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1,3-Oxazoline intermediates in reactive processing applications[†]: 3. Bis(1,3-xazolin-2-yl)-terminated oligotetrahydrofuran liquid rubbers and preparation of the corresponding segmented copolyetheresteramides

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Novel α,ω-bis(1,3-oxazolin-2-yl)-terminated oligotetrahydrofurans with number average molecular mass of 2000 and 3700 g mol^{-1} were prepared via endcapping of bis(carboxypropyl)-terminated oligotetrahydrofuran with 1,4-bis(1,3-oxazolin-2-yl)-benzene in bulk at 250°C. Such liquid rubbers were added as chain extenders during melt processing of poly(butyleneterephthalate) to produce within a few minutes at 240°C copolyetheresteramides containing oligotetrahydrofuran soft segments. Alternatively, bis(carboxypropyl)-terminated oligotetrahydrofuran together with carboxy-terminated PBT were chain extended with bisoxazolines. Thermal, mechanical and morphological properties of the resulting segmented copolyetheresteramides were investigated as a function of reactive processing conditions and oxazoline-functional liquid rubber content and molecular mass. © 1997 Elsevier Science Ltd.

(Keywords: reactive blending; liquid rubber; oxazoline)

INTRODUCTION

Reactive liquid rubbers, comprising oligomeric elastomers with well-defined end groups, play an important role in polymer processing. For example, in thermoset processing liquid rubbers, which are miscible with uncured resins, phase separate during cure to form dispersed rubber micro- and nanophases which enhance toughness/stiffness balance of brittle crosslinked polymers[1]. In polyurethane chemistry, liquid rubber polyols together with short chain diols are reacted with isocycanate resins to control material properties such as hardness and resilience[2]. End group and side chain coupling reactions of polymer backbones with functional groups of reactive oligomers are of particular interest with respect to producing novel block and graft copolymers during melt processing[3]. Reactive extrusion represents a solvent-free process which permits diversification of commodity polymers during processing without requiring development of new monomers or copolymerisation processes. In order to qualify for reactive extrusion application, reactive intermediates must react quantitatively in highly viscous reaction medium of polymer melts at elevated processing temperatures, usually above 200°C, within very short reaction times of a few minutes, typical for extruder hold-up times. Moreover, the coupling reaction should not yield byproducts which would remain as impurities in the polymer. Yet another requirement is to enable efficient coupling reaction at very low total concentration of functional groups and at sterically hindered locations at polymer interfaces.

Reactive processing requirements are met by 2-substituted 1,3-oxazoline intermediates, which are readily prepared from esters or nitriles, respectively, and 2-aminoethanol. As reported previously, model reactions clearly demonstrate that 1,3-oxazolines react with aromatic carboxylic acids within 2 min at temperatures of 220°C to give esteramides in yields of 99.5% via nucleophilic attack of the carboxylate group at C-5 position of the oxazoline ring, thus causing ring-opening of the oxazoline ring and formation of an esteramide group[4]. Several researchers have applied di- and polyfunctional 2-substituted 1,3-oxazolines as chain extenders and coupling agents in reactive extrusion. For example, oxazoline-functional styrene polymers, prepared by copolymerising styrene with vinyl-functional oxazolines, were used in reactive blending applications[5]. More recently, Birnbrich and Fischer[6] developed new families of maleinate-, fumarate- and acrylate-functional oxazolines, which are derived from fat and natural oils and are readily grafted onto various thermoplastics to provide the opportunity of interfacial coupling with carboxylate- and anhydride-functional polymers. This technology was applied by Seppälä *et al.*[7] to produce oxazoline-grafted polypropylene, useful as a compatibiliser in polypropylene blends with poly(butyleneterephthalate) or polyamide 6. Loontjens *et al.*[8,9] and Inata and Matsumura[10–12] have investigated polyester chain extension with low molecular weight bisoxazolines to build up polyester molecular weight

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and to convert carboxylate end groups which can catalyse hydrolytic degradation. Combining polyester chain scission with oxazoline-mediated chain extension represents a very versatile route to producing novel copolyesteramides and to recycling partially hydrolysed polyester wastes[9,13]. Trifunctional oxazoline chain extenders have been applied by Boehme *et al.*[14] to introduce long chain branches and to improve processing and mechanical properties of liquid crystalline polymers. Most oxazoline coupling agents reported so far have rather low molecular weight. The purpose of this research was to prepare oxazoline-terminated telechelics, especially liquid rubbers, and to examine them as new reactive intermediates for reactive processing of polyesters. Chain extension of bisoxazoline-functional telechelics with carboxylate-terminated oligo- and polyethers produce segmented copolyesteramides which should exhibit improved toughness.

EXPERIMENTAL

Materials

Polybutyleneterephthalate (PBT, Type RT-4) was purchased from Hoechst, Frankfurt/Main, and dried in vacuo at 200°C prior to use. Concentration of carboxylic acid chain end groups was 106 mmol kg^{-1}, determined by titration analysis. α,ω-Bis(3-carboxypropyl)-terminated oligotetrahydrofurans (PTHFCOOH1400 and PTHFCOOH3000) were purchased from BASF, Ludwigshafen, and dried in vacuo at 80°C prior to use. 1,4-Bis(1,3-oxazolin-2-yl)-benzene (OxaPhOxa) was synthesised according to literature procedures[15]. Antioxidant Irganox®1010 was purchased from Ciba AG, Basel.

Preparation of α,ω-bis[3-(N-(4-(1,3-oxazolin-2-yl)benzamide)ethyl)propyl]-terminated oligotetrahydrofuran (PTHFOxa2000) according to pathway III. 108.1 g (500 mmol) OxaPhOxa were melted at 250°C in a 500 mL flask. A mixture of 140 g (100 mmol) PTHFCOOH1400 (*Table 1*) and 0,14 g Irganox® 1010 was dropped into within 15 min. The homogeneous mixture was stirred for further 15 min at 250°C, followed by suspending in 250 mL THF. The product was isolated by centrifugation at 23 000 rev min^{-1}. Finally, excess OxaPhOxa was removed completely by means of thin film evaporation at 180°C *in vacuo*. 175 g (96%) PTHFOxa2000 (*Table 1*) were obtained as a slightly yellow coloured and viscous liquid.

*FT*i.r. (Film): $\tilde{\nu}$ [cm^{-1}] = 2940–2797 (CH), 1739 (C–O), 1667 (NHC=O), 1650 (C=N), 1541 (NH), 1112 (C–O).

^{1}H n.m.r. (300 MHz, $CDCl_3$): $\delta = 7.89$ (d, arom. H, 4H); 7.73 (d, arom. H, 4H); 7.03 (s, NH, 2H); 4.37 (t, $CH_2OC{=}N$, 4H); 4.22 (t, $COOCH_2$, 4H); 3.97 (m, $CH_2N{=}C$, 4H, $\mathrm{COOC}\mathit{H}_2\mathrm{CH_2CH_2}$, 0.6H); 3.61 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2COO}$, 4H, CH_2NH, 4H); 3.30 (s, CH_2OCH_2, 77H); 2.51 (m, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{COO}$, 4H); 1.54 (s, $\mathrm{OCH_2C}\mathit{H}_2$, 77H).

^{13}C n.m.r. (75 MHz, $CDCl_3$): $\delta = 172.0$ (COO); 166.8 (CONH); 163.8 (C=N); 136.5; 130.4; 128.2; 127.0 (arom. C); 70.0 (CH_2OCH_2); 67.7 ($CH_2OC{=}N$); 66.0 (OCH_2CH_2-COO); 63.1 (CH_2CH_2NH); 54.9 ($CH_2N{=}C$); 39.4 (CH_2NH); 35.1 (OCH_2CH_2COO); 26.4 (CH_2CH_2O).

*Preparation of α,ω-bis[3-(N-(4-(1,3-oxazolin-2-yl)-benzamide)ethyl)propyl]-terminated oligotetrahydrofuran (***1b***, PTHFOxa3700) according to pathway III.* The preparation of PTHFOxa3700 (*Table 1*) was performed according to preparation of PTHFOxa2000 via addition reaction of 43.7 g (202 mmol) OxaPhOxa and 150 g (40.5 mmol) PTHFCOOH3000 (*Table 1*). This yielded 158 g (94%) of waxy and slightly yellow coloured product.

*FT*i.r. (Film): $\tilde{\nu}$ [cm^{-1}] = 2941–2797 (CH), 1739 (C=O), 1669 (NHC=O), 1650 (C=N), 1540 (NH), 1113 (C–O).

^{1}H n.m.r. (300 MHz, $CDCl_3$): $\delta = 7.87$ (d, arom. H, 4H); 7.74 (d, arom. H, 4H); 7.08 (s, NH, 2H); 4.38 (t, $CH_2N{=}C$, 4H); 4.20 (t, $COOCH_2$, 4H); 3.95 (m, $CH_2OC{=}N$, 4H, $\mathrm{COOC}\mathit{H}_2\mathrm{CH_2CH_2}$, 0.9H); 3.62 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2COO}$, 4H, CH_2NH, 4H); 3.31 (s, CH_2OCH_2, 172H); 2.53 (m, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{COO}$, 4H); 1.52 (s, $\mathrm{OCH_2C}\mathit{H}_2$, 172H).

^{13}C n.m.r. (75 MHz, $CDCl_3$): $\delta = 172.2$ (COO); 166.9 (CONH); 163.6 (C=N); 136.2; 130.2; 128.1; 127.0 (arom. C); 70.2 (CH_2OCH_2); 67.8 ($CH_2OC{=}N$); 66.1 ($\mathrm{\mathit{O}CH_2CH_2}$-COO); 63.3 ($\mathrm{\mathit{C}H_2CH_2NH}$); 54.8 ($CH_2N{=}C$); 39.3 ($CH_2NH$); 35.3 ($\mathrm{OCH_2\mathit{C}H_2COO}$); 26.2 ($\mathrm{\mathit{C}H_2CH_2O}$).

Reactive processing

PBT chain extension (general procedures). PBT blends with liquid PTHF rubbers (PTHFOxa, PTHFCOOH): reactive blending was performed in a Haake Rheomix 90, equipped with a 60 ml double-screw blender which was preheated at 240°C and operated at 100 rev min^{-1}. Torque

Table 1 Characterisation of the carboxy- and oxazoline-terminated oligotetrahydrofuran liquid rubbers used in this study

	PTHFCOOH 1400	PTHFOxa 2000	PTHFCOOH 3000	PTHFOxa 3700
M_n (g mol^{-1})^a	1400	1970	3030	3780
M_n (g mol^{-1})^b	1350	1940	2950	3600
M_n (g mol^{-1})^c	1500	2000	3200	3790
M_n (g mol^{-1})^d	2540	3180	4650	5370
M_w/M_n^d	0.91	1.02	1.22	1.30
Functionality (mol kg^{-1})				
Calc.^{b}	1.48	1.03	0.68	0.56
Found^c	1.33	1.00	0.63	0.53
T_g (°C)^e	– 70.7	– 69.6	– 80.2	– 79.2
T_m (°C)^e	18.6	17.2	21.2	22.2
ΔH (J g^{-1})^e	88.4	74.1	81.5	72.0

^{a}Determined from ^{1}H n.m.r. spectroscopy
^{b}Determined by means of vapour pressure osmometry
^{c}Determined from titration analysis
^{d}Determined by means of SEC
^{e}Determined by means of d.s.c.

and temperature were recorded on-line. From 55.0 to 46.0 g PBT, stabilised with 0.1 wt% Irganox® 1010, were melted in the blender at 240°C. After 150 s, the PTHF component was injected via syringe within 1–2 min. After 2 min of additional kneading, the obtained materials were removed and compression moulded *in vacuo* at 240°C to produce sheets of 2 mm thickness, using a Schwabenthan Polystat 100 press.

PBT blends with additional OxaPhOxa chain extension reaction: if chain extending with OxaPhOxa is performed, OxaPhOxa was added immediately to the melt when rubber addition was completed, and kneaded for an additional 2 min.

Polymer characterisation

Vapour pressure osmometry experiments were carried out with a Perkin–Elmer Molecular Weight Apparatus Type 115 with $CHCl_3$ as solvent at 30°C. The GPC apparatus was equipped with refractive index and u.v. (254 nm) detections using polystyrene calibration (column PL-Gel; 10^6, 10^5, 10^4, 10^3 Å; 7.5·300 mm; flow rate 1 ml min^{-1}). For tensile testing, tensile bars (according to DIN 53455) were cut and machined. Tensile tests to determine Young's modulus and tensile strength at break, were performed at 10 mm min^{-1} crosshead speed on an Instron 4204 at 23°C. Scanning electron micrographs of polymer blends were taken on a Zeiss Model DSM 960 microscope. Samples were prepared by fracturing the blend in liquid nitrogen and sputtering it with gold to obtain a surface of 2–3 mm^2. Micrographs were taken in the magnification range 1000–10 000. Glass transition temperatures were measured by dynamic mechanical analysis on a Rheometrics solids analyser at 1 Hz and a heating rate of 5 K min^{-1}, and differential scanning calorimetry (d.s.c.) on a Perkin–Elmer DSC 7 with a heating rate of 20 K min^{-1}. ^{1}H (300 MHz) and ^{13}C (75 MHz) n.m.r. experiments were measured on a Bruker ARX 300, in $CDCl_3$ with TMS as internal standard.

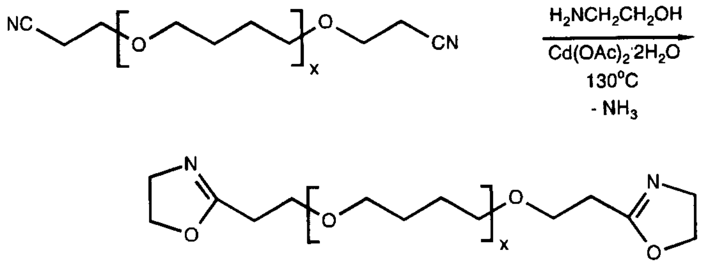
RESULTS AND DISCUSSION

Preparation of oxazoline-functional liquid rubbers

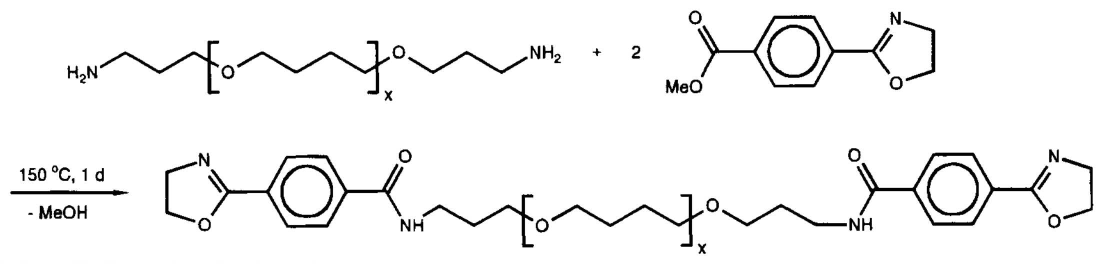
Novel bis(1,3-oxazolin-2-yl)-terminated oligotetrahydrofuran liquid rubbers (PTHFOxa) were prepared by converting nitrile, amine and carboxylate end groups of oligotetrahydrofuran (PTHF) into 2-substituted 1,3-oxazolines. Although such oxazoline-functional oligotetrahydrofuran liquid rubbers are not reported in the literature, there exist several reports on end group conversions yielding oxazoline end groups. For example, Sillion and Daccord obtained α,ω-bis(1,3-oxazolin-2-yl)-di-, tetra- and hexaphenylenesulfide by reacting nitrile-terminated oligophenylenesulfides with 2-aminoethanol[16]. Poor yields of this conversion below 80% with respect to the nitrile required extensive purification by recrystallisation. Percec *et al.*[17,18] reported oxazoline-terminated polyethersulfones where endcapping was performed by means of etherification with 2-(4-hydroxyphenyl)-1,3-oxazoline. Ester end groups of oligotetrafluoroethylenes were converted into 1,3-oxazolines in approximately 85% yield[19]. All these synthetic routes are not applicable to preparation of PTHFOxa because of low yield and poor functionality. In step-growth-type chain extension, only high purity difunctional intermediates with two functional groups afford high molecular weights.

According to *Scheme 1*, α,ω-bis(3-cyanopropyl)-terminated oligotetrahydrofuran, readily available by base-catalysed cyanoethylation of dihydroxy-terminated oligotetrahydrofuran[20], was reacted with stoichiometric amounts of 2-aminoethanol at 130°C in the presence of 2 mol% cadmium diacetate dihydrate catalyst. Although ammonia was split off, thus indicating oxazoline formation, oxazoline yield was only 40% with respect to nitrile groups. According to n.m.r. spectroscopic analysis, oxazoline formation was accompanied by formation of hydroxy end groups. Obviously, amine addition catalyses retro-Michael reaction of acrylonitrile to hydroxy-terminated oligotetrahydrofuran. This is in accord with reversibility of cyanoethylation reactions performed in solvents such as water and alcohols where Lewis bases accelerate the retro-Michael reaction[21]. Therefore, pathway I fails to produce PTHFOxa with adequate oxazoline functionality.

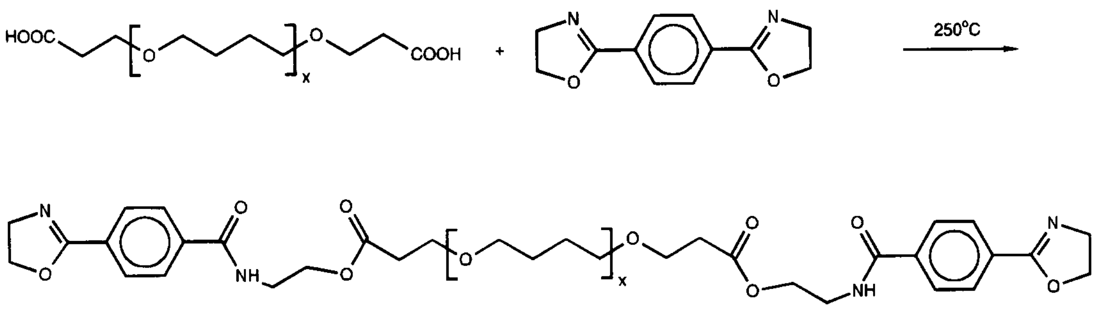
In pathway II, displayed in *Scheme 2*, α,ω-bis(3-aminopropyl)-terminated oligotetra-hydrofuran, corresponding to hydrogenated α,ω-bis(3-cyanopropyl)-oligotetrahydrofuran, was endcapped with 4-(1,3-oxazolin-2-yl)-benzoic



Scheme 1 Pathway I: Conversion of nitrile end groups



Scheme 2 Pathway II: Conversion of amine end groups



1a
1b

Scheme 3 Pathway III: Conversion of carboxylate end groups (**1a** PTHFOxa2000 with M_n = 2000 g mol^{-1}; **1b** PTHFOxa3700 with M_n = 3700 g mol^{-1} (*Table 1*))

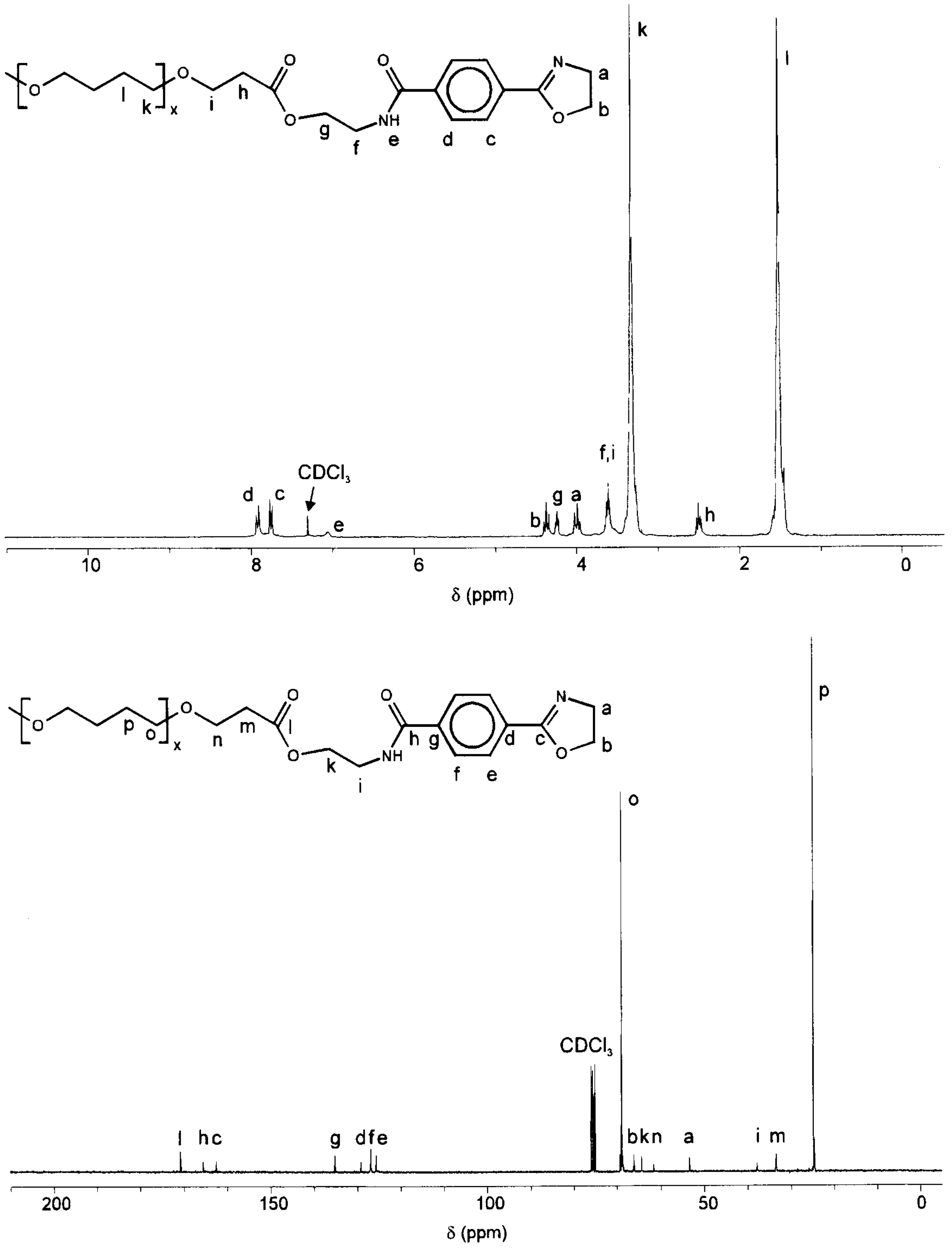


Figure 1 ^{1}H n.m.r. (300 MHz, $CDCl_3$, above) and ^{13}C n.m.r. (75 MHz, $CDCl_3$, below) spectra of PTHFOxa2000 (**1a**)

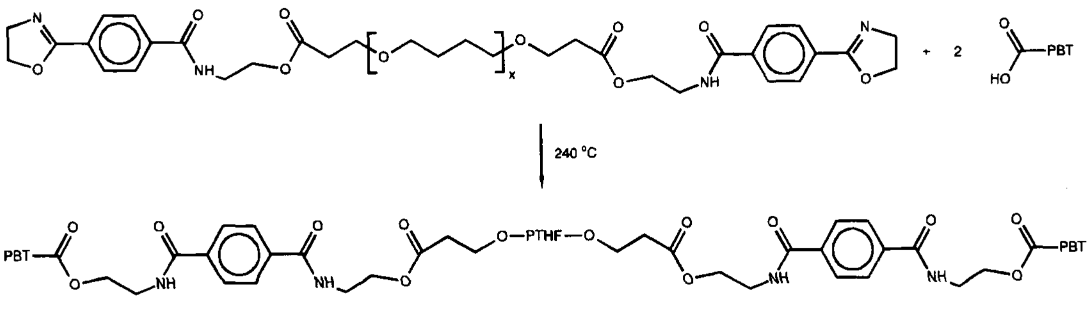
acid methyl ester which is obtained from monomethylterephthalate[22] and aminoethanol. Stoichiometric reaction of α,ω-bis(3-aminopropyl)-terminated oligotetrahydrofuran with 4-(1,3-oxazolin-2-yl)benzoic acid methyl ester (1 mol/ 2 mol) required 150°C. According to ^{1}H n.m.r. spectroscopy, the signal at 3.95 ppm (OCH_3) and 2.78 ppm (CH_2N) disappeared completely after 24 h reaction time. However, the intensity of the signals at 4.42 and 4.07 ppm (CH_2), which are typical for methylene groups of the 1,3-oxazoline ring, indicated a conversion of only 88%. Additional signals appearing between 2.2 and 2.9 ppm are likely to correspond to *N*-(2-alkylaminoethyl)carboxamides, formed via nucleophilic attack of the amine groups at the oxazoline ring and subsequent ring opening[23]. At elevated temperatures this side reaction consumes oxazoline end groups and accounts for inadequate functionality of the resulting PTHFOxa.

In contrast to pathway I and pathway II, side reactions are circumvented when α,ω-bis(3-carboxypropyl)-terminated oligotetrahydrofuran, commercially available by hydrolysis of α,ω-bis(3-cyanopropyl)-terminated oligotetrahydrofuran, is endcapped by reacting it with at least fivefold excess 1,4-bis(1,3-oxazolin-2-yl)-benzene (OxaPhOxa), in bulk at 250°C (*Scheme 3*). Such high temperatures are required because OxaPhOxa melts at 239°C. This reaction is completed within 15 min. Large excess of OxaPhOxa suppresses chain extension. Upon cooling residual OxaPhOxa crystallises and can be removed either by filtration or centrifugation. Preferably, quantitative removal is achieved by means of thin film evaporation at 180°C *in vacuo*. Excess OxaPhOxa, which is easy to sublime, is readily recovered and recycled. According to size exclusion chromatography as well as n.m.r. spectroscopy, no residual OxaPhOxa was detected in α,ω-bis[3-(*N*-(4-(1,3-oxazolin-2-yl)benzamide)-ethyl)propyl]-terminated oligotetrahydrofuran (PTHFOxa2000 and PTHFOxa3700 for M_n = 2000 and M_n = 3700 g mol^{-1}, respectively). Properties and functionalities of PTHFCOOH and PTHFOxa are listed in *Table 1*.

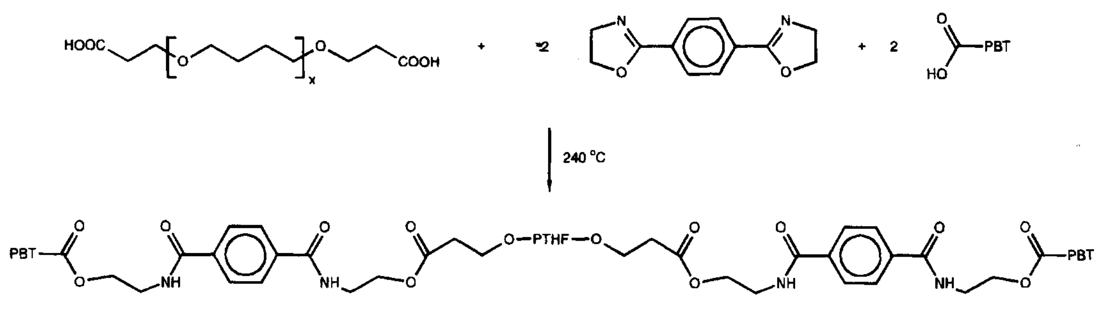
With exception of SEC, probably because of its calibration with polystyrene standards, functional group content and molecular mass determined by means of ^{1}H n.m.r. spectroscopy, vapour pressure osmosis, and end group titration were in excellent agreement with calculated values. ^{1}H and ^{13}C n.m.r. spectra of (1a) are displayed in *Figure 1*. In the case of higher molecular weight PTHFOxa3700, molecular mass distributions are slightly broader because chain extension took place without affecting the end group type. According to thermal analysis, the oxazoline end groups lower crystallinity, reflected by lower heat of fusion of PTHFOxa, whereas both melting temperatures and glass transition temperatures are very similar for liquid rubbers with carboxy and oxazoline end groups (cf. *Table 1*). The resulting viscous liquids meet the above mentioned stringent requirements for telechelic chain extenders and are also attractive toughening agents for thermoset resins.

Oxazoline-mediated reactive blending of PBT

Segmented copolyetheresters containing both poly(butyleneterephthalate) (PBT) hard segments and oligotetrahydrofuran soft segments are commercially available thermoplastic elastomers produced by traditional polycondensation of dimethyl terephthalate with butanediol and oligotetrahydrofurandiol[24–26]. When blended together with PBT such copolymers enhance low temperature toughness without sacrificing stiffness. In principle, coupling of oxazolines with carboxylate end groups of PBT could afford segmented copolyetheresteramides with property profile similar to that of copolyetheresters. This reactive processing technology could be an attractive solvent-free route to recycling of PBT waste by converting it into high-value-in-use thermoplastic elastomers based upon PBT and oligotetrahydrofuran. Since earlier model studies revealed that aromatic carboxylic acids react with 2-substituted 1,3-oxazolines within a few minutes in > 99% yield to form esteramides[13], reactive blending was performed in bulk at 240°C using a corotating twin-screw blender. Two chain



Scheme 4 Copolyesteramides via chain extension with PTHFOxa



Scheme 5 Copolyesteramides via chain extension with PTHFCOOH/OxaPhOxa

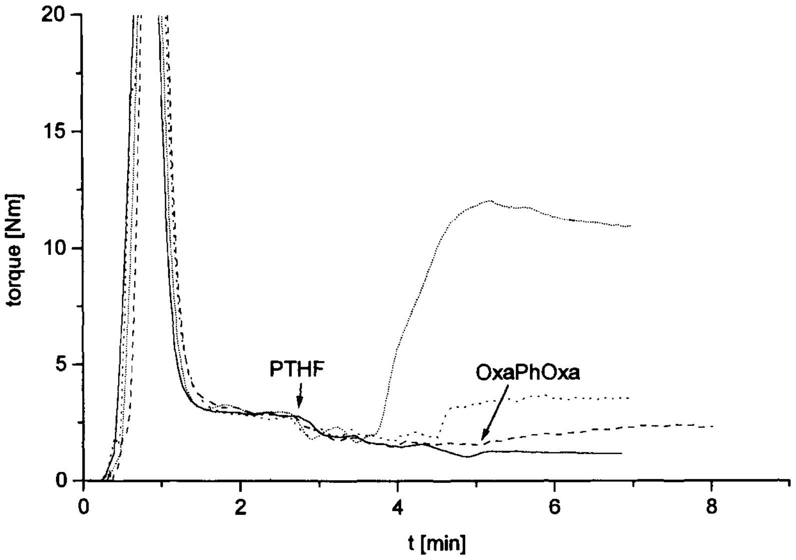


Figure 2 Torque as a function of the PTHF liquid rubber type (PBT containing 9 wt% PTHF liquid rubber) with PTHFCOOH1400 (solid line); PTHFCOOH/OxaPhOxa (dashed line); PTHFOxa3700 (dotted line) and PTHFOxa2000 (fine dotted line).

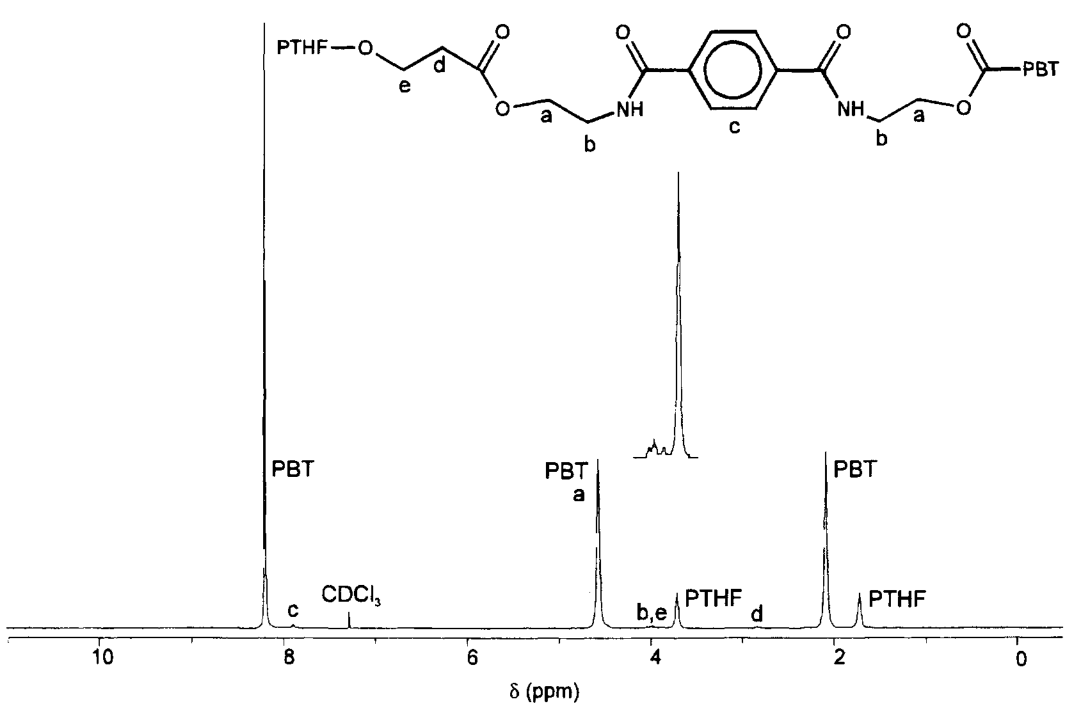


Figure 3 ^{1}H n.m.r. spectrum (300 MHz, $CF_3COOD/CDCl_3$ 1:1) of PBT containing 9 wt% PTHFOxa (blend sample PBT9PTox20, *Table 2*)

Table 2 Blend compositions and properties

Blend system	Liquid rubber Type	Liquid rubber wt%	OxaPhOxa (wt%)	Torque (Nm)	[η] (dL g^{-1})	Young's modulus (MPa)	Yield strength (MPa)	Elongation at break (%)	Charpy impact strength (kJ m^{-2})
PBTKneter	–	0	–	1.7	0.67	2230	–	2.9	6.1
PBT OxaPhOxa	–	0	1.1	8.2	1.09	2040	17.9	37.2	9.7
PBT9PTs14	PTHFCOOH 1400	9.3	–	1.2	0.52	1600	29.7	14.6	3.6
PBT9PTs30	PTHFCOOH 3000	9.3	–	1.3	n.d.	1540	30.0	8.8	3.4
PBT9PTox20	PTHFOxa 2000	9.3	–	11.0	1.25	1470	40.7	52.8	14.2
PBT9PTox37	PTHFOxa 3700	9.3	–	3.1	0.70	1480	39.5	29.8	8.9
PBT16PTs14	PTHFCOOH 1400	15.8	–	0.8	n.d.	1290	21.5	12.5	3.1
PBT16PTs30	PTHFCOOH 3000	15.8	–	0.9	n.d.	1230	22.8	10.3	3.2
PBT16PTox20	PTHFOxa 2000	15.8	–	3.7	0.72	1120	31.6	14.3	10.5
PBT16PTox37	PTHFOxa 3700	15.8	–	3.2	0.67	1150	26.0	30.6	10.5
PBT9PTs14 OxaPhOxa	PTHFCOOH 1400	9.3	2.4	2.4	0.68	1380	36.0	14.9	8.2
PBT9PTs30 OxaPhOxa	PTHFCOOH 3000	9.3	1.1	2.6	0.76	1570	35.1	17.8	8.1
PBT16PTs30 OxaPhOxa	PTHFCOOH 3000	15.8	2.1	1.8	0.59	1200	25.6	36.5	8.5

extension processes were investigated: first, chain extension of carboxylate-terminated PBT with novel PTHFOxa liquid rubbers (*Scheme 4*), and second, simultaneous chain extension of PTHFCOOH together with carboxy-terminated PBT (*Scheme 5*).

When molecular mass build up is monitored by the increase of torque in the kneader, both PTHFOxa and PTHFCOOH injection accounted for decreased torque which one minute after injection increased due to chain extension. Molecular weight build-up of PTHFCOOH/OxaPhOxa was much less effective with respect to PTHFOxa, especially PTHFOxa2000 (*Figure 2*). At 9 wt% PTHFOxa addition, the oxazoline/carboxylate molar ratio was 0.54. When liquid rubber content was increased to 16 wt%, the molecular weight increase was much less pronounced. Obviously, the stoichiometry of oxazoline/carboxylic acid groups plays an important role, as expected for step growth polymerisation. Also at higher liquid rubber content, the PTHFOxa liquid rubbers are much more effective than PTHFCOOH/OxaPhOxa.

The conversion of oxazoline end groups can be monitored by means of FTIR spectroscopy^{27} and also by high resolution ^{1}H n.m.r. spectroscopy. The peak assignment is displayed in *Figure 3* for the system where PBT was chain extended with PTHFOxa2000. Again oxazoline conversion to esteramide is not accompanied by side reaction such as cationic ring-opening polymerisation of oxazoline.

Various PBT blends have been prepared via reactive

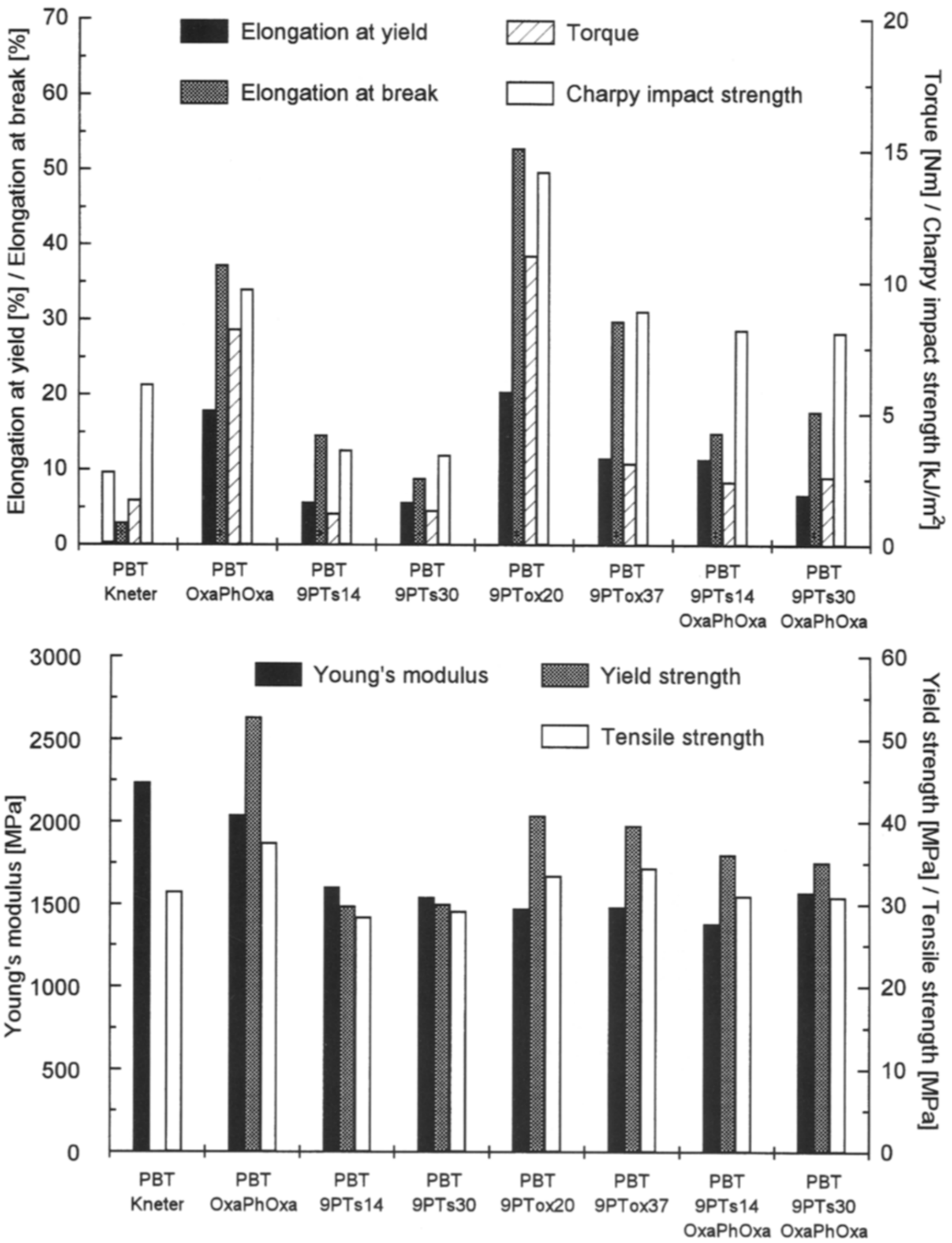


Figure 4 Mechanical properties of blends containing 9 wt% PTHF component

blending. Blend composition and properties are listed in *Table 2*. The influence of OxaPhOxa chain extender together with PBT and PTHFCOOH was compared with blends based upon PBT and PTHFOxa. In blend sample designation the first number represents the weight percentage of added PTHF component and the second number indicates the molecular mass of PTHF. For better comparison, torque and the mechanical properties such as Young's modulus, tensile strength, yield stress, elongation at yield, elongation at break and Charpy impact strength are displayed in *Figure 4* for blends containing 9 wt% of the PTHF component, and in *Figure 5* for blends containing 16 wt% of the PTHF component.

As expected for blends containing soft oligotetrahydrofuran, Young's modulus as a measure for stiffness and tensile strength decrease with increasing PTHF content, regardless of the PTHF type. Improvement of impact strength depends significantly on the PTHF type and also on PTHF content or oxazoline/carboxylic acid molar ratio, respectively. While PBT chain extension with OxaPhOxa accounts for substantial improvement of impact strength as a result of chain extension, the simultaneous addition of PTHFCOOH together with PBT in the absence of OxaPhOxa chain extender (blend series PBT–PTs) fails to increase toughness. In fact, PTHFCOOH does not appear to be a toughening agent at all. However, when OxaPhOxa chain extender is added together with PBT and PTHFCOOH the impact strength is increased but does not match the performance of PBT chain extended with OxaPhOxa without PTHFCOOH addition, which causes losses of

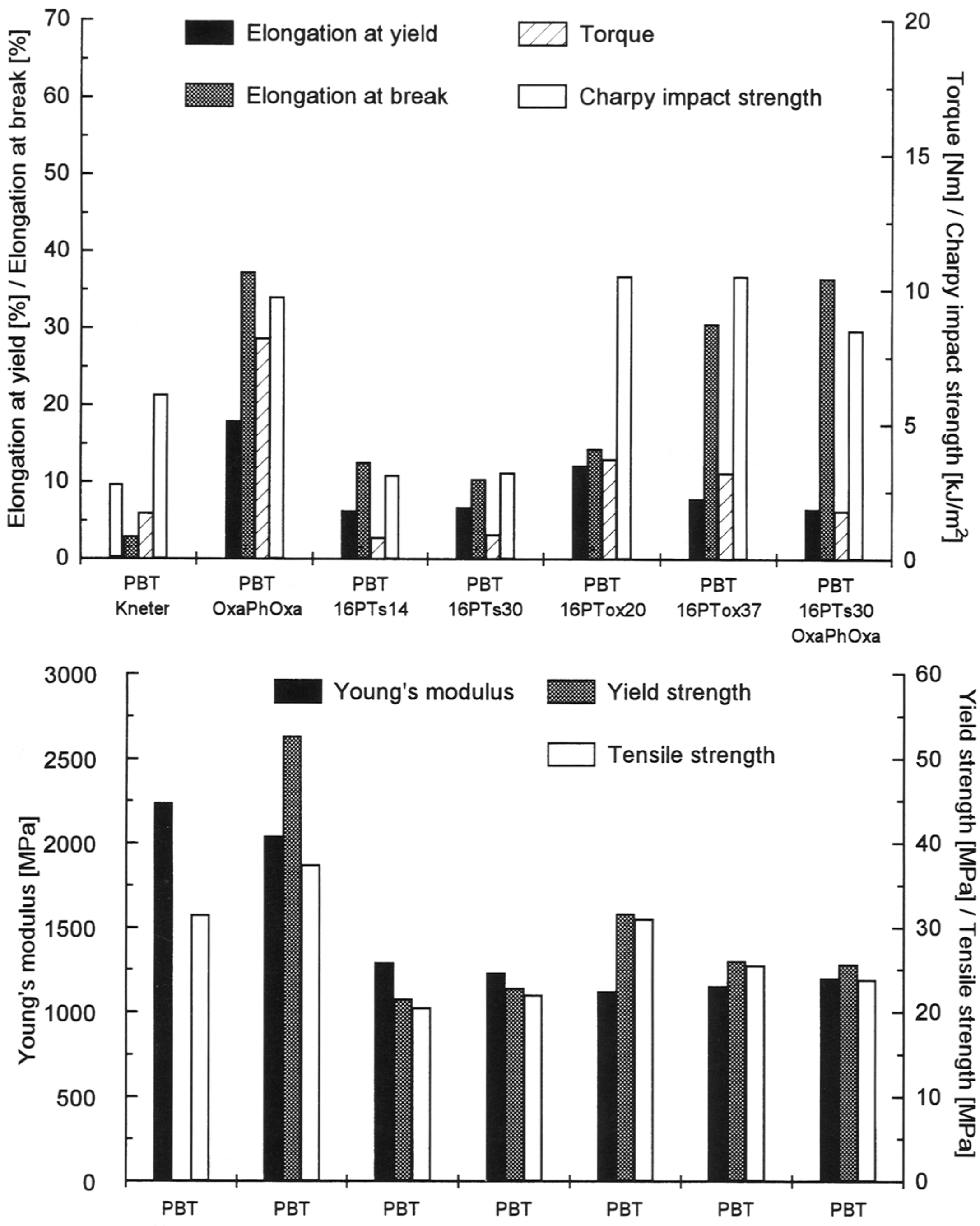


Figure 5 Mechanical properties of blends containing 16 wt% PTHF component

Table 3 Thermal and morphological properties of blends

Blend system	Liquid rubber		OxaPhOxa (wt%)	Domain diameter[a] (μm)	T_g^b PTHF-phase (°C)	T_g^b PBT-phase (°C)	T_m^b PTHF-phase (°C)	T_m^b PBT-phase (°C)	ΔH_m^b PBT-phase (J g^{-1})
	Type	wt%							
PBTKneter	–	0	–	–	–	56.0	–	226.6	48.2
PBT OxaPhOxa	–	0	1.1	–	–	52.0	–	222.9	34.3
PBT9PTs14	PTHFCOOH 1400	9.3	–	1–12	– 70.5	50.8	18.2	223.4	41.0
PBT9PTs30	PTHFCOOH 3000	9.3	–	5–25	– 79.2	51.3	23.8	225.3	42.5
PBT9PTox20	PTHFOxa 2000	9.3	–	homogeneous	–	45.0	–	219.3	34.8
PBT9PTox37	PTHFOxa 3700	9.3	–	0.6–1.6	– 74.8	50.3	23.9	223.4	40.1
PBT16PTs14	PTHFCOOH 1400	15.8	–	0.5–10	– 71.5	49.5	17.0	223.5	40.1
PBT16PTs30	PTHFCOOH 3000	15.8	–	5–20	– 76.7	50.0	21.3	224.2	40.6
PBT16PTox20	PTHFOxa 2000	15.8	–	0.1–0.5	– 69.5	44.5	16.5	219.2	34.9
PBT16PTox37	PTHFOxa 3700	15.8	–	1–5	– 73.1	49.0	24.0	222.7	40.0
PBT9PTs14 OxaPhOxa	PTHFCOOH 1400	9.3	2.4	0.2–1.0	– 76.1	48.6	16.5	221.1	40.1
PBT9PTs30 OxaPhOxa	PTHFCOOH 3000	9.3	1.1	3–10	– 76.1	50.2	22.4	224.9	41.2
PBT16PTs30 OxaPhOxa	PTHFCOOH 3000	15.8	2.1	2–10	– 75.6	50.1	23.7	223.2	38.0

[a] Determined by means of REM
[b] Determined by means of d.s.c.

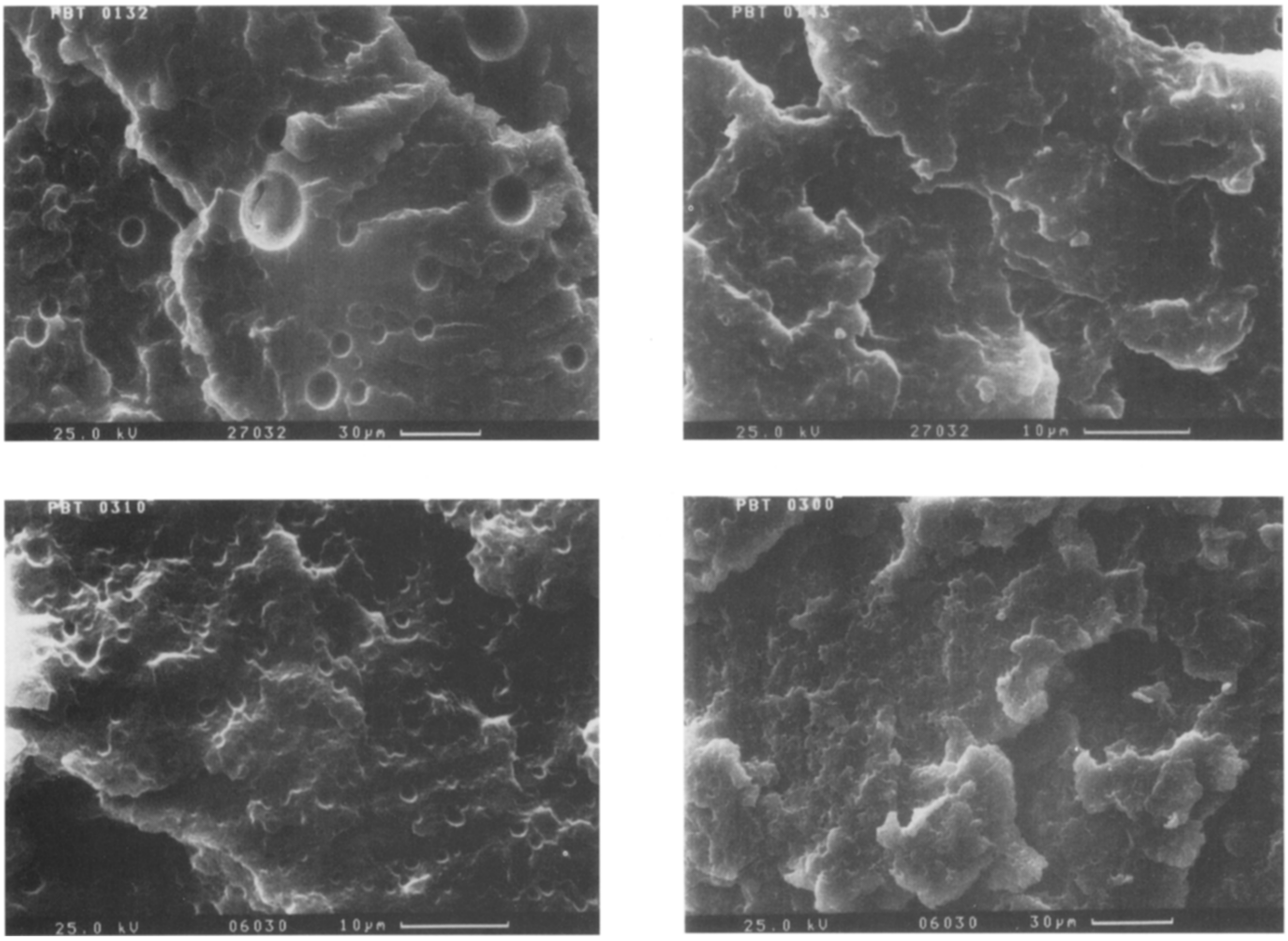


Figure 6 SEM images of fracture surfaces of blends containing 9 wt% PTHF component: PTHFCOOH1400 (above left), PTHFOxa2000 (above right), PTHFOxa3700 (below left) and PTHFCOOH/OxaPhOxa (below right)

stiffness and strength. In comparison to PTHFCOOH and PTHFCOOH/OxaPhOxa, the oxazoline-functional liquid rubbers PTHFOxa appear to be much more effective as toughening agents. Highest impact strength was found for blends containing 9 wt% PTHFOxa2000. Higher PTHFOxa content and higher molecular mass of PTHFOxa gave inferior stiffness/toughness balance with respect to that of PTHFOxa2000.

The thermal properties, determined by d.s.c. and DMA, are listed in *Table 3*. According to DMA analysis of blends, only the blend containing 9 wt% PTHFOxa2000 represents a single phase system, whereas all the other blends based upon higher molecular weight PTHFOxa3700 or all PTHFCOOH as well as all blends containing larger amounts of 16 wt% PTHF-based liquid rubbers represent two-phase systems containing separate PTHF-phases. The glass transition of the PTHF phase depends primarily on the PTHF molecular mass with glass transition temperature of approximately − 70°C for PTHFCOOH1400 and PTHFOxa2000, and − 80°C for PTHFCOOH3000 and PTHFOxa3700. The glass transition temperature of PBT was slightly lowered in the order of magnitude of 5°C when PTHF-based liquid rubbers were added. The melting temperature of PBT is lowered from 226 to 220°C in the case of blends containing 9 wt% PTHFOxa2000, whereas blends containing 9 wt% PTHFCOOH1400 melted at 223°C. Moreover, oxazoline-functional PTHF-based liquid rubber, especially PTHFOxa2000, accounted for up to 28% reduction of PBT melting enthalpy. The thermal analysis clearly provides experimental evidence for incorporation of PTHFOxa, resulting in reduced PBT melting temperature and reduced PBT crystallinity. This is also reflected by the blend morphology, imaged by means of scanning electron microscopy (SEM) in *Figure 6*.

Blend samples were fractured in liquid nitrogen to image topology of fracture surfaces and to examine the formation of separate PTHF-based phases dispersed in the PBT continuous matrix. As a rule, PBT/PTHFCOOH blends without chain extenders gave two-phase blends with very large PTHF phases, typically 1–12 μm for PTHFCOOH1400 and 5–25 μm for PTHFCOOH3000. Clearly, both components are highly incompatible and the resulting blends exhibit poor mechanical properties (cf. *Table 2*). When OxaPhOxa chain extender was added together with PTHFCOOH1400 and PBT, however, the interfacial coupling was much improved, as evidenced by reduction of the average particle size of the PTHF phase of 0.2–1 μm! With higher molecular mass PTHFCOOH3000, no such pronounced dispersion enhancement was found. In the case of blends containing 9 wt% PTHFOxa2000, in accord with results of the thermal analysis, no separate PTHF phase was detected. When PTHFOxa2000 content was raised to 16 wt%, a second phase consisted of spherical PTHF-based microparticles of 0.1–0.5 μm average diameter. Even the higher molecular weight PTHFOxa3700 gave fine particle dispersions of 0.6–1.6 μm at 9 wt% content and 1–5 μm at 16 wt% content. Oxazoline-mediated interfacial coupling, either by addition of OxaPhOxa chain extender or by introducing oxazoline end groups, enhances dispersion and compatibility of PTHF with PBT due to *in situ* formation of segmented copolyetheresteramides.

CONCLUSIONS

The toughness/stiffness balance of PBT is enhanced upon chain extension with low molecular weight bisoxazoline chain extenders such as 1,4-bis(1,3-oxazolin-2-yl)-benzene. This chain extension principle can be applied to *in situ* preparation of segmented copolyetheresteramides derived from PBT. Using either carboxylate-terminated oligotetrahydrofuran PTHFCOOH in conjunction with low molecular weight bisoxazoline chain extenders or using novel oxazoline-terminated PTHFOxa, respectively, dispersion and interfacial coupling of PTHF-based rubber is achieved. This is reflected by blend morphologies as well as improved mechanical properties, especially toughness. Clearly, blend performance depends upon polymer compatibility which is influenced by molecular mass, content or carboxylate/oxazoline molar ratio, respectively, and molecular architecture of the PTHF-based liquid rubber. In the case of bisoxazoline-functional oligotetrahydrofuran with M_n = 2000 g mol^{-1} (PTHFOxa2000) the end group coupling reaction is very effective and affords high molecular weight segmented copolyetheresteramides which do not phase separate. In conclusion, oxazolines are very versatile intermediates for reactive processing application to diversify and upgrade polyesters such as PBT. Moreover, oxazolines are excellent model systems to understand the role of interfacial coupling reactions and to design reactive blending technology with much improved control of blend architectures and compatibilisation.

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