

Segmented block copolymers based on poly(butylene terephthalate) and telechelic polyesters and polyamides of dimerized fatty acids

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Segmented block copolymers (SBCs) based on poly(butylene terephthalate) (PBT) and telechelics based on dimerized fatty acids have been synthesized in the melt. The dimerized fatty acids were coupled with diols or diamines to synthesize polyesters and polyamides of low molar mass. With these telechelic polyesters and polyamides we studied the influence of the different types of blocks and the block length on thermal transitions with differential scanning calorimetry and dynamic mechanical thermal analysis. The melting behaviour was compared to an SBC based on a dimerized fatty acid ($M_n = 565 \text{ g mol}^{-1}$) and PBT. Neither the compositions of the SBCs nor the block lengths of the telechelic polyesters and polyamides seemed to be of influence on the melting behaviour. The glass transition temperatures (T_g values) of the SBCs based on the telechelic polyester decreased, while the T_g of the SBC based on the primary polyamide increased. Higher reaction temperatures and longer reaction times increased T_g , owing to transesterification reactions in the melt.

(Keywords: dimer acid; dimerized fatty acid; segmented block copolymer; poly(butylene terephthalate); telechelic poly(ester ester); thermoplastic elastomer)

INTRODUCTION

Segmented block copolymers (SBCs) are polymers that consist of different types of segments that alternate along the polymer backbone. Each segment of the polymer backbone has its own properties and transition temperatures. When flexible monomers are chosen SBCs can be synthesized with elastomeric properties. One segment must possess a low elasticity modulus and a low glass transition temperature (T_g). This segment imparts elastomeric properties to the material and, therefore, is often called the soft phase. The other segment is designed to undergo some sort of association so that it can form physical crosslinks. This segment will then impart dimensional stability to the material and, therefore, is often called the hard phase. Since the crosslinks in the material are of a physical nature, the materials with the elastomeric properties can be molten and processed by thermoplastic moulding techniques. For that reason the materials are called thermoplastic elastomers (TPEs).

An example of a commercial TPE that has been studied extensively in the literature¹ is the segmented block copoly(ether ester). Commercial block copoly(ether ester)s are usually based on poly(tetramethylene oxide) (PTMO) and poly(butylene terephthalate) (PBT) as the rubbery and semi-crystalline components respectively. These materials and their modifications are known under

many trade names such as Hytrel (Du Pont), Arnitel (AKZO) and Pelprene (Toyobo). These materials couple interesting properties such as high melting temperature (T_m), low T_g , high tensile strengths and high tear strengths with ease of processing.

One of the disadvantages of PTMO in TPEs is that the ether group is prone to oxidative degradation²⁻⁵ and hydrolysis⁵ at elevated temperatures. These TPEs also degrade at ambient temperatures in sunlight^{6,7}. For these reasons commercial copoly(ether ester)s are stabilized with various additives^{2-5,7-10}.

An alternative to using polyethers in TPEs is to use saturated fatty acids. Hoeschele¹¹ synthesized SBCs with a C_{36} dimerized fatty acid as the soft phase. All the properties concerning degradation stability were improved while most other properties were not influenced significantly. The properties at lower temperatures, however, showed poorer results due to the higher T_g .

In an earlier article from our group, SBCs based on PBT and dimerized fatty acids with different molar masses ($565 < M_n < 1038 \text{ g mol}^{-1}$) were discussed¹². It was found that the T_g values of the SBCs were lower for the dimerized fatty acid with the larger molar mass (1038 g mol^{-1}). The melting temperature increased concomitantly.

If T_g is influenced by the lengths of the amorphous segments, another possibility to lower T_g is through the use of telechelics based on dimerized fatty acids as the

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soft phase. The dimerized fatty acids can be coupled with diols or diamines to synthesize telechelic polyesters and polyamides respectively.

The aim of this work is therefore to study the synthesis and properties of SBCs with PBT as the hard phase and telechelics based on dimerized fatty acids as the soft phase.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT), 1,4-butanediol (BDO), 1,6-hexanediamine (HMDA), piperazine, *N,N'*-dimethylethylenediamine (DMEDA), *N,N'*-dimethyl-1,6-hexanediamine (DMHDA), tetrabutyl orthotitanate (all synthetic grade) and methanol (analytical grade) were purchased from Merck, Hohenbrunn, Germany. The dimerized fatty acids were obtained from Unichema Chemie, Gouda, The Netherlands.

The properties of the dimerized fatty acids were discussed in a previous paper¹². (Pripol 1008 has 36 C atoms of which 13 C atoms lie directly between the carboxy groups, a concentration of carboxy end groups of 3.46 meq g⁻¹ and an iodine value of 3.8 mg I per 100 g, and is composed of 0.1 wt% monomer, 0.5 wt% intermediate, 99.0 wt% dimer and 0.5 wt% trimer.) In this article another dimerized fatty acid – Pripol 1009 – is also used. This dimerized fatty acid has largely the same properties, but is a trifle less pure (0.1 wt% monomer, 1.0 wt% intermediate, 98.5 wt% dimer and 0.5 wt% trimer) and more unsaturated (iodine value of 5.3)

Synthesis of telechelic amorphous polymers (dimerized fatty acid with diol/diamine)

Telechelic polyesters. Batches of 50 g of polymer were synthesized by placing dimerized fatty acid and diol in an agitated round bottomed flask fitted for distillation. A stainless steel stirrer with a paddle cut to conform with the internal radius of the flask was positioned at a few millimetres above the bottom of the flask. Agitation was started while nitrogen was led into the flask. The flask was placed in an oil bath at 160°C, agitated for 5 min and then 0.1 wt% tetrabutyl orthotitanate was added. Water distilled from the reaction mixture as the temperature was slowly raised to 230°C over a period of 1 h. The reaction mixture was agitated for another 1.5 h at 230°C. The polyesters PPEB1 to PPEB5 were then allowed to cool down slowly to room temperature.

For the polyesters PPEB6 and PPEC1, however, the reaction continued under reduced pressure to get higher molar masses. For PPEC1 the reaction continued for 0.5 h under a reduced pressure of 15 mmHg. For PPEB6 the pressure was reduced to 0.5 mmHg in 2 h and the reaction was continued for another 4 h under these conditions.

All telechelic polyesters were transparent, viscous liquids.

Telechelic polyamides. For the synthesis of the telechelic polyamides the same procedure as described for the polyesters was followed. In these syntheses the catalyst was 0.1 wt% MeOLi from a solution of 0.3 g Li in 25 ml MeOH. The starting temperature of the oil bath was lower: 120°C. The temperature was raised to 230°C in 2 h and then held at that level for 1 h. The telechelic polyamides were then allowed to cool down slowly to room temperature.

For the polyamide PPAH1, however, the reaction continued under reduced pressure. The pressure was reduced to 0.5 mmHg in 15 min and held at that level for 75 min.

All products were transparent, yellow, viscous liquids except PPAH1 and PPAH2, which were yellow (slightly transparent) solids.

Synthesis of segmented block copolymers

The segmented block copolymers (SBCs) were synthesized with the same procedure as described for the polyesters. In these syntheses the reactants were BDO, DMT and polyester or polyamide. After heating from 160 to 230°C in a period of 45 min, the pressure was reduced in 15 min to 0.5 mmHg and the reaction was continued for 45 min. For samples PPEB2/DMT to PPEB6/DMT the procedure was slightly different. They were heated from 160 to 240°C in a period of 1 h, the pressure was reduced in 15 min to 0.5 mmHg and the reaction was continued for 1 h.

For two SBCs other starting materials were used. These copolymers were based on a telechelic polyester and prepolymerized PBT of low molar mass. This low-molar-mass PBT was synthesized by heating DMT and BDO with 0.1 wt% Ti(OC₄H₉)₄ from 180 to 230°C in 40 min and reacting at that temperature for 2 h. With this low-molar-mass PBT the SBCs PPEB1/PBT and PPEC1/PBT were synthesized. In this reaction the materials were heated from 210 to 230°C in 10 min. In another 10 min the pressure was reduced to 0.5 mmHg and held at that level for 40 min.

With the telechelic polyesters as starting material, white solid polymers were formed. With the telechelic polyamides, brown-yellow solid polymers resulted.

Characterization

End group titration. The amorphous polyesters were titrated to determine the concentration of carboxy end groups. The concentration was measured by dissolving 200 mg product in freshly distilled benzyl alcohol followed by titration with KOH in tert-BuOH. Titration was carried out with a glass calomel electrode under nitrogen, to minimize oxidation of benzyl alcohol, in a titroprocessor Metron 636.

The concentration of amine end groups was determined by titration of a solution of 200 mg material in an 80/20 (v/v) phenol/water mixture with trifluoromethanesulfonic acid in tert-BuOH. Phenol was freshly distilled before use. Titration was carried out with a glass calomel electrode in a titroprocessor Metron 636.

The concentration of hydroxy end groups was determined by reaction of the material with an excess of acetic acid anhydride (5 ml of a solution of 25% acetic acid anhydride in pyridine) at 80 to 100°C for 1 h. The excess acetic acid anhydride was titrated with a solution of KOH in tert-BuOH.

All chemicals (analytical grade) were purchased from Merck, Hohenbrunn, Germany.

Differential scanning calorimetry (d.s.c.). Thermal properties were measured with a Perkin-Elmer DSC-7. Samples of 4 to 8 mg of the as-prepared copolymers were dried in vacuum at 100°C for 24 h prior to testing. D.s.c. curves were obtained with the following procedure (heating/cooling rate 20°C min⁻¹): first heating run from 50°C to 40°C above the melting temperature,

equilibration for 8 min, and a cooling run to 50°C; second heating run to 40°C above the melting temperature. The crystallization and melting temperatures were taken as the maxima in the cooling run and second heating run respectively. The crystallization and melting enthalpies were also taken from this run. The absolute error in the melting and crystallization temperatures was $\pm 2^\circ\text{C}$. The absolute errors in the melting and crystallization enthalpies were $\pm 4\text{ J g}^{-1}$ and $\pm 2\text{ J g}^{-1}$ respectively.

Dynamic mechanical thermal analysis (d.m.t.a.). Torsion bars of approximate dimensions $80 \times 9 \times 2\text{ mm}$ were prepared by compression moulding of the as-prepared segmented block copolymers. Hereto the copolymers were placed between the heating plates of a hydraulic press (Laufer), compressed, and kept at a temperature approximately 40°C above the melting temperature for 7 min, after which cooling of the heating plates was started. The bars were subsequently dried for 18 h in vacuum at 100°C. Torsion moduli were studied with a computer controlled Myrenne torsion pendulum in a temperature range from -100°C to the onset of melting at a heating rate of 1°C min^{-1} and at a resonance frequency of 1 Hz. The maximum of the loss modulus was taken as the glass transition temperature T_g . The absolute error in T_g was $\pm 2^\circ\text{C}$. The relative error in the moduli was $\pm 5\%$.

The T_g values of the telechelic amorphous polymers were determined by an indirect route. First a piece of cloth with the right dimensions was cut. The piece of cloth was then impregnated with the polymer and dried at 40°C for 5 h. The specimens were tested under the same conditions as described above.

RESULTS AND DISCUSSION

Telechelic amorphous polyesters and polyamides

Molar masses. In Table 1 the molar masses determined from calculation and end group concentrations are given.

The telechelic polyesters were prepared with an excess of dimerized fatty acid but despite this excess in acid some diol distils from the flask during the polymerization. The hydroxyl concentrations of these esters were low. The lower molar masses of the telechelic esters than aimed at is thus due to loss of diol during the reaction.

The telechelic polyamides were synthesized with an excess of diamine. Excess diamine was used to give amide groups in the coupling to the PBT segment.

Glass transition temperatures. In Table 1 the glass transition temperatures (T_g) as measured by d.m.t.a. on the telechelic amorphous polyesters and polyamides are collected.

T_g is a function of the structure of the repeating monomer units. The T_g values of the polyesters are lower than those of the polyamides. The T_g values of the secondary polyamides lie between those of the polyesters and the primary polyamides.

The T_g of the primary polyamide PPAH2 is high because hydrogen bonds can be formed in the material.

The T_g values of SBCs will depend in part on the structure of the soft blocks. It is to be expected that the T_g will be lower if a soft block with a lower T_g is used. SBCs based on the telechelic polyesters are therefore the most promising materials. They were synthesized as well as a few SBCs based on the telechelic secondary polyamides.

Segmented block copolymers

Differential scanning calorimetry. D.s.c. data for the dried copolymers are collected in Table 2. From this table several conclusions can be drawn.

The melting temperatures are, within experimental error, equal for all samples (that have the same weight fraction of PBT: 60%). The use of PBT instead of DMT/BDO as the starting material for the SBC hard segment does not seem to influence T_m (or the other d.s.c. data). Also, the melting temperature is not influenced by

Table 1 Calculated and experimental molar masses and glass transition temperatures of the synthesized low-molar-mass polyesters/polyamides

Code ^a	Materials				End-group analysis			
	Acid ^b	Diol or diamine ^c	Ratio acid/other ^d (mol mol ⁻¹)	M_{aimed}^e (g mol ⁻¹)	Acid (meq g ⁻¹)	OH/NH ₂ (meq g ⁻¹)	M_n (g mol ⁻¹)	T_g (°C)
PPEB1	1008	BDO	1.16	4450	0.93	0.02	2100	-55
PPEB2	1008	BDO	2.00	1200	1.66	0.02	1200	-50
PPEB3	1008	BDO	1.50	1800	1.20	0.04	1800	-
PPEB4	1008	BDO	1.33	2400	0.91	0.02	2150	-
PPEB5	1008	BDO	1.20	3650	0.75	0.16	2200	-
PPEB6	1008	BDO	0.90	∞	0.00	<0.14	>14000	-56
PPEC1	1008	C ₃₆ diol	1.22	5000	0.70	-	<2850	-52
PPAH1	1009	HMDA	0.67	1600	0.04	1.22	1600	-
PPAH2	1009	HMDA	0.77	2500	0.02	0.79	2450	-10
SPAP1	1008	Piperazine	0.79	2400	0.03	0.77	2500	-24
SPAE1	1008	DMEDA	0.85	3800	-	0.69	<2900	-30
SPAH1	1008	DMHDA	0.88	5600	-	0.44	<4500	-38

^a Notation: first letter Primary or Secondary; second and third letters PolyEster or PolyAmide; fourth letter denotes the diol/diamine used

^b Pripol 1008 and 1009 from Unichema Chemie were used

^c BDO = 1,4-butanediol; C₃₆ diol = dimerized fatty acid diol based on Pripol 1009; HMDA = 1,6-hexanediamine; DMEDA = *N,N'*-dimethylethylenediamine; DMHDA = *N,N'*-dimethyl-1,6-hexanediamine

^d Ratio acid/alcohol or acid/amine

^e $M_{\text{aimed}} = M$ calculated from the ratio of reactants

Table 2 D.s.c. data and torsional data of SBCs based on low-molar-mass amorphous polyesters/polyamides and DMT or PBT

Code ^a	T_m (°C)	T_c (°C)	ΔT (°C)	ΔH_m (J g ⁻¹)	$-\Delta H_c$ (J g ⁻¹)	T_g (°C)	$G'_{20^\circ\text{C}}$ (MPa)
1008H60	185	146	45	21	32	-26	60
PPEB1/DMT	185	144	41	27	16	-35	54
PPEB1/PBT	176	137	39	21	22	-35	63
PPEB2/DMT	^b	126	-	-	28	-31	58
PPEB3/DMT	^b	142	-	-	27	-31	50
PPEB4/DMT	185	135	50	13	29	-31	63
PPEB5/DMT	184	148	37	22	26	-31	60
PPEB6/DMT	186	140	46	24	29	-28	55
PPEC1/DMT	184	133	51	24	28	-27	50
PPEC1/PBT	180	129	51	21	25	-33	50
PPAH1/DMT	170	130	40	21	19	-6	92
PPAH2/DMT	186	142	44	33	18	10	85

^a 1008H60 is an SBC based on Pripol 1008 ($M_n = 565 \text{ g mol}^{-1}$) and DMT/BDO; PPEB1/DMT is an SBC based on PPEB1 as the soft phase and DMT/BDO as the hard phase. PBT was of low molar mass and used as the hard phase

^b No melting peaks could be detected

the molar mass of the amorphous polymer used. This can be seen by comparing 1008H60 (based on unpolymerized dimerized fatty acid, $M_n = 565 \text{ g mol}^{-1}$) with the other materials (with increased M_n). The melting temperature was expected to increase with increasing molar mass of the amorphous polymer, because this also would increase the block length of the hard PBT segments.

The crystallization temperature, ΔH_m and ΔH_c behave analogously to T_m , although the errors in these data are somewhat larger than for T_m . In an earlier paper¹² it was shown that the enthalpy is influenced by composition only.

The use of telechelic polyamide compared to the use of telechelic polyester does not seem to have any influence on the melting behaviour.

Dynamical mechanical thermal analysis. D.m.t.a. data for the compression moulded samples are also collected in Table 2.

From the table it can be concluded that T_g is influenced by the length and type of soft block. Increasing the length of the soft block from 565 g mol^{-1} (Pripol 1008 alone) to around 2000 g mol^{-1} (amorphous polyester PPEB1) results in a decrease in T_g of 10°C . When polyamides are used the glass transition temperature is increased considerably, as was expected. The moduli of these polyamide based materials are also increased significantly.

Employment of polyester PPEC1 does not seem to give an advantage over the use of telechelic polyesters from BDO with dimerized fatty acid (PPEB). The use of PBT instead of DMT/BDO does not seem to influence T_g or the modulus. Also, for the amorphous polyesters PPEB2 to PPEB6 there seems to be no influence of the molar mass of the telechelic on T_g or $G'_{20^\circ\text{C}}$. It was expected that an increased M_n would cause a decreased compatibility between PBT blocks and the amorphous phase such that T_g would probably decrease. The T_g values for the materials PPEB2/DMT to PPEB6/DMT are higher than that of PPEB1/DMT, although M_n for PPEB1 is of the same order as the M_n values for PPEB4 and PPEB5. This possibly is caused

by the different polymerization times. Long reaction times allow a considerable amount of transesterification to take place, leading to a decrease in the molar mass of the aliphatic polyester block.

To test the influence of the reaction conditions a few copolymers were synthesized based on PPEB4 under different conditions. In Table 3 the reaction conditions and T_g values of the corresponding materials are contained.

The table shows that the T_g is influenced by the reaction conditions. Longer reaction times and higher reaction temperatures increase T_g . This effect is not quite unexpected. If the catalyst is not killed transesterification will always occur when heating polyesters to their melting temperature. From this table it is evident that the reaction conditions do influence the properties of the SBCs. Possibilities to overcome this problem are already described in the literature. AKZO, for example, produced a poly(ester ester) by reacting a hydroxy terminated PBT of low molar mass with an isocyanate terminated amorphous telechelic polyester^{13,14}. It is also possible to couple hydroxy terminated hard and soft polyesters with diisocyanates¹⁵. Snijder used another approach still¹⁶. He took poly(ethylene terephthalate) and a copolyester of ethylene terephthalate and ethylene sebacate, both of high molar mass. By transesterification reactions in the melt, the molar masses of both polymers decreased until a homogeneous melt was formed. This route, however, is not so suitable for commercial products because the reaction cannot be adequately controlled.

CONCLUSIONS

In this work segmented block copolymers (SBCs) based on telechelic dimerized fatty acid polymers and DMT/BDO or PBT were synthesized.

The dimerized fatty acids were first polymerized with diols or diamines to give polyesters or polyamides respectively. The T_g in the SBC decreased in the order secondary polyamides > tertiary polyamides > polyesters. To synthesize SBCs with low T_g values the telechelic polyesters are therefore preferred as soft building blocks.

Compared to a sample based on a dimerized fatty acid the use of a telechelic of a dimerized fatty acid does not seem to influence the melting behaviour of the SBC significantly. The glass transition temperature is increased by using primary polyamides and decreased by polyesters compared to the SBC based on a dimerized fatty acid. The use of prepolymerized PBT again shows no significant effect.

Longer reaction times and higher reaction temperatures increase T_g owing to transesterification reactions that occur in the melt.

Table 3 Reaction conditions^a used in the synthesis of SBCs based on the low-molar-mass amorphous polyester PPEB4 and the resulting T_g values

Code	t_{heat} (h)	t_{polym} (h)	t_{tot} (h)	T_{max} (°C)	T_g (°C)
PPEB4/A	0.92	0.92	1.84	220	-36
PPEB4/B	0.75	1.50	2.25	230	-32
PPEB4/C	1.00	1.25	2.25	240	-31
PPEB4/D	1.50	1.75	3.25	240	-24

^a t_{heat} = warming-up time; t_{polym} = polymerization time; t_{tot} = total time of heating up and polymerization; T_{max} = maximum temperature used

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