEEIs **5e'** or **6** (see curve B, Figure 5). The comparison of the PEEIs **5e'** and **6** revealed the expected differences. The longer soft segment of **6** has the consequence of lower tensile stress values, whereas the elongation at break was slightly higher (Figure 5).

For comparison with the previously described PEEI **5a** [1] and poly(ether-ester) **7** [1] the characterization of PEEI **5e'** (having a polyether soft segment of

**Figure 5.** Stress-strain measurements of: (A) PEEI **5e'**, (B) PEEI **6**.



**Figure 6.** Dynamic rheological measurements of PEEI **5e'** in the melt at 240°C after A preheating of 5 minutes (□) or 15 minutes (◇).

the same Mn as **5a** and **7**) was extended to rheological measurements, dynamic mechanical thermoanalysis (DMTA) and hysteresis measurements. The dynamic rheological measurements were performed in the melt at 240°C over a broad frequency range. As illustrated in Figure 6, the viscosity changed little with the frequency suggesting a nearly Newtonian flow and different periods of preheating again had little effect indicating an excellent melt stability. Exactly the same results were obtained for both PEEI **5a** [1] and PEE **7** [1]. The DMTA measurements summarized in Figure 7 showed a pattern which largely agreed with the DMTA curves found for PEE **7** [1]. A first steep decrease of the storage modulus and increase of the loss modulus were found at the glass transition around  $-20^{\circ}\text{C}$  and a steep decrease of both storage and loss moduli in combination with the melting process of the hard segments around  $200^{\circ}\text{C}$ . In the case of PEE **7**, the glass transition is lower ( $-50^{\circ}\text{C}$ ) due to the higher flexibility of the PTMO chains. However, both TPEs have in common that the pattern of the DMTA curves corresponds to a simple two-phasic system, consisting of crystalline hard segments and amorphous hard plus soft segments. In the case of **5a** and similar PEEIs based on PTMO [1] the DMTA pattern showed characteristic differences due to an incomplete microphase separation and a more complex amorphous phase. This result is remarkable, because in the molten state during the polycondensation the PTMO based systems showed macrophase separation whereas not the PEO based PEEIs did not. The most likely explanation is the

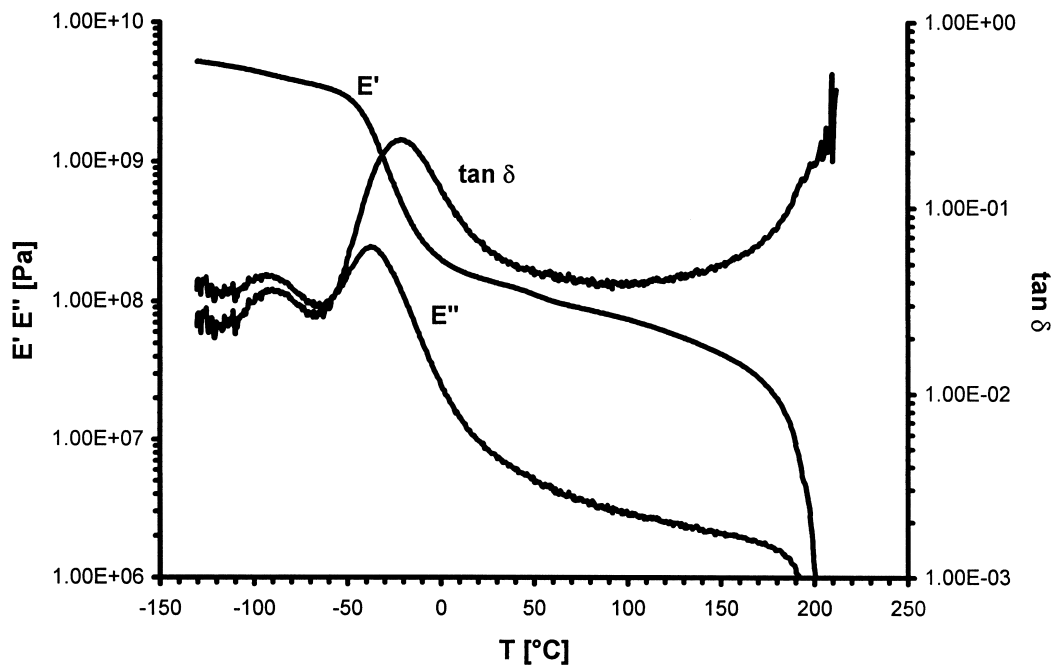


Figure 7. DMTA-measurements of PEEI 5e'.

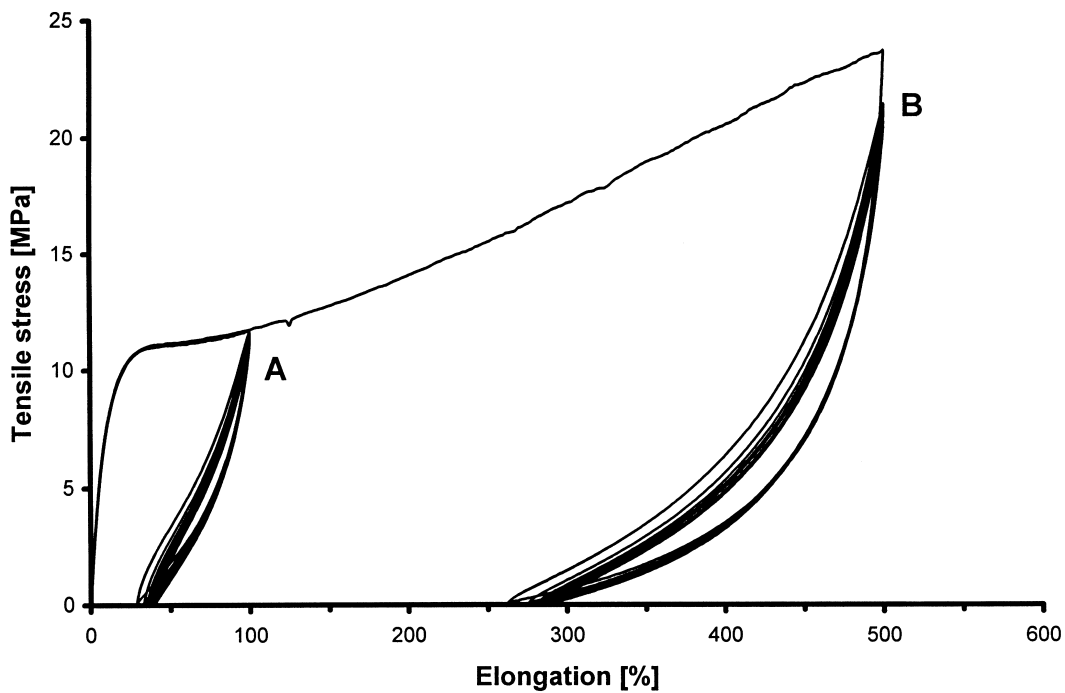


Figure 8. Hysteresis measurements of PEEI 5e': (A) elongation of 100%, (B) elongation of 500%.

assumption that the macrophase separation (in the case of PTMO) generates a broader distribution of compositions with the consequence of broader phase-transitions.

The hysteresis measurements were conducted with an elongation of 100 and 500% (Figure 8). At 500% elongation, the hysteresis curves of **5e'** are almost identical with those obtained for PEEI **5a**. The relaxation down to an elongation of 260–290% (so-called permanent set) was observed, whereas in the case of PEE **7** the relaxation stopped around 400%. In summary, depending on the mechanical method the PEEI **5e'** either showed a good agreement with PEEI **5a** or with PEE **7**.

## CONCLUSION

The present study of PEO containing PEEIs allows several unpredictable and interesting conclusions. Firstly, the admixture of PEO-1000 to PTMO-1000 does not completely suppress the macrophase separation which occurs near the end of the polycondensation process. Secondly, this macrophase separation was completely avoided, when neat PEO-1000 or PEO-1550 was used as soft segment. Thirdly, the partial demixing of PTMO-1000 containing reaction mixtures did not have negative consequences for the mechanical properties in stress-strain measurements. Fourthly, the properties of the PEO-1000 based “homopolymer” **5e'** resemble either the properties of the PTMO based PEEI **5a** or the properties of PEE **7** depending on the analytical method used for the characterization. Remarkable are the better mechanical properties of PEEI **5e'** relative to PEE **7** in hysteresis measurements. The incorporation of PEO accelerates the crystallization of the hard segments, but this acceleration does not suffice for the requirements of injection molding. However, the PEO containing PEEIs may be useful for a production of oil and gasoline repelling elastic films or water vapor permeable membranes.

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