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Synthesis and characterization of poly[(2,6-dimethyl-1,4-phenylene oxide)-block-isoprene] diblock copolymers

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SUMMARY:
As a first stage in the synthesis of a new class of thermoplastic elastomers, a suitable synthetic route for elastomeric tailor-made diblock copolymers based on poly(2,6-dimethyl-1,4-phenylene oxide), PPE, as the thermoplastic block and on 1,4-polyisoprene, PIP, as the elastomeric block, is outlined. The 2,6-dimethyl-1,4-phenylene oxide-block-isoprene diblock copolymers were synthesized via an amidation coupling route between the ammonium salt of PPE and the monocarboxylic acid of PIP in the presence of dicyclohexylcarbodiimide, DCC. Preliminary studies were focused on the synthesis of a well-defined low molar mass diblock copolymer ($M_n=10000$) in order to facilitate the quantitative characterization by proton NMR spectroscopy. The developed amidation coupling route was successively applied to the synthesis of a similar diblock copolymer with a number-average molar mass of 40000 in order to obtain optimum overall properties.

Introduction
In the past decades, block copolymers have been widely investigated. The large importance of and interests in this class of engineering materials arises from their unique properties in solution as in the solid state. The specific properties of block copolymers are related to their molecular structure. In particular, sequences of two or more chemically different blocks are usually incompatible and therefore have a tendency to segregate into microdomains. Moreover, the combination of the properties of both homopolymers within a block copolymer yields a material with improved overall properties. Most of the interests are related to elastomeric systems and especially to thermoplastic elastomers. The unique properties of thermoplastic elastomers can be attributed to the physical crosslinking of the rubbery microphase by dispersed glassy domains. The continuous rubbery phase provides for the exceptional extensibility of these materials. The most widely investigated systems are styrene/butadiene and styrene/isoprene triblock copolymers (e.g. Kraton®, Shell). These thermoplastic elastomers possess excellent mechanical properties; however high temperature applications (e.g. automotive industry) are limited since the polystyrene block possesses a glass transition temperature ($T_g$) of 100 °C. This limitation can be overcome by using another type of amorphous thermoplastic segment like poly(2,6-dimethyl-1,4-phenylene oxide), PPE, possessing a $T_g$ of 220 °C.

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As a first stage in the synthesis of a new class of thermoplastic elastomers, the main objective of this work is the development of a synthetic route for a well-defined diblock copolymer based on PPE as the thermoplastic block and on 1,4-polyisoprene (PIP) as the elastomeric block ($M_n = 40000$). A relatively high molar mass was chosen in order to combine the properties of both homopolymers within the final 2,6-dimethyl-1,4-phenylene oxide-block-isoprene diblock copolymer. The synthesis of 2,6-dimethyl-1,4-phenylene oxide-block-isoprene diblock copolymer was achieved via amidation coupling in the presence of dicyclohexylcarbodiimide (DCC). In this respect, the two components of the copolymer, PPE and PIP, were first synthesized and endcapped with an ethylamino and a carboxylic acid group, respectively. In order to facilitate the quantitative characterization of the synthesized copolymer, it was essential to synthesize low molar mass endcapped PIP and PPE possessing a $M_n$ of 4900 and 3500, respectively. However, requirements with respect to the block length must be fulfilled, resulting from the combination of the properties of each segment in order to obtain a compound with better overall properties. Therefore, high molar mass endcapped PIP ($M_n = 26000$) and PPE ($M_n = 14500$) were synthesized as well.

**Experimental part**

**Materials**

Low molar mass poly(2,6-dimethyl-1,4-phenylene oxide), PPE ($M_n = 3500$), was prepared as described in literature. PPE-803 ($M_n = 11000$) was provided by General Electric Plastics (Bergen op Zoom, The Netherlands). Chloroethylamine (70 wt.-% solution in water), trioctylmethylammonium chloride (TOMA), dicyclohexylcarbodiimide (DCC), and sec-butyllithium (sec-BuLi) 1.3 M in cyclohexane/hexane (92/8) were used as received from Janssen Chimica (Tilburg, The Netherlands). BTS catalyst (BASF, Germany) was activated by passing through a hydrogen/nitrogen gaseous mixture (90/10) at 120°C during 8 h. Nitrogen was purified and dried at room temperature over molecular sieves and activated BTS catalyst subsequently. Isoprene (Janssen Chimica) was dried over calcium hydride for 16 h and freshly distilled under argon before use. Toluene was dried over calcium hydride before use and stored under argon. Tetrahydrofuran was freshly distilled under argon from sodium-benzophenone before use. Cyclohexane was dried over a molecular sieve (4 Å) column at room temperature. Carbon dioxide was used as received from Hoek Loos (Schiedam, The Netherlands).

**Characterization techniques**

$^1$H NMR spectra were recorded at room temperature on a 400 MHz spectrometer (Bruker AM 400), using CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal standard. Fourier transformed infrared (FT-IR) spectra were recorded on a Mattson Polaris FT-IR spectrometer, after accumulating 5 scans at a resolution of 4 cm$^{-1}$. Glass transition temperatures were determined using a Perkin-Elmer DSC-7 differential scanning calorimeter calibrated with indium ($T_{\text{fus}} = 156.6°C$ and $\Delta H_f = 28.45$ J/g). The samples were first heated to 230°C quenched to room temperature with a cooling rate of 200 K/min and subsequently run with a heating rate of 20 K/min. Gel permeation chromatography (GPC) measurements were performed on a Waters chromatograph equipped with a
refractometer detector, and two PL Gels columns (500 Å and 1000 Å) calibrated with monodisperse polystyrene standards. The samples were eluted in THF (PIP) and chloroform (PPE, copolymer) (2 mL/min).

Eluting components were detected via refractive index. The functionality in carboxylic end-groups of PIP-COOH was determined by titration at room temperature with a Schott N37A titration instrument equipped with an electrode type Ankersmit A141. The carboxylic end-groups of PIP-COOH were titrated in toluene/methanol (90/10) by a 2,4·10⁻³ M tetramethylammonium hydroxide (TMAH) solution in toluene/methanol (90/10, v/v), previously gauged with oxalic acid. Transmission electron microscopy (TEM) was performed using a Jeol JEM 2000 FX transmission microscope, operating at 80 kV. The TEM samples were prepared by solution casting from a 1 wt.-% solution of the diblock copolymer in dry toluene. The samples were embedded in epoxy and thin sections were obtained by ultramicrotomy. The cut sections were stained in a 2 wt.-% ruthenium tetroxide (RuO₄) solution at room temperature for 24 h, and coated with a carbon layer. Finally, the cut sections were stained again with RuO₄ vapours for 5 h. Dynamic mechanical thermal analysis (DMTA) experiments were performed in the tensile mode using a DMTA MK2 (Rheometric Scientific) equipped with a cooling unit. The sample was measured at a frequency of 1 Hz and at a heating rate of 2 K/min.

Monocarboxylic polyisoprene (PIP-COOH): 1 (1a: $M_n = 4900$ and 1b: $M_n = 26000$)

The anionic polymerization of isoprene was carried out in a 1,5 L-glass reactor (Büchi, Switzerland) under 2 bars nitrogen overpressure. After having evacuated and purged the polymerization reactor five times with nitrogen at 80°C, the reactor was quenched to 10°C. At this temperature, 500 mL of cyclohexane and 70 g (1 mol) of isoprene were charged under 2 bars of nitrogen overpressure. At a stirring rate of 200 rpm and under nitrogen flow, 11 mL of a 1,3 M solution of sec-butyllithium in cyclohexane/hexane (92/8, v/v) was added with a purged hypodermic syringe. The reaction mixture was heated to 60°C and stirred with a stirring rate of 800 rpm. After 1 h of polymerization at 60°C, the living polymeric solution was transferred under nitrogen overpressure into 500 mL of a stirred tetrahydrofuran solution saturated with carbon dioxide and previously cooled down to 0°C. Hereafter, the mixture was acidified with concentrated HCl (till pH = 2) and precipitated in 10 volumes of methanol containing 1 wt.-% of Irganox 1011 (antioxidant). PIP-COOH (1a) was obtained as a sticky viscous liquid after decantation and drying in vacuo at 50°C for 24 h (yield: 98%). The functionality of 1a was found to be higher than 95% (NMR and titration).

$^1$H NMR (CDCl₃): $\delta = 0.8$ (t, 3H, terminal CH₃), 1.2-2.3 (m, CH₂-CH-CH₂ [cis-and trans-1,4], CH-C=C-CH₂ [−3,4], CH=CHCH₃ [cis- and trans-1,4] and C(CH₃)=CH₂ [−3,4], 3.05–3.15 (s + s, 2H, CH₂COOH [cis- and trans-1,4]), 4.6–4.8 (m, C(CH₃)=CH₂ [−3,4] and 5.1–5.2 (m, CH=C(CH₃) [cis- and trans-1,4]); microstructure: −1,4/−3,4/−1,2: 94/6/0, cis-1,4/trans-1,4: 72/28.

FT-IR (KBr): 1709 cm⁻¹ (C=O).

GPC: $M_n = 4900$, $M_w/M_n = 1.09$.

DSC: $T_g = -56$°C.

The same procedure was applied for the synthesis of the monocarboxylic acid of PIP possessing a $M_n$ of 26000, 1b.

$^1$H NMR (CDCl₃): see above; microstructure: −1,4/−3,4/−1,2: 95/5/0; cis-1,4/trans-1,4: 75/25.

FT-IR (KBr): 1709 cm⁻¹ (C=O).

GPC: $M_n = 25900$, $M_w/M_n = 1.06$.

DSC: $T_g = -50$°C.
**Ethylammonium salt of PPE (PPE-OCH₂CH₂NH₃⁺Cl⁻): 5 (5a: $M_n = 3500$ and 5b: 14500)**

At room temperature, 5 g of PPE ($M_n = 3500$, 43 mmol) was charged in a 250-mL three-necked round bottomed flask equipped with a dropping funnel, a cooler and a thermometer, and containing 140 mL of toluene. After 1 h stirring, 2.31 g of TMA (5,72 mmol) and 6 mL of aqueous 12.5 M solution of NaOH (75 mmol) were added, and the reaction mixture was heated to 90°C. At this temperature, 1.43 mL of 70 wt.-% aqueous solution of chloroethylamine (36 mmol) was added dropwise. Hereafter, the reaction mixture was vigorously stirred at 90°C for 20 h. The reaction was followed by thin layer chromatography (TLC) using a chloroform/methanol mixture (95/5, v/v) as eluent.

The reaction product was precipitated in 1 liter of acidified methanol, filtered, washed twice with methanol and dried *in vacuo* at 70°C for 8 h. The ammonium salt of PPE (4,8 g), 5a, was obtained as a light brown powder in a yield of 95%. The functionality of 5a was found to be higher than 95% (NMR).

$^1$H NMR (CDCl₃): $\delta = 2.08$ (s, 6H, terminal phenolic CH₃), 2.12 (s, inner CH₃), 2.20 (s, 6H, terminal aromatic CH₃), 3.35 (t, 2H, OCH₂⁻), 3.98 (t, 2H, C—CH₂—N⁺), 6.43 (s, 2H, terminal phenolic C₆H₅), 6.51 (s, inner C₆H₅) and 7.13 (m, 3H, terminal aromatic C₆H₃).

$M_n = 4700$ (determined by $^1$H NMR).

DSC: $T_g = 190°C$

The same procedure was applied for the amination of the commercial PPE-803 possessing a $M_n$ of 11 200, yielding the ethylammonium salt 5b. Due to repeated precipitations in methanol during purification, the molar mass of 5b is found to be 14 500 instead of 11 200.

$^1$H NMR (CDCl₃): see above.

$M_n = 14 500$ (determined by $^1$H NMR), $M_w/M_n = 2.5$.

DMTA: tan $\delta_{max} = 220°C$.

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**2,6-Dimethyl-1,4-phenylene oxide-block-isoprene diblock copolymer: 10a ($M_n = 10000$)**

At room temperature, 66 mg of the ethylammonium salt of PPE 5a ($M_n = 4700$, 0.014 mmol) and 69 mg of PIP-COOH 1a ($M_n = 4900$, 0.014 mmol) were dissolved in 2.5 mL of chloroform. After one hour stirring, 2 mg of DCC (0.014 mmol) was added and the reaction mixture was stirred at 60°C for 16 h. The copolymer was precipitated in 250 mL of methanol. The precipitate was separated from the non-solvent by centrifugation and subsequently decanting. After drying at 70°C *in vacuo* for 8 h, the diblock copolymer PPE/PIP 10a was obtained as a sticky, brown coloured and transparent material in a yield of 80%. The conversion was found to be higher than 95% by $^1$H NMR spectroscopy.

$^1$H NMR (CDCl₃): $\delta = 3.65$ (t, 2H, O—CH₂—C), 3.75 (t, 2H, C—CH₂—NHCO—).

GPC: $M_n = 10000$, $M_w/M_n = 1.8$.

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**2,6-Dimethyl-1,4-phenylene oxide-block-isoprene diblock copolymer: 10b ($M_n = 40000$)**

At room temperature, 5 g of the ethylammonium salt of PPE-803 5b ($M_n = 14500$, 0.3 mmol) and 8.9 g of PIP-COOH 1b ($M_n = 26000$, 0.3 mmol) were dissolved in 120 mL of chloroform. After 3 h stirring at room temperature, 42 mg of DCC (0.34 mmol) was added to the homogeneous polymeric solution and the reaction mixture was stirred at 60°C for 16 h. After precipitation in 1 L of methanol, filtration and drying at 70°C *in vacuo* for 8 h, the diblock copolymer 10b was obtained as a sticky white powder in a yield of 90%. The conversion was found to be higher than 90% by $^1$H NMR spectroscopy.
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$^{1}$H NMR (CDCl$_3$): see above.

GPC: $M_n = 38600$, $M_w/M_n = 2.8$.

DMTA: $\tan \delta_{\text{max}1} = -50^\circ$C $\tan \delta_{\text{max}2} = 10^\circ$C and $\tan \delta_{\text{max}3} = 185^\circ$C.

Results and discussion

The syntheses of PIP-COOH, 1a ($M_n = 4900$) and 1b ($M_n = 26000$), were performed via anionic polymerization with sec-butyllithium in apolar media, using gaseous carbon dioxide as endcapping agent, yielding monocarboxylated polyisoprene with a high content of 1,4-microstructure. This feature is of crucial importance to deliver the obtained polyisoprene good elastomeric properties. It was reported by Quirk et al.$^8$ that the carboxylation of polydienyllithium in apolar media occurred with completion by adding 25 vol.-% of tetrahydrofuran; the addition of THF as a polar co-solvent prevents the formation of dimeric ketone, due to chain-ends association, during the endcapping reaction. However, contrary to Quirk’s affirmations, the best result obtained was 60% of monocarboxylated PIP and 40% of dimeric ketone. In order to promote dissociation of the PIP chain-ends and to control the rate of the endcapping reaction, the carboxylation of PIP was performed by slowly transferring the living polymeric solution into a stirred tetrahydrofuran solution, previously saturated with gaseous carbon dioxide and cooled to 0°C. The monocarboxylated PIP’s 1a and 1b were both obtained after precipitation in acidified methanol in a yield of 90%. The functionality of 1a and 1b in carboxylic end-groups was found to be higher than 95% after analysis by titration. Thin layer chromatography revealed the presence of a single spot corresponding to PIP-COOH.

In Fig. 1, the $^{1}$H NMR spectrum of 1a shows two peaks at 2.95 and 3 ppm in a ratio 3:1 characteristic of the last methylene group in the cis- and trans-1,4-microstructures, respectively. After integration, the carboxylation of PIP chain-ends is found to have occurred quantitatively. Similar results were obtained for 1b.

The GPC chromatograms of 1a and 1b clearly show one single peak corresponding to a $M_n$ of 4900 and 26000, respectively. This confirms the absence of dimeric ketone. This result was confirmed by infrared spectroscopy. Both IR spectra of 1a and 1b contain a typical carboxylic vibration at 1 709 cm$^{-1}$ and no ketonic vibration at 1 680 cm$^{-1}$. The previous analyses demonstrate that the carboxylation of low and high molar mass PIP’s has occurred with completion.

The ethylamination of PPE$^9$ was performed in toluene at 90°C using 25 equivalent of a 70 wt.-% solution of chloroethylamine in water in the presence of 4 mol equivalent of trioctylmethylammonium chloride (TOMA) as a phase transfer catalyst and 50 equivalent NaOH as a base. The ethylammonium salt of PPE, PPE–$\text{OCH}_2\text{CH}_2\text{NH}_3^+$ 5, is required for the coupling reaction with PIP-COOH 1. This requirement is inherent to two factors: i) the mechanism of the amidation reaction between 1 and 5 in the presence of dicyclohexylcarbodiimide (DCC), which requires the presence of an extra acidic proton (Scheme 1), and ii) the ionic interactions occurring between the ethylammonium end-group of PPE and the carboxylate end-group of PIP which promote the coupling reaction and minimize the shielding of the chain-ends. Both endcapping reactions resulting in 5a and 5b were followed
Scheme 1:

\[
\begin{align*}
\text{PIP-C-CH}_2\text{CH}_2\text{O} + & \quad \text{N}=\text{C}=\text{N} + \quad \text{PIP-C-CH}_2\text{CH}_2\text{O} \\
\text{5} & \quad \text{down} \quad \text{5} \\
\text{PPE} & \quad + \quad \text{NH}=\text{C}=\text{N} + \quad \text{PPE} \\
\text{6} & \quad \text{down} \quad \text{7} \\
\text{5a} & \quad \text{down} \quad \text{6} \\
\text{PPE-OC\text{H}2\text{CH}2\text{NH}_2} & \quad \text{PPE-OC\text{H}2\text{CH}2\text{NH}_2} + \quad \text{PPE-OC\text{H}2\text{CH}2\text{NH}_2} \\
\text{8} & \quad \text{down} \quad \text{9} \\
\text{10} & \quad \text{down} \quad \text{10}
\end{align*}
\]

by means of thin layer chromatography using a chloroform/methanol mixture (95/5) as the eluent. After 20 h, no unmodified PPE was observed anymore. 5a and 5b were both isolated by precipitation in acidified methanol in a yield of 95%.

As illustrated in Fig. 1, the spectrum of 5a shows two characteristic triplets of the methylene end-group at 3.35 and 4.05 ppm. After integration it can be concluded that the ethylamination of PPE has occurred with completion. Similar results were obtained for 5b.

The synthesis of the 2,6-dimethyl-1,4-phenylene oxide-block-isoprene diblock copolymer was performed via the amidation coupling between the ethylammonium salt of PPE and the monocarboxylic acid of PIP in the presence of one mol equivalent of DCC. As explained in the introduction, a low molar mass compound, 10a, possessing a $M_n$ of 10000, was synthesized using PPE-OC\text{H}2\text{CH}2\text{NH}$_2$ 5a and PIP-COOH 1a as endcapped homopolymers. A similar diblock copolymer, 10b ($M_n = 40000$), was synthesized as well using PPE-OC\text{H}2\text{CH}2\text{NH}$_2$ 5b and PIP-COOH 1b.
Fig. 1. $^1$H NMR spectrum of (A) PIP-COOH 1a, (B) PPE-OCH$_2$CH$_2$NH$_3^+$Cl$^-$ 5a and (C) diblock copolymer 10a
as endcapped homopolymers. The mechanism of the coupling reaction (Scheme 1) and the results obtained for 10a and 10b are presented and discussed hereafter. As explained previously, the use of the ethylammonium salt of PPE instead of the free ethylamine derivative is essential for the occurrence of the coupling reaction with PIP-COOH (Scheme 1). First, DCC reacts with PIP-COOH 1 resulting in the carboxylate anion of PIP-COOH 2 and protonated DCC 3, which upon recombination afford ester 4. Subsequently, 4 reacts with the ethylammonium salt of PPE 5, resulting in the free ethylamine derivative of PPE 6 and the protonated ester 7. In the latter step, the ethylammonium salt of PPE reacts as a Lewis base to activate ester 4. When the free ethylamine derivative of PPE is used instead of the ethylammonium salt, the reaction terminates after the second step yielding a mixture of 6 and 4 in a ratio 1 to 1. Finally, nucleophilic attack by 6 on the acyl group of 7 generates the N,N-dicyclohexyl urea 9 and the 2,6-dimethyl-1,4-phenylene oxide-block-isoprene diblock copolymer 10. 10a and 10b were obtained after precipitation in methanol as a non-solvent in an overall yield of 70% and 85%, respectively.

By comparing the 1H NMR spectrum of diblock copolymer 10a with the spectra of PIP-COOH 1a and PPE-CH₂CH₂NH₂Cl⁻ 5a (Fig. 1), it may be noted that the two characteristic peaks of the terminal methylene groups of the PPE block are shifted to 3.65 ppm for the methylene adjacent to the final phenoxide group, and to 3.75 ppm for the methylene adjacent to the amide linkage. This result is in agreement with the lower negative inductive effect of the amide group, as compared to the ethylammonium group. The two characteristic peaks of the terminal methylene group of the PIP block are shifted as well to 3 ppm in the NMR spectrum. Furthermore, by comparing the integral area of the individual methylene peak with the one of the terminal methyl group of the PIP chain, it can be concluded that the coupling reaction resulting in 10a has occurred with a conversion higher than 95%. As a result of the increase of the molar mass, the end-group concentration in 10b (0.8% for PPE and 0.3% for PIP) is much lower than in the previously studied low molar mass system 10a. However, by using a concentrated NMR solution (30 wt.-% solution), the characteristic peaks of the two methylene groups, located in between the final phenylene group of the PPE block and the amide linkage group, are well observed at 3.65 and 3.75 ppm and it can be concluded that the coupling reaction had occurred with a conversion higher than 90%.

As shown in the FT-IR spectrum of diblock copolymer 10a (Fig. 2), the characteristic carboxylic and ammonium vibrations at 1710 and 3500 cm⁻¹ respectively, have vanished completely. However, the characteristic carbonyl vibration of the amide group at 1680 cm⁻¹ is not observed due to an overlap with the olefinic vibrations of the PIP chain. The same observations are made for copolymer 10b.

The number-average molar masses (\(\bar{M}_n\)) and the molar mass distributions of 10a and 10b were determined using gel permeation chromatography (GPC). The GPC chromatogram of copolymer 10a possesses a monomodal distribution corresponding to a \(\bar{M}_n\) of 9500 after correction from the polystyrene standard, using the Mark-Houwink constants for PPE and PIP in THF at 25°C in the following relationship¹⁰:

\[
\log_{10} \bar{M}_w (\text{PPE}) = 1.073 \log_{10} \bar{M}_w (\text{PS}) - 0.5055
\]
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The previous results, doubling of the molar mass and monomodal distribution, confirm again that the coupling reaction between 1a and 5a had occurred with completion. The gel permeation chromatogram of 10b possesses a monomodal distribution as well corresponding to a $M_n$ of 38600 after correction from the polystyrene standard, as displayed in Eq. 1. These results confirm that the synthesis of diblock copolymer 10b had occurred successfully as well.

Since the microdomains in block copolymers are expected to be smaller than 50 nm\textsuperscript{11}, the morphology of the diblock copolymer 10a was investigated by transmission electron microscopy (TEM). The TEM micrograph of 10a shown in Fig. 3, demonstrates the presence of dispersed PPE particles in the PIP matrix. The particle size of the PPE microdomains is between 20 and 30 nm. At this moment, investigations concerning morphological studies on diblock copolymer 10b are in progress.

DMTA measurements were performed in order to identify the thermal transitions of 10b. This technique was preferred to DSC, because of the possibility to detect secondary transitions. Since a few grammes of material are necessary to prepare the tensile bar, DMTA experiments were investigated only for 10b, which was synthesized on a larger scale (10 g). In Fig. 4, the modulus $E^*$ and the loss factor tan $\delta$ are plotted as functions of the temperature.

From the tan $\delta$ curve, three different transitions $T_{g1}$, $T_{g2}$ and $T_{g3}$ can be derived at $-50^\circ$C, 10$^\circ$C and 185$^\circ$C, respectively. The first and third transitions correspond to
the glass transition temperatures of the PIP block and of the PPE block, respectively. The second transition temperature, \( T_{g2} \), is assumed to be correlated to the molar mass distributions of PPE and PIP. Since PIP is close to monodisperse (\( D = 1.06 \)) and since PPE possesses a broad molar mass distribution (\( D = 2.5 \)), the short PPE segments might be partially miscible with part of the PIP chains. As a consequence, this part of PIP possesses a higher glass transition temperature located at 10°C. Nevertheless, this particular phenomenon requires further investigations.

Conclusions

The amidation coupling route between the ethylammonium salt of PPE and the monocarboxylic acid of PIP, in the presence of DCC, was successfully applied to the synthesis of 2,6-dimethyl-1,4-phenylene oxide-block-isoprene diblock copolymers with molar masses of 10000 (10a) and 40000 (10b). The conversion yield of both coupling reactions was found to be higher than 90%. The typical morphology of 10a displays very small PPE domains (20–30 nm) dispersed in the PIP matrix. Further, the thermal analysis of 10b revealed three distinct glass transitions. Two of the transitions correspond to the PPE (190°C) and to the PIP (−50°C) blocks; the
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third transition (10°C) is assumed to result from partial miscibility of the short PPE chains into the PIP microphase.

Fig. 4. $E^* (\alpha)$ and tan$\delta$ (+) curves of diblock copolymer 10b