TRIBLOCK COPOLYMER BASED ON MONODISPERSE ARAMIDE SEGMENTS - SYNTHESIS, MECHANICAL AND RHEOLOGICAL PROPERTIES

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Introduction

Well known are triblock copolymers and they are usually made of SBS type copolymers.[1] The styrene blocks have a molecular weight of about 25,000 gr./mol and are phase separated by liquid-liquid demixing. Triblock copolymers can also be made from polyether-nylon 6 systems.[2] The amide length is about 2000 g/mol and the amide content is often more than 50 wt%. Triblock copolymers with aromatic ester LCP blocks have been reported.[3] These short ester blocks have however rather low melting temperatures. Lately has also been studied triblock copolymers with H-bonding groups forming click like macromolecules.[4] These H-bonded copolymers have interesting thermo responsive rheological behavior, however the mechanical properties leaves to be desired. We studied triblock copolymers with monofunctional diamide blocks. The diamide blocks are short and mono-disperse in length so that they mix with the mid block in the melt and crystallize on cooling. With decreasing molecular weight of the copolymer the melt viscosities are expected to decrease strongly. A (very) low melt viscosity of the copolymer is an advantage in several applications like in overmoulding and in injection molding of electronic components. The use of mono-disperse diamide segments in multi-block copolymers has been studied.[5] The amide segments in segmented block copolymers crystallize fast and to a large extend. The mono-disperse character of the amide segments is maintained on melt synthesis and melt processing. The properties of these block copolymers can be varied with the soft segment length. Interesting is to study is the influence of H-bonding amide end-blocks on the melt rheological and solid state behavior. The question is do crystalline end-blocks contribute to the properties differently than mid-blocks. In this paper we reported the synthesis and the properties of poly(aramide- poly(tetramethylene oxide)-aramide) triblock copolymer. The properties are compared to segmented block copolymers with similar aramide segments.[5] Studied are the synthesis of the mono functional diamide, the synthesis of the triblock copolymer, the structure analysis by AFM, the DMA spectrum and the melt rheological behavior.

Experimental

Materials. Dimethyl terephthalate (DMT), and N-methyl-2-pyrrolidone (NMP) were purchased from Merck. Tetraisoprophyl orthotitanate (Ti(i-OC$_3$H$_7$)$_4$), obtained from Merck, was diluted in anhydrous m-xylene (0.05 M), obtained from Fluka. Poly(tetramethylene oxide) (PTMO, *M* = 1000 g/mol) was provided by DuPont. Irganox 1330 (1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene) was obtained from CIBA. 4$^-$-aminobenzanilide was purchased from Aldrich. Methyl(4-chlorocarbonyl)benzoate (MCCB) was obtained from Dalian (No.2 Organic Chemical Works, China).

Synthesis of TΦB-mono methyl (Scheme 1). MCCB (3 g, 0.015 mol) was dissolved in 25 mL of NMP at room temperature in a 250 mL flask, equipped with mechanical stirrer, nitrogen inlet, condensed and calcium chloride tube. 4$^-$-aminobenzanilide (3.4 g, 0.016 mol), previously dissolved in 125 mL of NMP was added dropwise over a period of 30 min, and methanol (25 mL) was added after 2 h reaction time. After a further 2 h, the reaction mixture was filtered off in a soxhlet extraction thimble and washed with hot toluene, and twice in hot acetone. The product was subsequently dried in a vacuum oven at 70°C. Yield = 60%.

^{1}H NMR spectra were recorded on a Bruker AC 300 spectrophotometer at 300.1 MHz. Deuterated trifluoroacetic acid (TFA-d) was used as the solvent. ^{1}H NMR for TΦB (TFA-d, δ): 8.3 (2H, d, marked as 'a'), 8.1 (2H, d, marked as 'b'), 7.9 (2H, d, marked as 'c'), 7.6-7.8 (7H, m, marked as 'd') and 4.1 (3H, s, marked as 'e'). The purity of the hard segment (TΦB-mono methyl) was calculated using the formula,

$$Purity = \frac{I_c}{I_b} \times 100 \qquad (\%)$$

Where, I_b = Integral value of proton b and I_c = integral value of proton c.
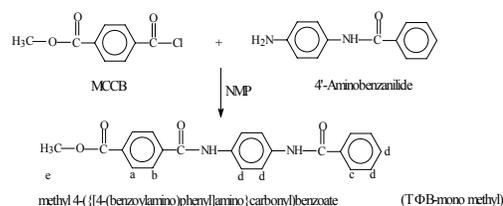
Scheme 1. Synthetic route of TΦB-mono methyl.

Synthesis of triblock copolymer BΦT-(PTMO$_{1000}$-T)$_x$-PTMO$_{1000}$-TΦB. The preparation of BΦT-(PTMO$_{1000}$-T)$_{9000}$-PTMO$_{1000}$-TΦB is shown as an example. The reaction was carried out in a 250 mL stainless steel vessel with a nitrogen inlet and mechanical stirrer. The reactor was charged with TΦB-mono methyl (3 g, 0.008 mol), PTMO$_{2900}$ (34.8 g, 0.012 mol), DMT (1.55 g, 0.008 mol), 1 wt% of Irganox 1330 (0.364 g), the catalyst solution (1.2 mL of 0.05 M Ti(i-OC$_3$H$_7$) in m-xylene), and 75 mL of NMP under nitrogen flow. The stirred reaction mixture was heated to 180°C for 30 min and subsequently the temperature was raised in steps to 250°C within the 1 h, followed by 2 h stirring. Subsequently, the pressure was carefully reduced (P<20 mbar) to distil off the NMP and further the pressure was reduced to <0.3 mbar for 1 h. After that the reaction mass was cooled slowly with maintaining the low pressure. The molecular weight of the copolymer was tuned by changing the soft segment length by taking appropriate mole ratios of PTMO and DMT. The chemical structure of the triblock copolymer was presented in the Scheme 2.
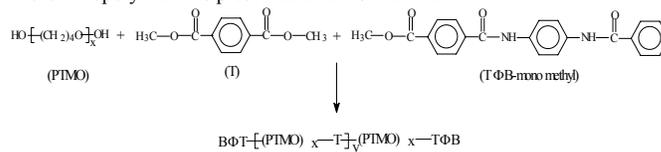
Where,
X = 1000 and Y = 2000 or 5000 or 9000 or 19000

Scheme 2. Synthesis of Triblock copolymer BΦT-(PTMO$_{1000}$-T)$_x$-PTMO$_{1000}$-TΦB.

Inherent viscosity, AFM, injection moulding and DMA of the copolymers were done according to the procedure given by Schuur et. al.[6]

Melt rheology. Rheology measurement was carried out on a Paar Physica UDS200 rheometer with a Paar Physica TC 20 temperature control unit. A parallel plate set up was used with a fixed EHH-TEK 350 plate and MP 306 rotating plate.

Results and Discussion

The mono functional mono ester diamide TΦB-mono methyl was prepared with a high purity (>99%). The triblock copolymers with TΦB end-segments were made with varying TΦB-mono methyl content by changing the soft segment length, the PTMO$_{1000}$ was extended with terephthalic groups -(PTMO$_{1000}$-T)$_x$-PTMO$_{1000}$-(Table 1). The triblock copolymers were transparent materials. The inherent viscosities increased with expected molecular weights. The triblock copolymers are compared to multi-block copolymers with the difunctional TΦT units.[5]

Table 1. Inherent viscosity and DMA results of triblock copolymer BΦT-(PTMO$_{1000}$-T)$_x$-PTMO$_{1000}$-TΦB.

Expected Mol.Wt. (g/mol)	TΦB (wt %)	η_{inh} (dl/g)	T_{flex} (°C)	T_g (°C)	T_{flow} (°C)	G'$_{25°C}$ (MPa)	tan δ (-)
2800	22.4	0.27	5	-70	245	39	0.05
6200	10.2	0.58	10	-65	175	11	0.07
10700	5.9	0.71	15	-65	150	6	0.11
20900	3.0	1.1	15	-65	135	4.5	0.10

AFM analysis. The structure analysis is studied on spin coated films by the AFM method using the phase angle mode. The crystalline regions appear as white areas. The AFM picture of the triblock copolymer having 3% of hard segment reveal a ribbon like crystalline morphology with a high aspect ratio of the ribbons (Figure 1). The AFM picture is of the surface and

the long ribbons bend out of the surface, therefore the total length of the ribbons is very difficult to determine, but was found to be more than 1μm..
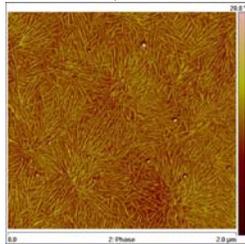

Figure 1. AFM phase image pictures of Triblock copolymers having 3% of hard segment.

DMA. The storage modulus verses temperature graph of BΦT-$(PTMO_{1000}-T)_x-PTMO_{1000}-T\Phi B$ triblock copolymers were presented in the Figure 2. Three transitions were observed, the T_g of the polyether phase, the T_m of the PTMO and the T_m of the TΦB. The T_g of the PTMO phase was found to be around -70°C in the triblock copolymer and this is a very low temperature. This suggests that the concentration of the TΦB in the polyether phase is very low. The PTMO melting is at about 10°C and is in the DMA storage modulus graph noticeable as a shoulder and is given in Table 1 as the T_{flex}. These copolymers show a temperature independent rubbery plateau which is a typical of copolymers with the mono disperse crystallisable segments. The flow temperature (T_m) of the TΦB segments in these copolymers was sharp and it increasing with increasing the TΦB content in the polymer (or decreasing the soft segment length). Sharp T_{flow} of these polymers is due to the mono dispersity of the crystallisable segments. The change in the flow temperature by changing the TΦB content was due to the solvent effect of the soft phase for which the theory of Flory can be used.[7]
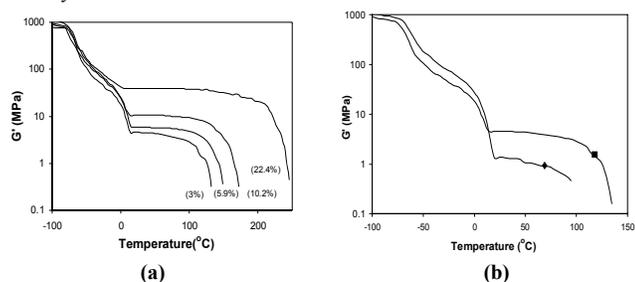

(a)

(b)

Figure 2. The storage modulus curve of (a) triblock copolymers and (b) comparative graph between the triblock and multiblock[5] copolymers having 3% of hard segment : ■ , triblock; ♦, multiblock.

The moduli at room temperature increase strongly with amide content. The thermo mechanical behavior of the BΦT-$(PTMO_{1000}-T)_x-PTMO_{1000}-T\Phi B$ triblockcopolymer was compared to the -(-$(PTMO_{1000}-T)_x-PTMO_{1000}-T\Phi T)_b$- multi-block copolymer[5] (Figure 2b). The low temperature behavior of the tri- and muliti-block copolymers seems to be similar. For the triblock copolymer the moduli were even higher than for the multi-block copolymer and the melting temperature was surprisingly also higher. The storage moduli increase logarithmic with the amide content (Figure 3a). The moduli of the triblock copolymers were over the whole concentration range high than those of the multi-block copolymer. At low amide contents the $G'_{25°C}$ of triblock had three fold increases in the storage modulus over multi block copolymer. The higher values of the storage modulus of the triblock copolymer can be due to a higher crystallinity and/or the higher aspect ratio of the crystallites. The copolymer melting temperatures (T_{flow}) decrease with increasing soft segment length (Figure 3b). Also, the T_{flow} of triblock copolymers were at higher temperatures that that of the multi-block copolymers. The T_{flow} value is dependant on the crystallite thickness, the crystallinity and the crystallite/amorphous phase interaction. The diamide length of TΦB and TΦT is very similar and thus also the crystallite thickness. Also both TΦB and TΦT are expected to have a high crystallinity. Thus as yet it is not yet clear why the T_{flow} and $G'_{25°C}$ for the triblock copolymer are higher.
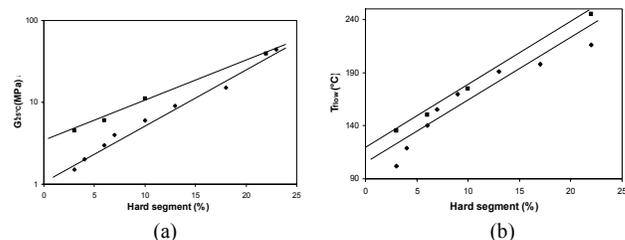

(a)   **(b)**

Figure 3. Comparative graph between the triblock and multiblock[5] copolymers as function of amide content (a) G' (b) T_{flow} : ■ , triblock; ♦, multiblock.

Melt rheology (dynamic test). The storage (G') and the loss modulus (G") in the linear viscoelastic region of triblock and multiblock copolymer were studied (Figure 4). In both the case, the concentration of the hard segment was kept at 3%. The multi-block copolymers G' and G'' decreasing very sharply (with high terminal slope) without a crossover and the tan δ (G"/G') even increase in value. The triblock copolymer graph shows that on decreasing the oscillation frequency leads to decrease in modulus values (G' and G'') and crossover point occurs at a low frequency. A cross over (tan δ =1) suggests a network formation. Also the high G' combined with the small terminal slope suggest that there is a strong interaction between the hard segment of the polymer chain in the molten state leading to the ordered arrangement in the melt.[8] The network formation is thought to be due to H-bonding of the amide segments.
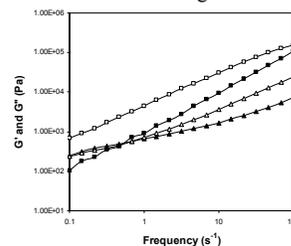

Figure 4. Melt rheology behavior of copolymers on 1% strain at 160 °C: ▲, G' triblock; Δ, G'' triblock; ■, G' multiblock; □, G'' multiblock.

Conclusion

Novel hard mono functional diamide segment TΦB with high purity was synthesized and used for the triblock synthesize. Triblock copolymers having different concentration of hard segment were synthesized. Compared to the multi-block copolymer had the triblock copolymer an unusual melt rheological behavior. At low shear rates network forming seem to take place. Also the rubbery modulus and the flow temperature (melt temperature) were higher. Aggregation of hard segment through hydrogen bonding in the molten state seems to have also an effect on the polymer properties in the solid state. Low melt viscosity with high rubbery modulus of the triblock copolymers will be a great advantage for many industrial applications.

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