Melt Rheological Behavior of a Triblock Copolymer Based on Aramide End-Segments

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ABSTRACT: Melt rheological behavior of a **ABA** triblock polymer made of poly(tetramethylene oxide) (PTMO) (M_n = 2,900 g mol^{-1}) soft segment and aramide hard segment was studied. The aramide end-segments (**A**) were short and mono-disperse in length. The mid-segment (**B**) consisted of PTMO$_{2900}$ extended with terephthalate units to a molecular weight of 9000 g mol^{-1}. The molecular weight of the triblock was 9700 g mol^{-1}. Rheological behavior of this material was studied by parallel-plate and capillary method. The **ABA** triblock copolymer was compared with a **B** polymer (PTMO-terephthalate) of a similar molecular weight. The low molecular weight **B** polymer had a Newtonian behavior. The low molecular weight triblock copolymer had at high frequencies a low complex viscosity. However, at low frequencies the tri-block copolymer had a very high complex viscosity. Also the G''/G' ratio decreased with decreasing frequency to values less then one and the G' seemed to have at low frequencies a plateau value. The activation energy of the process increased in value with decreasing shear rate. All these results indicate that the triblock copolymer at low frequencies had a gel-like behavior and this probably due to the clustering of the aramide segments. The aramide clusters are thought to be the (weak) network points of the gel. This network was also found to have a time dependant rheological response and thus a thixotropic behavior. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2663–2668, 2009

Key words: aramide; triblock; rheology; thixotropic

INTRODUCTION

ABA triblock copolymers with H-bonding end-segments have interesting properties.[1–10] Triblock copolymers have been studied with uridopyrimidinone,[1–4] urethane,[5–8] and amide[8–10] end-groups. If the structure is regular, the H-bonding end-segments can crystallize and as the end-segments are more mobile, they crystallize faster and have a higher crystallinity than mid-segments.[6–10] If the end-segments were made with a regular structure and mono-disperse in length, the crystallinity was very high, near 100%.[9,11,12] These triblock copolymers had a relatively high modulus and relative high elongations at break. Particular interesting are block copolymers with aromatic diamide units, similar to aromatic units in the highly crystalline aromatic fibers as these diamide units have a high crystal-linity combined with a high melting temperature.[11,13–15] The diaramides ($-$TΦB) in the triblock copolymer are mono functional compounds that were mono-disperse in length (Fig. 1).

The diaramide end-segments like amide segments in multiblock copolymers can H-bond with both neighboring amide segments and crystallized out in nanoribbons with a high aspect ratio.[8,11,16] As the crystallization of the amide segments was so fast, it was questioned whether the amide segments were in the melt preordered.

Another type of triblock copolymers is whereby two end groups associate and thereby form a high virtual molecular weight linear copolymer.[1,2,17,18] The rheological behavior of the polymers with associating ends showed nongelling behavior in the melt.[1,2,17] Whereas introducing an extra urethane group along with the association ends leads to gelation at low frequencies.[18] It was concluded that the presence of lateral hydrogen bonding end groups, forming H-bonding with two neighboring aramide segments, facilitate the gelation in the melt.

It is interesting to study the rheological behavior of a triblock copolymer with the amide units. The amide units can form H-bonding with both neighboring amide units. The question is if in the melt the mono-disperse diaramide endgroups are randomly
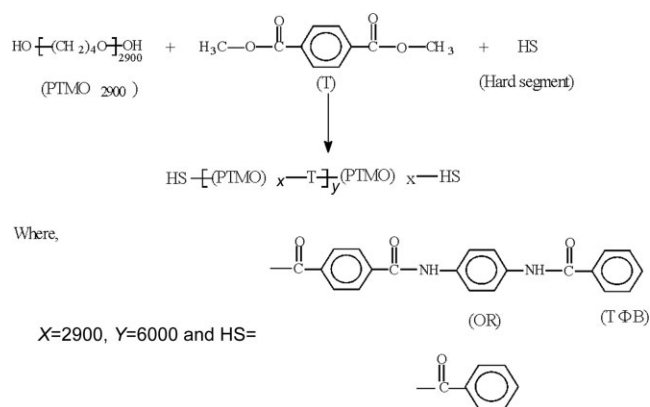
Figure 1 The chemical structure of the copolymer segments.

dispersed or clustered. To study the effect of the diaramide end-segments, copolymer without the diaramide end-segments was also studied.

EXPERIMENTAL

Materials

The synthesis and some properties of monoblock polymer (Ph-(PTMO$_{2900}$-T)$_{9000}$-Ph) and the triblock copolymer (TΦB-(PTMO$_{2900}$-T)$_{9000}$-TΦB) has been described.[9,12]

Viscometry

The inherent viscosity of the polymers at a concentration of 0.1 g/dL in a 1 : 1 (molar ratio) mixture of phenol-1,1,2,2-tetrachloroethane at 25°C was determined using capillary Ubbelohde 0C.

Parallel-plate rheology measurements

Rheology measurement was carried out on a Paar Physica UDS200 parallel-plate rheometer and Kayeness capillary flow rheometer. A parallel-plate set up was used with a fixed EHH-TEK 350 plate and MP 306 rotating plate. The diameter of the upper plate was 25 mm, and the gap between the two parallel-plates was 0.5 mm. Paar Physica software was used for all the rheology calculations. Low amplitude oscillatory shear experiment were performed over the frequency range of 0.1–100 s^{-1} on polymer samples. Initially, the copolymer was allowed to stand in between the two parallel-plates at a set temperature for 300 s. Dynamic frequency sweep was performed on the triblock copolymer at different strain percentage. The complex viscosity of the polymer at low shear rate 0.1–100 s^{-1} was measured using parallel-plate method. Similarly, the creep and recovery behavior was measured using parallel-plate rheometer. This consists of two parts, creep and elastic recovery. The triblock copolymer was allowed to

stand at a set temperature for 300 s. In the creep phase, small (1–10 Pa.s) constant shear stress was applied instantaneously and the applied shear stress was removed after 120 s. The recovery phase was monitored for 300 s.

Capillary rheology measurements

The apparent viscosity of the polymers at high shear rate was measured by capillary method. The length and the diameter of the capillary were 30.48 and 1.016 mm, respectively. The inner diameter of the barrel was 9.525 mm. The force (*F*) necessary to push the melt polymer through the capillary was measured and the melt viscosity was calculated from the equation,

$$\eta = \frac{F * r_c^4}{8\pi * R_b^4 * L_c * S} \qquad (1)$$

where, F = Force on piston [N], r_c = Inner radius of the capillary [m], R_b = Inner radius of the barrel [m], L_c = Length of the capillary [m], and S = piston speed [ms^{-1}].

RESULTS AND DISCUSSIONS

The rheological behavior of an **ABA** triblock copolymer and a **B** polymer (monoblock) both with a molecular weight of 9700 and 9200 g mol^{-1}, respectively, was studied in detail. The triblock copolymer had a polyether mid-segment (**B**) and monodisperse mono functional diaramide end-segments (**A**) (Fig. 1). The ether segment of the mid-segment of the triblock copolymer consist of PTMO with a molecular weight of 2900 g mol^{-1} extended with terephthalate groups to a soft segment length of 9000 g mol^{-1}. The monodisperse mono functional diaramide end-segments used were TΦB and with these end-segments the triblock copolymer had a molecular weight of 9700 g mol^{-1} (Fig. 1). The **B** polymer (monoblock) consists of poly(tetramethylene oxide) (PTMO$_{2900}$) extended with terephthalate groups, endcapped with benzyl groups (Fig. 1) and had a molecular weight of 9200 g mol^{-1}. The inherent viscosity of these two polymers were similar (∼ 0.8 dL g^{-1}), and thereby, the properties of these materials can be compared conveniently. The mid-segment of the triblock copolymer had a similar composition and molecular weight as the **B** polymer (monoblock). Some properties of these materials are given in Table I.

The **B** polymer (monoblock) was a brittle semi-solid material with a melting temperature of 25°C (by DSC) which is the T_m of the melting of crystalline PTMO$_{2900}$. The **ABA** triblock copolymer is an elastic material with a flow temperature (melting

TABLE I
Properties of Tri and Monoblock Copolymers

Polymer type	Mol. wt.[a] (g/mol)	η_{inh} (dL/g)	HS (wt %)	$T_{m,s}$[b] (°C)	T_{flow}[b] (°C)	$G'_{35°C}$[b] (MPa)	ΔG[b] (%/°C)
Triblock[9]	9700	0.86	7	28	160	7.5	0.2
Monoblock[12]	9200	0.80	0	25[c]	25	–	–

[a] M_n based on feed composition.
[b] DMA data.
[c] DSC data.

temperature) of 160°C. This T_m is of the melting of crystalline TΦB segments. The triblock copolymer crystallized fast had a high crystallinity and good tensile properties.[8–10] The molecular weight of these copolymers is relatively low and thus entanglements are expected hardly to be present. A Newtonian or a near Newtonian melt rheological behavior is expected. The melt rheological behavior of the polymer melt was studied using dynamic test. In dynamic test, the complex modulus can be represented as $G^* = G' + iG''$, where, G' and G'' are the storage and the loss modulus, respectively. Also determined was the complex viscosity (η^*).

Effect of frequency

The complex viscosity of the mono- and triblock copolymers (9200–9700 g mol^{-1}) was studied as function of frequency at a $\sim$ 30°C temperature higher than the flow temperature (TΦB melting temperature) at, respectively, 50 and 190°C (Fig. 2).

The monoblock copolymer had a low melt viscosity, which did not change with frequency. The monoblock copolymer had a Newtonian behavior as expected for low molecular weight polymer.[3,19] The complex viscosity of the triblock copolymer was at high frequencies low, as low as that of the monoblock copolymer. However, on decreasing the oscil-

Figure 2 Complex viscosity η^* as function of shear rate at 1% strain: ▲, monoblock at 50°C; ■, triblock at 190°C.

lation frequency the complex melt viscosity of the triblock copolymer increased strongly. With three decades of frequency a complex melt viscosity increase of a factor 100 was observed. This strong increase in melt viscosity of the triblock copolymer at low shear rates when compared with the monoblock copolymer suggest that the TΦB end-segments can form loose associates in the melt and that dissociates upon increasing the frequency.[3,18] These associates must have been due to interactions between TΦB end segments in the triblock copolymer. This observation was consistence with the earlier reports for copolymers with lateral H-bonding end-groups, forming H-bonding with two neighboring segments.[4,11,18] From these results, it is not clear whether the end-segment associates are homogeneously mixed with the mid-segment phase or phase separated as small aggregates. The triblock copolymer melt was transparent, but the end-segment aggregates might have been so small that they did not scatter light. Also under polarized microscope no birefringence was observed. The increased viscosity at low shear rates might be due to an increased virtual molecular weight but may be also to the formation of clusters of diaramide end-segments.

Effect of strain

On the triblock copolymer, the effect of strain on the melt rheological behavior at 190°C was studied at 1 and 10% strain (Fig. 3).

With decreasing the frequency, both G' and G'' decreased and the G''/G' crossed over. At the crossover point ($G''/G' = 1$) the tan δ is one and this is a characteristic value for the onset of gel formation.[18] With increasing strain the crossover point shifted to a lower frequency, which is typical for a melt with a transient network structure.[18,20] Also, at low frequency, the G' values reached a plateau value and with increasing strain the onset of a plateau shifted to higher frequencies. The onset of the G' plateau value is regarded as the frequency at which the associates form as fast as they break up.[15] The appearance of the plateau modulus confirms the presence of a tight polymer network formed by the end-segments of the triblock copolymer in the melt.[3,11,19] Just entanglements would not show this
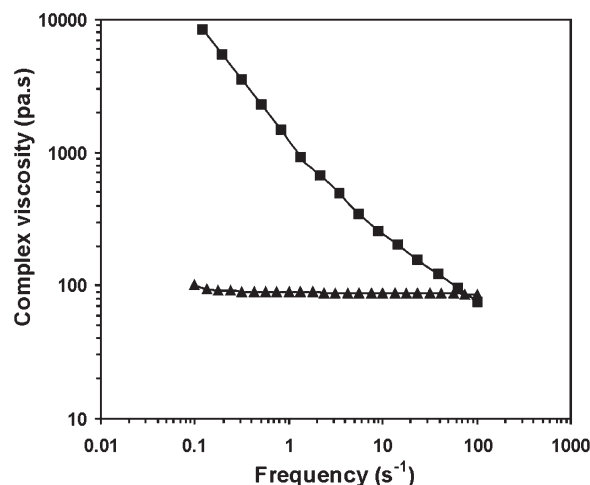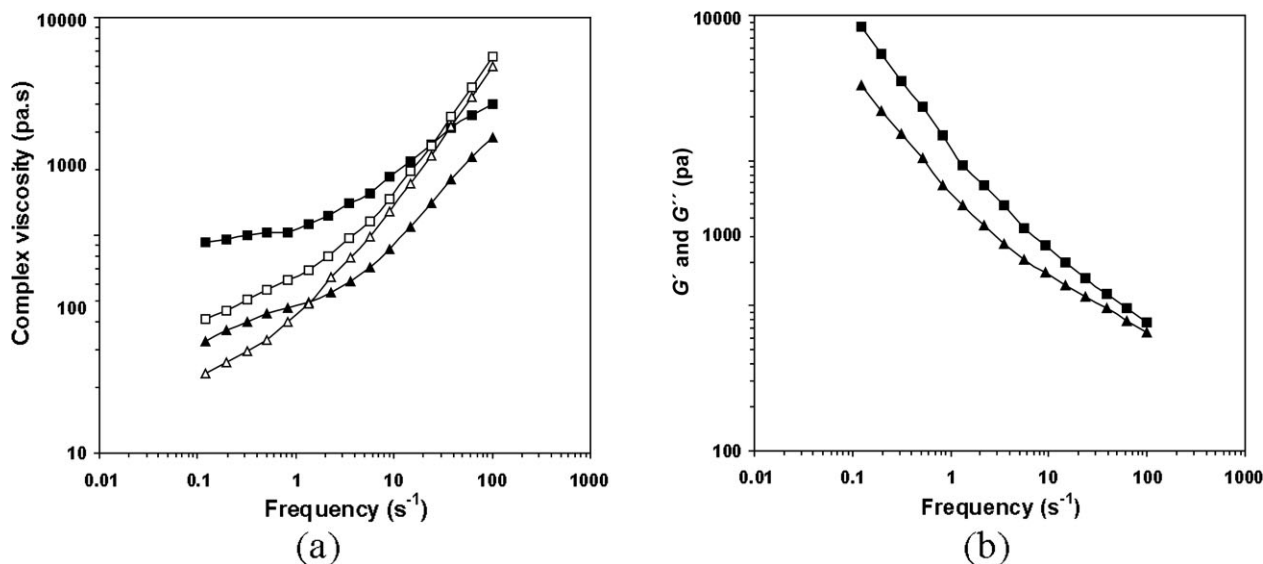
Figure 3 Effect of strain% (■, 1; ▲, 10) on the tri-block at 190°C, (a) G' (closed symbols) and G (open symbols) and (b) complex viscosity.

behavior. This suggests that the diaramide end-groups associates are not only increasing the virtual molecular weight but also form a network structure. Increasing the strain, the G' and G'' values decreased and the crossover point was at a lower frequency. This is due to the fact that at higher strain the chain relaxation is less.

On increasing the temperature, the G' and G'' changed similar to the frequency effect (Fig. 4).

As the temperature increased, the chain mobility increased and the crossover point frequency is shifted to the lower frequency. Higher G' with a smaller terminal slope confirmed that there is a

strong interaction between the hard segment in the melt leading to the ordered arrangement in the melt.

Activation energy

The melt viscosity of the triblock copolymer was next to the parallel-plate measurements also studied by a capillary technique and this at higher strain rates (Fig. 5).

The apparent melt viscosities in the strain rate region 100–3000 s^{-1} still decreased with increasing strain rate, but now slower that at low frequencies. As the temperature increased, the melt viscosities
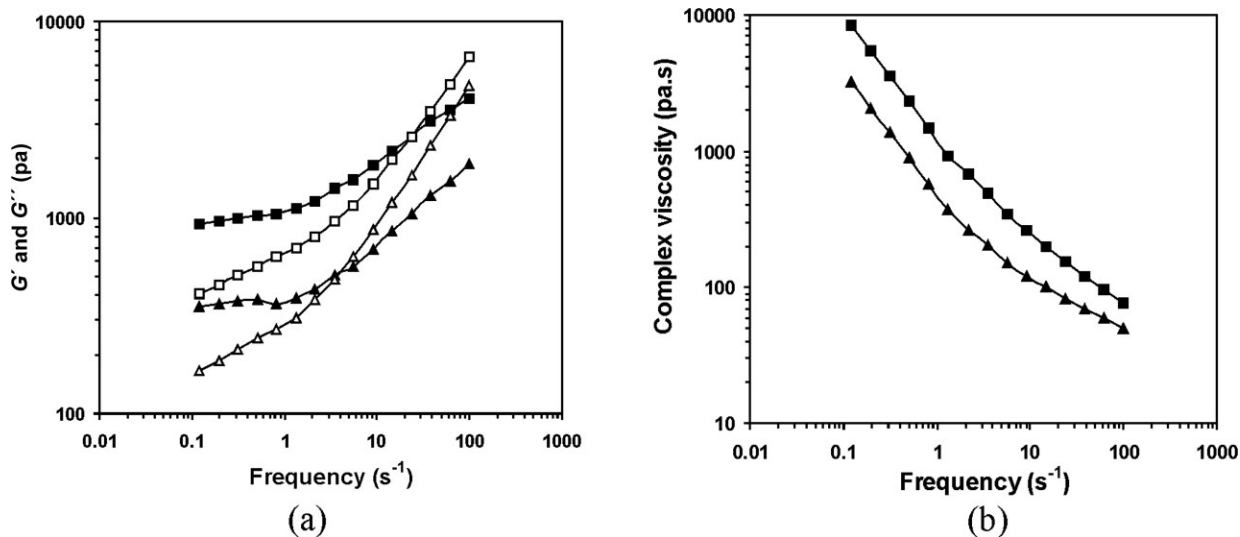

Figure 4 Effect of temperature (■, 190; ▲, 200°C) on the triblock at 1% strain, (a) G' (closed symbols) and G (open symbols) and (b) complex viscosity.
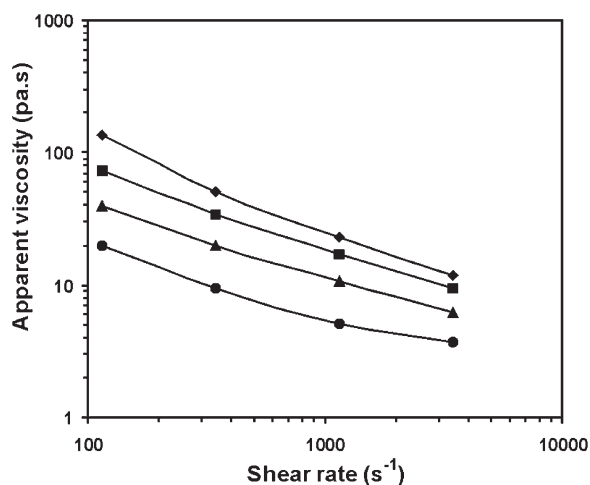
Figure 5 Viscosity curve of triblock copolymer by capillary rheometer at different temperature: ◆, 180; ■, 190; ▲, 200, and ●, 210°C.

decreased. The viscous flow activation energy was calculated using the Arrhenius equation.

$$\ln \eta = \ln A - E_a/RT,$$

where η is the melt viscosity and E_a is the activation energy. An Arrhenius plot was made both for the parallel-plate as for the capillary measurements (Fig. 6).

The apparent viscosities of the parallel-plate method at 0.1–100 s^{-1} and the capillary method at 100–3000 s^{-1} were nearly in line with each other. From the slopes, the activation energy of the melt flow was calculated (Fig. 7).

The activation energy was not a constant but decreased linearly on increasing the shear rate. The fact that the activation energy decreased with increasing strain rate must mean that the structure of the melt changed with strain rate. Such an effect
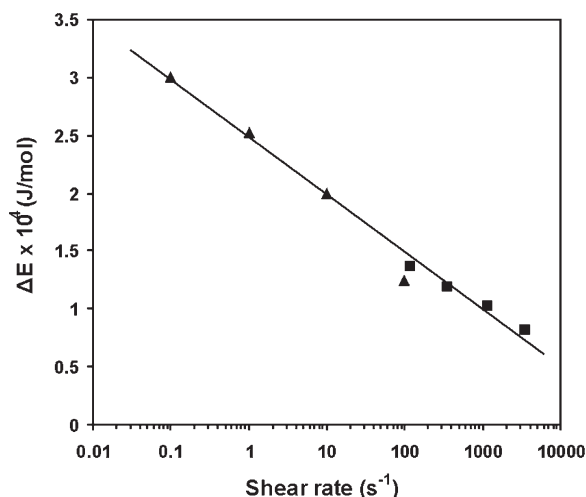

Figure 7 Viscous flow activation energy of tri-block against the share rate: ▲, parallel-plate method; ■, capillary method.

can be expected from a transient network. The apparent viscosity of the triblock at low shear rates is more sensitive to the temperature due to the high activation energy of the cluster deformation.

Effect of time

A disentangling network might have a time dependant behavior. A creep recovery experiment was conducted by applying a constant known value of shear stress to the sample using parallel plate rheometer. The resulting compliance and strain was monitored as a function of time. The imposed stress was suddenly released after 120 s and the recovery monitored for 200 s. From Figure 8, we can see that triblock copolymer at low applied shear stresses has a noticeable time dependent response of the strain recovery.[20]
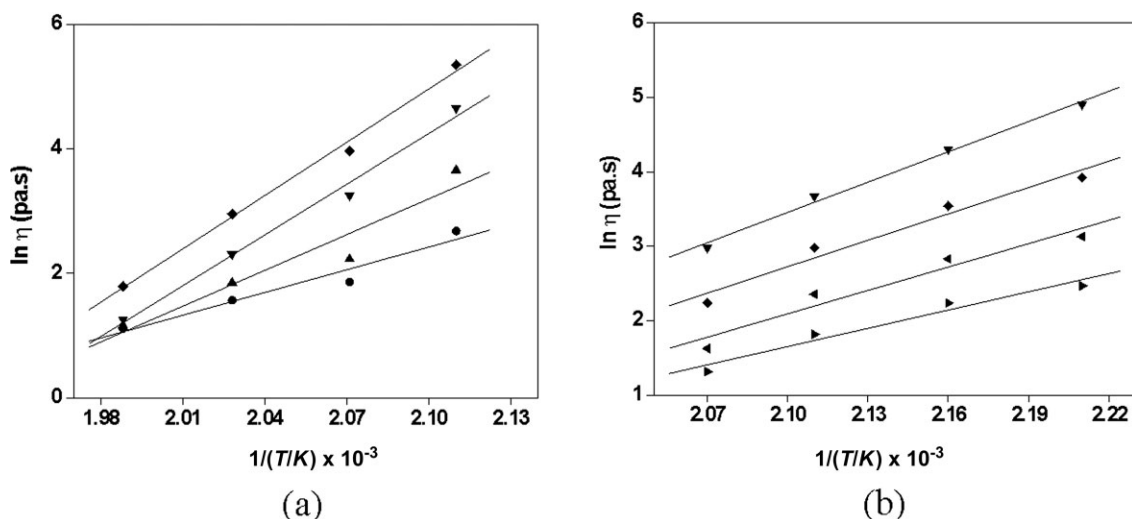

(a)

(b)

Figure 6 Temperature dependency of apparent viscosity at different shear rates: (a) parallel-platemethod: ◆, 0.1; ▼, 1; ▲, 10; ●, 100 s^{-1}; (b) capillary method: ▼, 115; ◆, 344; ▲, 1147; ▼, 3442 s^{-1}.
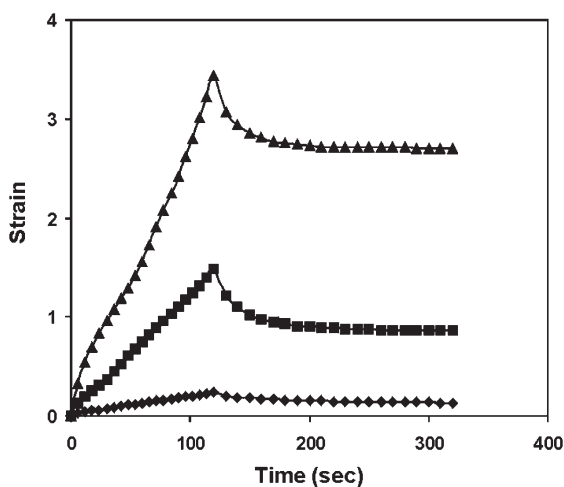
Figure 8 The creep recovery behavior of the tri-block co-polymer at 200°C and different stresses: ◆, 3 pa; ■, 8 pa; ▲, 10 pa.

These results suggests that at low strains (low shear rates) the triblock copolymer had a time dependant melt rheological response, a thixotropic behavior.

CONCLUSION

The melt rheological behavior of an ABA triblock copolymer was studied and compared with a B polymer (monoblock) with a similar molecular weight (9200–9700 g mol^{-1}). The A block was a short aramide diamide. At high frequency, both the mono- and triblock copolymer had low melt viscosities. The monoblock polymer showed Newtonian behavior with a frequency independent complex viscosity. The triblock copolymer at low frequencies had high melt viscosities. Also at low frequencies, the triblock copolymer had G''/G' ratios lower than one and the G' reached a plateau value. The activation energy of the polymer is calculated by the parallel-plate and capillary flow method. The activation energy of the triblock copolymer increased with decreasing shear rate. All these effects suggest that the triblock copolymer melt had at low frequencies a gel-like behavior

and this explains the high complex viscosities at low shear rates. This gelling of the triblock copolymers must have been due to the clustering of the diamide end-segments. The diamide clusters are the (weak) network points of the gel. The deformation of this network was not only shear rate but also time dependant and the triblock copolymer had a thixotropic behavior.

References

1. Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer A. J. B.; Hirschberg, K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. Science 1997, 278, 1601.
2. Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. Adv Mater 2000, 12, 874.
3. Loontjens, T.; Put, J.; Coussens, B.; Lange, R.; Palmen, J.; Sleijpen, T.; Plum, B. Macromol Symp 2001, 174, 357.
4. Yamauchi, K.; Kanomata, A.; Inoue, T.; Long, T. E. Macromolecules 2004, 37, 3519.
5. Kuo, M. C.; Jeng, R. U.; Su, W. C.; Dai, S. A. Macromolecules 2008, 41, 682.
6. Ojelund, K.; Loontjens, T.; Steeman, P.; Palmans, A.; Maurer, F. Macromol Chem Phys 2003, 204, 52.
7. Arun, A.; Baack, K. K. J.; Gaymans, R. J. Polym Prepr 2007, 48, 483.
8. Arun, A.; Gaymans, R. J. Polym Prepr 2007, 48, 856.
9. Arun, A.; Gaymans, R. J. Polymer 2008, 49, 2461.
10. Arun, A.; Gaymans, R. J. J Appl Polym Sci 2009, 111, 1780.
11. Arun, A.; Gaymans, R. J. Macromol Chem Phys 2008, 209, 854.
12. Arun, A.; Dullaert, K.; Gaymans, R. J. Polymer 2009, 210, 48.
13. Niesten, M. C. J. E.; Feijen, J.; Gaymans, R. J. Polymer 2000, 41, 8487.
14. Rabani, G.; Rosair, G. M.; Kraft, A. J Polym Sci Part A: Polym Chem 2004, 42, 1449.
15. Yamakawa, H.; Miyata, H. In Handbook of Condensation Thermoplastic Elastomers; Fakirov, S., Eds.; Wiley-VCH: Weinheim, 2005; Chapter 5, p 141.
16. Sauer, B. B.; McLean, R. S.; Gaymans, R. J.; Niesten, M. C. J. E. J Polym Sci Part B: Polym Phys 2004, 42, 1783.
17. Kautz, H.; van Beek, D. J. M.; Sijbesma, R. P.; Meijer, E. W. Macromolecules 2006, 39, 4265.
18. Van Beek, D. J. M.; Spiering, A. J. H.; Peters, G. W. M.; te Neijenhuis, K.; Sijbesma, R. P. Macromolecules 2007, 40, 8464.
19. Lange, R. F. M.; Van Gurp, M.; Meijer, E. W. J Polym Sci Part A: Polym Chem 1999, 37, 3657.
20. Wang, Y. D.; Zhao, Q. X.; Liu, M. Y.; Wang, Z. M.; Liu, Y. K.; Cao, S. K.; Zha, T. Z. J Appl Polym Sci 2005, 98, 1643.