HIGH Tg SEGMENTED COPOLYMERS WITH MONODISPERSE CRYSTALLISABLE SEGMENTS

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Introduction

Segmented copolymers consisting of amorphous poly(2,6-dimethyl-1,4-phenylene ether) (PPE) (also called PPO) segments, crystallisable tetra-amide units (up to 20 wt%) and spacer groups (-spacer-T-PPE-spacer-T6T6T-) have been investigated. 1,11 The monodisperse tetra-amide units T6T6T are two and a half repeat units of PA-6,12 The copolymers are semi-crystalline materials with a high Tg (170-180 °C) combined with a not too high melting temperature (260-275 °C) and have thus an extremely high Tg/Tm ratio (>0.8). This is very particular because crystallization is normally absent in (co)polymers with a high Tg/Tm ratio. 1,3 The uniform length T6T6T segments form ribbon-like crystalline structures with a very high aspect ratio dispersed in the amorphous matrix. 1,4 The copolymers are good melt processable and have good solvent resistance and low water absorption. Increasing the spacer group length decreases the Tg of the system a bit but increases the storage modulus between Tg and Tm. 15 Interesting is to study if high molecular weight PPE-T6T6T copolymers can be made without spacer units and what the properties of these copolymers are. Without spacer units the copolymer synthesis is in less steps and thus simpler. The starting telechelic PPE has two hydroxyl groups (PPE-2OH) (Fig. 1) and a molecular weight of 3500 g/mol. 11

Experimental

Materials. N-methyl-2-pyrrolidone (NMP) was purchased from Merck. Tetra-isopropyl orthotitanate ([Ti(O-i-OC3H7)4]), obtained from Merck, was diluted in anhydrous m-xylene (0.05M), obtained from Fluka. A poly(2,6-dimethyl-1,4-phenylene ether) ethoxy dimethyl ether, PPO-8058 (11,000 g/mol), was obtained from GE Plastics (The Netherlands). Telechelic PPE-2OH with a number average molecular weight of 3500 g/mol and 450 μmol OH/g was made according to. 11 All chemicals were used as received. Uniform T6T6T-diphenyl (>95% uniform), 6T-diamine and diphenyl terephthalate (DPT) were synthesised as described before. 12

Synthesis of -PPE-T6T6T- copolymers

The preparation of an alternating segmented block copolymer of PPE-2OH and T6T6T-diphenyl is given as an example. For copolymers with lower T6T6T contents part of the T6T6T-diphenyl was replaced by DPT to retain stoichiometry and high molecular weight. The reaction was carried out in a 50 ml glass reactor with a nitrogen inlet and outlet. The reaction was carried out in air. The reaction temperature was 280 °C. Subsequently the pressure was then carefully reduced (P<2 mbar) to distill off the remaining NMP in 60 minutes and then further reduced (P<1 mbar) for 60 minutes. Finally, the vessel was allowed to slowly cool to room temperature whilst maintaining the low pressure. Then the polymer was removed from the reactor and powdered.

Viscometry. The inherent viscosity of the polymers was determined with a capillary Ubbelohde type 1B at 25 °C, using a polymer solution with a concentration of 0.1 g/dl in phenol/1,1,2,2-tetrachloroethane (50/50, mol/mol).

Differential Scanning Calorimetry. DSC spectra were recorded on a Perkin Elmer DSC 7 apparatus, equipped with a PE7700 computer and TASS 7 software, measured with a heating and cooling rate of 20 °C/min. The (peak) melting temperature and enthalpy were obtained from the second heating scan. The crystallisation temperature was defined as the maximum of the peak in the cooling scan.

Results and Discussion.

The bifunctional PPE telechelic with hydroxyl end groups (PPE-2OH) was reacted with DPT and/or T6T6T-diphenyl. The used PPE-2OH had a number average molecular weight of 3500 g/mol and a Tg of 182 °C. Due to the aromatic nature and steric hindrance of the 2,6-dimethyl groups have the phenolic end groups a low reactivity. Also present in PPE are Mannich base type OH-end groups which are expected to have a very low reactivity too. 12 In view of this was the final reaction step in the polymerization carried out at 280 °C. The PPE-T6T6T/T copolymers from PPE-2OH and T6T6T-diphenyl copolymers were prepared with varying T6T6T content (11 - 0%). The PPE-T6T6T/T copolymers from PPE-2OH and T6T6T-diphenyl were reacted with DPT and T6T6T-diphenyl. The copolymer without T6T6T is -PPE-T- and the copolymer without DPT is -PPE-T6T6T-. If both T6T6T and DPT are used the copolymer is abbreviated as -PPE-T6T6T/T-. The copolymers were obtained by a solution/melt polymerisation and had relative high inherent viscosities (0.31-0.38 dl/g) despite the low reactivity of the phenolic end groups of PPE-2OH. Increasing the DPT content did not seem to have an effect on the inherent viscosities. The reactivity of the T6T6T-diphenyl is thus not lower than DPT and the miscibility of T6T6T-diphenyl with PPE-2OH not a problem. The copolymers were transparent. The melting temperature and enthalpy were obtained from the second heating scan. The crystallisation temperature was defined as the maximum of the peak in the cooling scan.
difference should have been less than 30°C. The heats of melting and crystallisation were hardly measurable and were about 1 J/g. The copolymers could be injection moulded into bars and these were tested by DMA (Fig. 2).

**Figure 2:** The storage ($G'$) and loss modulus ($G''$) as function of temperature as measured by DMA with different T6T6T contents: □, 0 wt%; ○, 7 wt%; ●, 9 wt%; ■, 10 wt%.

The PPE-T copolymer (0 wt% T6T6T) is an amorphous material which is not expecting to crystallise. This copolymer had a $T_g$ at 195 °C and a flow temperature ($T_{flow}$) of 220 °C. The $T_g$ of the copolymer is thus higher than the prepolymer ($T_g$ = 182 ºC) and this probably due to the increase in molecular weight. Increasing the T6T6T content decreased the $T_g$ to 183 °C and increased the $T_{flow}$ to 250-260 °C. As the $T_g$ of the copolymers with T6T6T is lower than that of the amorphous copolymer PPE-T, some T6T6T units are expected to be mixed with the amorphous PPE phase. The flow temperature increased with T6T6T content due to crystallised T6T6T segments. The $T_g$ of the amorphous T6T6T is present in the PPE phase and a part as an amorphous PA phase with a glass transition temperature of 130°C. The crystallinity in the copolymers can probably be improved by optimizing the molecular weight and the processing conditions.

The properties of the -PPE-T6T6T- copolymers are fairly comparable and also with those of the copolymer with spacer units: -PPE-T-spacer-T6T6T-spacer-T-. However, the crystallinities and the crystallization rates were higher with the -PPE-T-spacer-T6T6T-spacer-T-copolymer.

**Conclusions**

High molecular weight copolymers could be obtained from PPE-2OH and T6T6T-diphenyl. The phenolic terephthalate ester is apparently sufficient reactive for making these block copolymers. The amide concentration could be lowered by replacing some of the amide units by DPT. With T6T6T units the segments are mono disperse in length. The copolymers have a high $T_g$ and a high melting temperature. The $T_{m}$s are somewhat lower that that of pure PPE (PPO-803) but higher than that of the starting prepolymer. The flow temperatures increase from 220 ºC without T6T6T to 255-265 ºC with 9-11 wt% -T6T6T-. The crystallinity of the amide segments in the studied copolymers is however not so high (~20%). Also the $T_g$-$T_c$ is not so low, suggesting that the crystallization rate is not very fast. A part of the non crystalline T6T6T is present in the PPE phase and a part as a separate T6T6T phase.

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