# Tensile and Elastic Properties of Triblock Copolymer Based on Aramide End-Segments and Polyether Mid-Segments

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**ABSTRACT:** The tensile and elastic behavior of triblock copolymers containing uniform aramide (TΦB) hard end-segments (HS) and poly(tetramethylene oxide) (PTMO, $M_n = 2900$ g/mol) soft segments (SSs) was studied. The molecular weight of the copolymer was varied by changing the length of the soft mid-segment; by extending the PTMO$_{2900}$ with terephthalate units, the SS length was increased from 2900 g/mol to 21,000 g/mol and concurrently the aramide concentration decreased from 18 to 3 wt %. The mechanical properties were investigated by means of tensile testing, stress relaxation (SR) experiments, and cyclic tensile set (TS) tests. The E-modulus was found to increase with increasing aramide content. The low molecular weight copolymers were brittle whereas the high molecular weight copolymers displayed large fracture strain values. The transition from brittle to ductile seemed to occur at a triblock copolymer molecular weight of 6600 g/mol. A strain-induced crystallization was observed at strains above 250%, and both the fracture strain and stress were found to be highly dependant on the molecular weight of the copolymer. Cyclic tensile experiments showed that the materials had low TS values up to the strain hardening point. On the other hand, the SR data at 10% strain seemed to be little dependant on the molecular weight. The higher molecular weight copolymers did not display lower SR values than their low molecular weight counterparts. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1780–1785, 2009

**Key words:** block copolymers; triblock; elastomers; polyamides

## INTRODUCTION

Triblock copolymers are interesting two phase materials,[1,2] and polymers such as styrene-butadiene-styrene (SBS) usually display liquid–liquid demixed phase structures with dispersed amorphous polystyrene phases. To obtain good mechanical properties, the molecular weights of the SBS copolymers needs to be high and the hard polystyrene segment often displays molecular weights on the order of 25,000 g/mol. Because of their high molecular weight, the segments are immiscible and even in the melt. Moreover, these SBS triblock copolymers demonstrate low moduli as well as low maximum use temperatures.

Segmented block copolymers such as polyetheresters are multiblock copolymers with excellent mechanical and thermal properties.[3–8] These multiblock copolymers have short segments and consequently give rise to homogenous melts. The hard end-segments phase separate by crystallization upon cooling and the crystallites provide the copolymers with relatively high moduli and high maximum use temperatures. Seeing as these segmented block copolymers are semicrystalline materials, the dispersed crystalline phase shears upon straining and yielding takes place. At high strains (>200%), a strain hardening can occur because of a strain-induced crystallization. Strain hardening significantly increases the maximum stress of the material. If the hard segments in the multiblock copolymers are monodisperse in length, the crystallization occurs very fast and the crystallinity of the hard segments (HS) is high.[9,10] As a result of using monodisperse HS, both low and high temperature properties can be improved. Moreover, even very short segment lengths (450 g/mol) of the monodisperse HS have been found to give rise to a good crystallization and this down to very low contents (3 wt %).[11]

Triblock copolymers with monodisperse monofunctional amide end-segments are relatively new.[12] The amide end-segments can form H-bonds with the two neighboring chains in the crystal, thus leading to the formation of long H-bonded crystalline structures. The crystallinity of the monodisperse amide end-segments reported herein was very high and a

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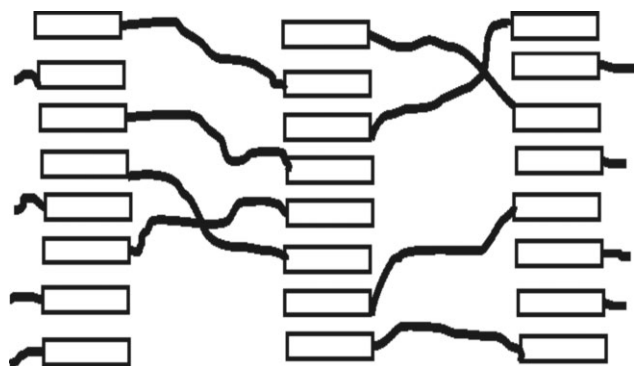*Correspondence to:* R. J. Gaymans (r.j.gaymans@tnw. utwente.nl).

**Figure 1** A schematic representation of a crystallized triblock copolymer.

network formation was thus expected to take place with these triblock copolymers (Fig. 1). The triblock copolymers displayed relatively high shear moduli that were little dependant on the temperature. In these triblock copolymers, the diamide end-segments were of constant length (375 g/mol) and by increasing the mid-segment length, the molecular weight of the copolymer could be varied. However, at the same time, the amide content decreased. These triblock copolymers combined a relatively low molecular weight with a good dimensional stability as well as a very low melt viscosity.

Generally, low molecular weight materials are known to be very brittle because of a lack of entanglements. It would thus be interesting to study the tensile and elastic behavior of triblock copolymers with nearly fully crystallized end-blocks. The question is whether low molecular weight triblock copolymers with crystallized end-blocks would supply the required "entanglements" in order for the material to display a ductile deformation behavior. The triblock copolymers in this study comprised a readily strain-hardening poly(tetramethylene oxide) with a molecular weight of 2900 g/mol (PTMO$_{2900}$), terephthalate units extending the PTMO$_{2900}$ segments to longer soft segments (SSs), and monofunctional monodisperse diaramide (T$\Phi$B) segments (Scheme 1). The triblock copolymers were synthe-

sized using a one-pot melt polymerization procedure described in detail elsewhere.[12]

## EXPERIMENTAL AND METHODS

### Materials

The synthesis and analysis of the triblock copolymers used in this study have been reported elsewhere.[12]

### Injection molding

Test specimens, i.e. bars of 70 × 9 × 2 mm$^3$, were prepared in an Arburg H manual injection molding machine. In the case of the monodispersed amide segments, the barrel temperature was set to 40–50°C above their flow temperature as measured by Dynamic Mechanical Thermal Analysis. The injection molded test bars were stored at room temperature for approximately 2 days prior to measuring. All samples were dried overnight in vacuum at 70°C before use.

### Tensile testing

Stress–strain curves were obtained from tensile testing on injection molded dumbbell-shaped specimens (ISO37 Type 2). The analysis was carried out on a Zwick Z020 universal tensile machine equipped with a 500N load cell at a strain rate of 0.4 s$^{-1}$ (test speed of 60 mm min$^{-1}$). The strain was measured with extensometers. The E-modulus was determined at a strain of 0.1–0.25%, and the yield point was calculated using Considere's construction.[13] For each material, three samples were tested and the best possible data was chosen to be presented herein. The scattering in the moduli, yield, and fracture data was less than 10%.

### Stress relaxation tests

Injection molded ISO37 Type 2 dumbbells were used as samples for the relaxation experiments. The stress relaxation (SR) was measured on a Zwick Z020
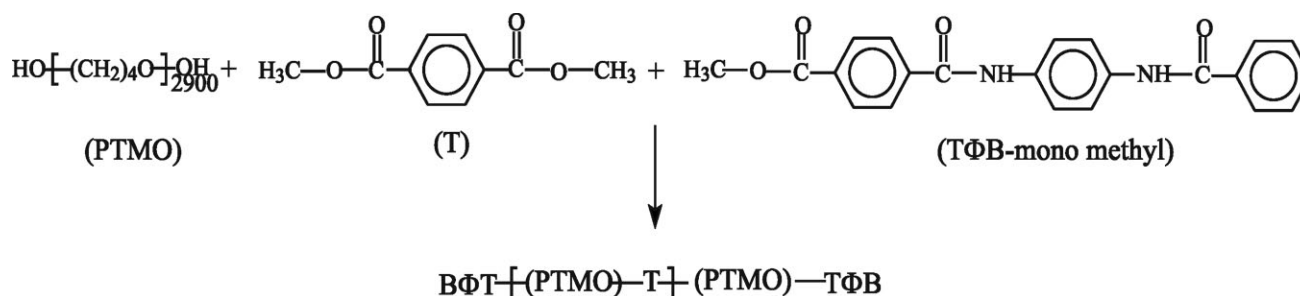


**Scheme 1** The chemical structure of the triblock copolymer.

## TABLE I
### Tensile and Elastic Properties of the BΦT-(PTMO$_{2900}$-T)$_y$-PTMO$_{2900}$-TΦB Triblock Copolymers

| $M_n$ (g/mol)[a] | TΦB (wt %) | $\eta_{inh}$ (dL/g) | $G'_{30°C}$ (MPa)[b] | $E$ (MPa) | $\sigma_{yield}$ (MPa) | $\sigma_{fra}$ (MPa) | $\varepsilon_{fra}$ (%) | $\sigma_{true}$ (MPa) | SD$_{10\%}$ (%) | SR$_{10\%}$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| 3600 | 18 | 0.37 | 29 | 88 | – | – | 5 | 3.3 | – | – |
| 6600 | 10 | 0.60 | 10 | 33 | – | – | 37 | 4.4 | 16 | 4.4 |
| 9600 | 7 | 0.86 | 8 | 23 | 2.6 | 4.23 | 332 | 18.3 | 25 | 11.2 |
| 21,700 | 3 | 1.40 | 4 | 12 | 1.5 | 13 | 1171 | 165 | 29 | 13.3 |

$\sigma_{yield}$, yield stress; $\sigma_{fra}$, fracture stress; $\sigma_{true}$, true fracture stress; $\varepsilon_{fra}$, fracture strain.
[a] $M_n$ calculated from the monomer feed.
[b] Taken from Ref. 12.

universal tensile machine equipped with a 500N load cell. The strain was measured as the clamp displacement with a starting clamp distance of 35 mm, and the samples were strained at a rate of 0.33 s$^{-1}$. The decay of the stress was measured for 10,000 s, and the initial stress decay (SD), i.e., the decay in the first 100 s, was calculated as:

$$\text{initial stress decay (\%)} = \frac{\sigma_{max} - \sigma_{100}}{\sigma_{max}} \quad (1)$$

Further, the normalized SR (SR$_n$) was calculated as:

$$SR_n = \frac{\sigma_{100} - \sigma_{10000}}{\sigma_{100} \times \Delta \log t} \quad (2)$$

### Cyclic tensile tests

Cyclic stress–strain experiments were conducted on the injection molded bars cut into dumbbell-shaped samples (ISO 37 Type 2) to measure the tensile set (TS) of the block copolymer. A Zwick Z020 universal tensile machine equipped with a 500N load cell was used and the stress and strain for each loading–unloading cycle was measured. For each subsequent cycle, the maximum strain was increased (staircase loading) by 25% and the TS was determined as a function of the applied strain according to the following relation:

$$\text{Tensile set (\%)} = \frac{\Delta\varepsilon_{remaining}}{\Delta\varepsilon_{cycle}}$$
$$= \frac{\varepsilon_{r,cycle(i)} - \varepsilon_{r,cycle(i-1)}}{\Delta\varepsilon_{cycle}} \times 100 \quad (3)$$

where, $\varepsilon_{r,cycle(i)}$ is the remaining strain at the end of cycle I and $\varepsilon_{r,cycle(i-1)}$ is the remaining strain at the end of the preceding cycle, i.e., $i - 1$.

### RESULTS AND DISCUSSION

The tensile and elastic properties of triblock copolymers with highly crystalline diaramide TΦB end-segments (Scheme 1) were investigated and are presented in Table I. The molecular weight of the

studied triblock copolymers ranged from 3600 to 21,700 g/mol and the inherent viscosity ($\eta_{inh}$) increased linearly with increasing molecular weight.

### Tensile properties

The tensile behavior was studied on injection molded samples of the experimental triblock copolymers and Figure 2 displays the obtained stress–strain curves. The low molecular weight copolymer samples were fractured before the yield point and thus had a brittle nature. The higher molecular weight copolymers ($\eta_{inh} > 0.6$) displayed distinct yield points with high fracture strains. The copolymer with $\eta_{inh} = 1.40$ even demonstrated a fracture strain of over 1100%. By increasing the molecular weight of these copolymers, the HS content was lowered. It was thus expected that both increasing the molecular weight and decreasing the HS content would render the material more ductile.

The E-modulus strongly increased with increasing HS content, and was found to be approximately
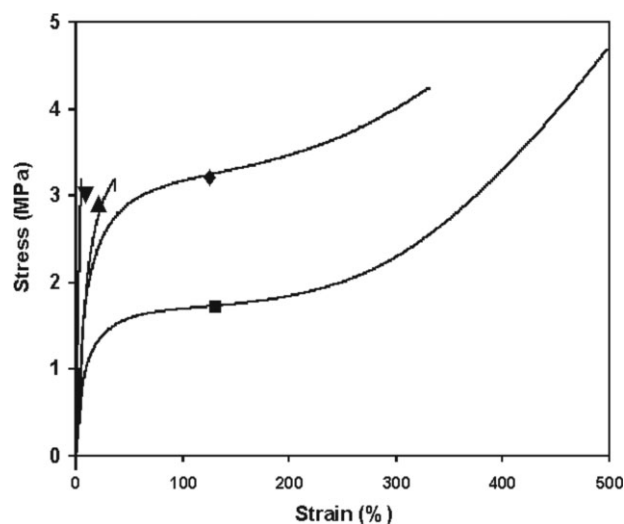


**Figure 2** Stress–strain (up to 500% strain) curves of the triblock copolymers: ▼, $\eta_{inh} = 0.37$; ▲, $\eta_{inh} = 0.6$; ◆, $\eta_{inh} = 0.86$; ■, $\eta_{inh} = 1.4$. (fracture strain 1170% not given).
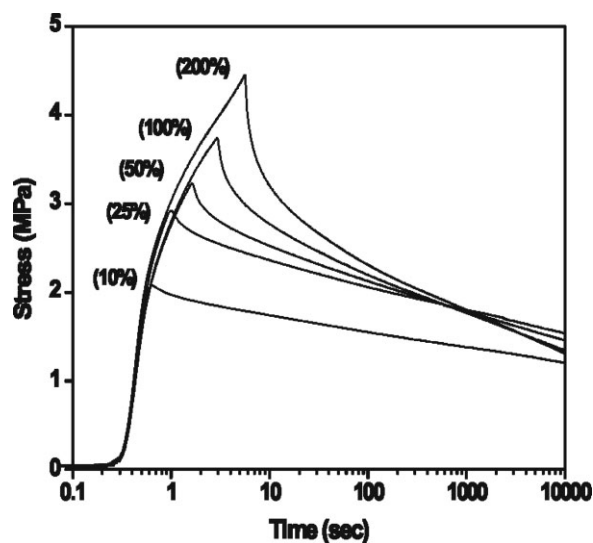
**Figure 3** The effect of strain (%) on the stress relaxation of the copolymer with $\eta_{inh} = 0.86$ (7 wt % T$\Phi$B) (strain % is presented within parentheses).



**Figure 4** SD ($\blacklozenge$) and SR ($\blacksquare$) as functions of the strain for the polymer with $\eta_{inh} = 0.86$.

three times higher than the G-shear modulus.[12] The Poison ratio calculated from the $E/G$ values was 0.5, suggesting an ideal rubber-like behavior at small strains.[14] The higher molecular weight copolymers displayed clear yield points as a result of the presence of a crystalline hard phase. The copolymers thus behaved like semicrystalline materials. Furthermore, the yield stress was found to decrease and the yield strain to increase with decreasing T$\Phi$B content (Table I). A similar behavior has been observed for multiblock copolymers.[8,15] The transition from brittle to ductile under the test conditions occurred at approximately $\eta_{inh} = 0.6$, which corresponded to an $M_n$ of $\sim$ 6600 g/mol. The copolymers thus demonstrated a ductile behavior with high fracture strains at relatively low molecular weights.

After the yield point at a strain of about 250% the stress was found to increase as a result of strain hardening, i.e., a strain-induced crystallization of the PTMO$_{2900}$ segments.[16,17] In general terms, strain hardening stabilizes the deformation of a material, and a high fracture stress can thus be combined with a high fracture strain. High fracture strains are typical for high molecular weight block copolymers with monodisperse HS.[8,16,18] Thin crystallites have a limited resistance to the plastic deformation and as a result the deformation of the copolymers can be higher than the natural draw ratio of a crosslinked rubber (700%). The fracture stress and the fracture strain data can be combined into one value known as the true fracture stress [i.e., fracture stress $\times$ (fracture strain + 1)]. The true fracture strains of the copolymers were found to increase very strongly with molecular weight (Table I).
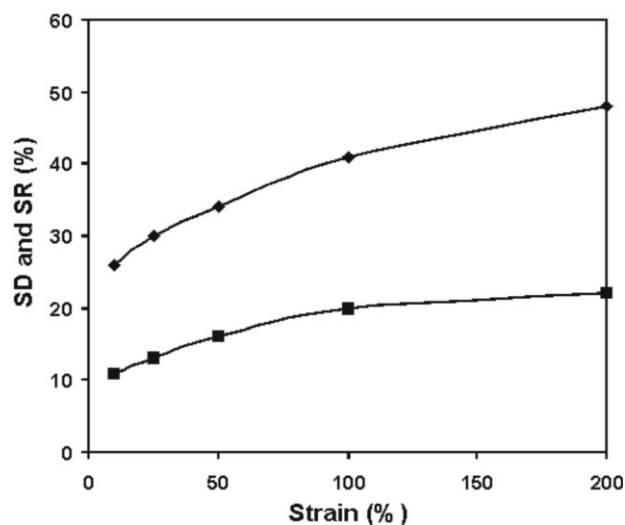
## Stress relaxation

The time-dependent deformation behavior of the triblock copolymers was studied by means of a SR experiment. The effect of the percentage of strain on the SR of the polymer with $\eta_{inh} = 0.86$ (7 wt % T$\Phi$B) was investigated and the results can be seen in Figure 3. The graph clearly shows two distinct regions: a fast relaxation during the first 100 s, followed by a slow linear relaxation (viscoelastic) process on log time scale. The SD was calculated over the first 100 s and the second relaxation process (SR) was calculated from 100 to 10,000 s and was normalized by the stress value at 100 s.[16] Figure 4 displays the initial SD and the normalized SD as functions of the percentage of strain.
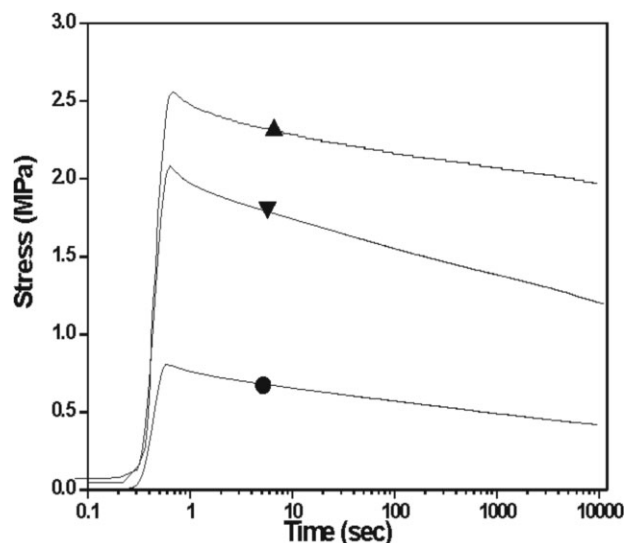


**Figure 5** The effect of the HS content on the stress relaxation at a strain of 10%: $\blacktriangle$, 10; $\blacktriangledown$, 7; $\bullet$, 3 wt % T$\Phi$B.
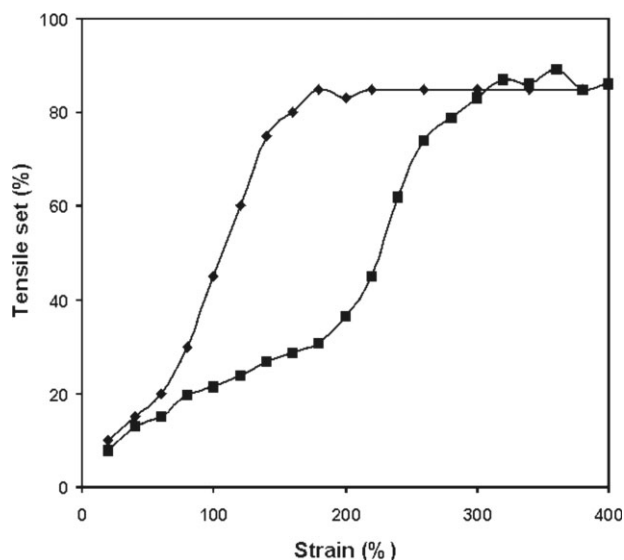
**Figure 6** The effect of strain on the tensile set in a cyclic test of two copolymers: ◆, $\eta_{inh} = 0.86$; ■, $\eta_{inh} = 1.4$.

Both the initial SD and the SR were found to increase when the applied strain was increased, and their respective values for the copolymer with $\eta_{inh} = 0.86$ were high as compared with those of a high molecular weight block copolymer.[16,19] The SR was also studied on the other copolymers, at an applied strain of 10%, and the results can be seen in Figure 5. The SR curves obtained at strains above 10% (as seen in Fig. 5) were representative of other strains. The 18 wt % TΦB copolymer with $\eta_{inh}$ of 0.37 was too brittle for this test.

The 10% SD and SR values were calculated from the curves, and the resulting values are presented in Table I. The SD and SR values of high molecular weight multiblock copolymers normally increase with HS content.[16] However, in the case of our triblock copolymers, the SD and SR values decreased with HS content despite the fact that the molecular weight in this series increased. Surprisingly the 10 wt % TΦB copolymer with $\eta_{inh}$ of only 0.6 demonstrated low SD and SR values.

### Cyclic tensile set

The elastic behavior of the triblock copolymers was studied by cyclic TS tests. In these experiments, the strain was applied in cyclic loadings with an increasing strain per cycle. The TS of the strain increment was determined and plotted as a function of the applied strain for the polymers with $\eta_{inh} = 0.86$ and 1.4 (Fig. 6). As can be seen in the figure, the TS values were low for strain values below that where strain hardening started to occur. The high molecular weight triblock copolymer displayed low TS values for strains up to 200% after which the TS started to increase. At high strains, TS values close to 90%

were obtained because of the strong strain hardening effect of the PTMO$_{2900}$. For the low molecular weight material, the sharp increase in TS started at ∼ 60% strain. This was a result of low molecular weight materials having higher HS contents and thus higher moduli and yield stresses. In such materials, the stress displays a faster increase and because of the higher stress values, the plastic deformation of the HS becomes more significant.

### CONCLUSIONS

This study reports on the tensile and elastic properties of triblock copolymers with monodisperse monofunctional diamide end-segments. The TΦB segments displayed a high crystallinity, and the length of the SS was varied by extending PTMO$_{2900}$ with terephthalate groups. Consequently, the molecular weight of the triblock copolymer could be altered. As the molecular weight of the polymer increased, the TΦB segment content decreased. The E-moduli of the copolymers were found to be relatively high. The low molecular weight copolymers with high TΦB contents demonstrated a brittle nature, whereas the high molecular weight copolymers with low TΦB contents were very ductile. The transition from brittle to ductile took place at a molecular weight of about 6000 g/mol, and the copolymers thus displayed a ductile behavior at relatively low molecular weights. The yield stress was found to increase with increasing HS content, and at a strain of about 250%, a strain-hardening effect was observed. This strain-hardening was a result of a strain-induced crystallization of the PTMO$_{2900}$ SSs. Moreover, the fracture stress and the fracture strain increased strongly with molecular weight. The SR behavior of the copolymers was also studied. When increasing the strain, both the initial relaxation (SD) and the long-term relaxation (SR) were found to increase. At 10% strain, the copolymers with the highest molecular weight displayed the lowest SD and SR values. With respect to the TS tests, the materials demonstrated low TS values at low strains and high TS values at higher strains. These high TS values at high strains for the high molecular weight copolymers were probably due to the strong strain hardening effect of the PTMO$_{2900}$ segments.

Triblock copolymers with monodisperse crystallizable end-segments showed good low strain properties and a ductile behavior, already, at low molecular weights (>6000 g/mol). Hence, they combine a low melt viscosity with good mechanical properties.

## References

1. Bates, F. S.; Fredrickson, G. H. Phys Today 1999, 52, 32.
2. Holden, G.; Legge, N. R.; Quirk, R. P.; Schroeder, H. E. Thermoplastic Elastomers, 2nd ed.; Hanser publishers: Munich, 1996.
3. Niesten, M.; Feijen, J.; Gaymans, R. J. Polymer 2000, 41, 8487.
4. Niesten, M.; ten Brinke, J. W.; Gaymans, R. J. Polymer 2001, 42, 1461.
5. Sheth, J. P.; Xu, J.; Wilkes, G. L. Polymer 2003, 44, 743.
6. Niesten, M.; Bosch, H.; Gaymans, R. J. J Appl Polym Sci 2001, 81, 1605.
7. Niesten, M.; Tol, R.; Gaymans, R. J. Polymer 2001, 42, 931.
8. Niesten, M.; Gaymans, R. J. Polymer 2001, 42, 6199.
9. Krijgsman, J.; Feijen, J.; Gaymans, R. J. Polymer 2004, 45, 4685.
10. Husken, D.; Feijen, J.; Gaymans, R. J. J Polym Sci Part A: Polym Chem 2007, 45, 4522.
11. Sauer, B. B.; McLean, R. S.; Gaymans, R. J.; Niesten, M. C. J. E. J Polym Sci Part B: Polym Phys 2004, 42, 1783.
12. Arun, A.; Gaymans, R. J. Polymer 2008, 49, 2461.
13. McCrum, N. G.; Buckley, C. P.; Bucknall, C. B. Principles of Polymer Engineering; Oxford University Press: Oxford, 1988.
14. Halpin, J. C.; Kardos, J. L. J Appl Phys 1972, 43, 2235.
15. Cella, R. J. J Polym Sci Polym Symp 1973, 42, 727.
16. Biemond, G. J. E.; Feijen, J.; Gaymans, R. J. J Mat Sci 2008, 43, 3689.
17. Niesten, M.; Harkema, S.; van der Heide, E.; Gaymans, R. J. Polymer 2001, 42, 1131.
18. Krijgsman, J.; Gaymans, R. J. Polymer 2004, 45, 437.
19. Le, H. H.; Lupke, T.; Pham, T.; Radusch, H. J. Polymer 2003, 44, 4589.