

The Melt Rheological Behavior of AB, ABA, BAB, and $(AB)_n$ Block Copolymers With Monodisperse Aramide Segments

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The melt rheological behavior of segmented block copolymers with high melting diamide (A) hard segments (HS) and polyether (B) soft segments was studied. The block copolymers can be classified as B (monoblock), AB (diblock), ABA (triblock, diamide end segment), BAB (triblock, diamide mid-segment) and $-(AB)_n-$ (multiblock) block copolymers. Varied were the number of HS in the chain, the HS concentration, the position of the HS (in the chain or at the end of the chain) and the molecular weight of the copolymers. The melt rheological behavior of the copolymers was studied with a plate–plate method. The materials B (monoblock), BAB (triblock, diamide mid-segment), and $-(AB)_n-$ (multiblock) block copolymers had a rheological behavior of a linear polymer and the complex viscosity increased with molecular weight. Surprisingly, the diblock copolymers AB and the triblock copolymers ABA at low frequencies and near the melting temperature of the copolymers had the behavior of a gelled melt. The diamide segments at the chain end seemed to form aggregates, whereas the diamide mid-segments did not. Also, time-dependent rheology of diblock copolymer confirmed the network structure built up in the melt. The block copolymers with H-bonding diamide end segments had a thixotropic behavior. *POLYM. ENG. SCI.*, 50:756–761, 2010. © 2009 Society of Plastics Engineers

INTRODUCTION

Segmented block copolymers are multiblock copolymers with a continuous phase with a low T_g and a dispersed crystalline phase with a high melting temperature [1–3]. The melts of these segmented block copolymers

are transparent and homogeneous. These materials are easy melt processable and, at room temperature, they display an elastic, rubber-like behavior combined with a high fracture stress. The function of the hard segments (HS) was to crystallize on cooling, thus providing an efficient network structure for good elastic properties. They should also provide the material with a dimensional stability up to the melting temperature and permit reprocessing. Very interesting are block copolymers with crystallizable segments of monodisperse in length [3–16]. With monodisperse crystallizable segments, the crystallization rate and the crystallinity are increased [11–16]. With that, the processability improved, the modulus is raised and the elastic properties are enhanced.

High molecular weight multiblock copolymers have high melt viscosities and a shear thinning behavior due to a disentangling of their chains [2, 3]. For certain linear polymers with H-bonding end groups, a gelled melt is observed [17, 18]. If a linear PTMO₂₅₀ end capped with imide units is mixed with melamine units comprising three H-bonding sites, a multiarm physical network structure was formed [17]. The melt rheological behavior of ABA triblock copolymers with H-bonding ureidopyrimidinone end segments has been reported by Meijer and co-workers [19–21]. Such UPS can dimerize and thereby increase their virtual molecular weight. These dimerized UPS do not form a network structure in the melt. However, if the H-bonding ureidopyrimidinone end segments contained an additional urea H-bonding unit, a gel behavior has been observed [18] but not for those copolymers with an additional urea or urethane H-bonding unit in the chain [21].

ABA-type triblock copolymers with monodisperse amide [22–27] and urethane HS [28–30] represent novel kinds of materials with H-bonding possibilities to both its neighbors. These triblock copolymers have a homogeneous melt, and the HS end groups crystallize rapidly on

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cooling displaying a very high crystallinity. The crystallization is in lamellae (ribbons) with a high aspect ratio [23, 24, 27, 29]. The first results on the melt rheological behavior of these copolymers suggest that such **ABA** triblock copolymers have at low frequencies a network structure, whereas the similar multiblock copolymers $-(\mathbf{AB})_n-$ with the amide units in the chain do not [26]. Thus, in block copolymers with H-bonding end segments network, structures in the melt can be formed if the end segments can H-bond to both its neighbors.

It would be interesting to study the effect of the number of diamide segments in the chain as well as their positions in the chain on the rheological properties and particularly the network formation in the melt. The amount association of the HS in the melt is expected to be directly related to the melting temperature and therefore the measurements were conducted at a constant temperature above the melting temperature. The block copolymers that were studied had either diamide end segments or diamide mid-segments, and the studied polyether-amide copolymers were composed of diamide (**A**) HS and poly(tetramethylene oxide) (PTMO) (**B**) soft segments. To increase the molecular weight of the polyether segment, a PTMO with a molecular weight of 2900 g/mol was extended with terephthalate units (-PTMO₂₉₀₀-(T-PTMO₂₉₀₀)_p-) according to a procedure described elsewhere [12, 13, 27]. The used diamide segments were monodisperse in length and based on aramides. They were either difunctional for a mid-block (Fig. 1a) or monofunctional for an end block (Fig. 1b).

The PTMO chains could also be endcapped with a benzoate group. The melt rheological behavior was studied on: monoblock (**B**), diblock (**AB**), triblock (**ABA** and **BAB**), and multiblock $((\mathbf{AB})_n)$ copolymers.

EXPERIMENTAL

Materials

The preparation of the block copolymers used in this study as well as their solid-state properties has been described elsewhere [27].

Viscometry

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

Differential Scanning Calorimetry

Differential Scanning Calorimetry spectra were recorded on a Perkin-Elmer DSC-7 apparatus, equipped with a PE7700 personal computer and TAS-7 software. Dried samples (10 mg) were heated at a rate of 20°C/min

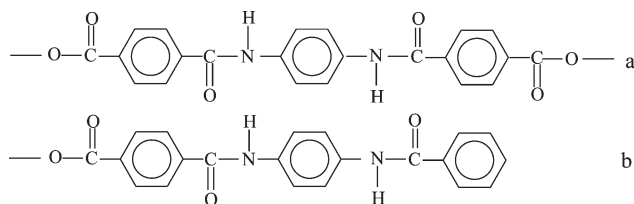


FIG. 1. The chemical structures of the diamide hard segments in (a) the mid-block (T Φ T and b) the end block (T Φ B).

and, after cooling, a second heating scan was used to determine the melting temperature of the polymer. The melting temperature (T_m) was taken as the temperature of the maximum of the endotherm. The cooling curve was used to determine the crystallization temperature.

Rheological Measurements

Rheological measurements were carried out on a Physica MCR300 rheometer with a temperature control unit. A parallel plate set-up was used to measure the rheological behavior of the polymers. The diameter of the upper plate was 25 mm and the gap between the two parallel plates was 1 mm. A Physica software was used for all the calculations. Initially, the copolymer was allowed to rest between the two parallel plates at a set temperature for 10 min. All the rheological experiments were measured at a minimum of 40°C above the melting point of the polymer, as determined by DSC (or the flow temperature in DMA measurements). The shear stress as a function of time was measured at a constant shear rate using the same instrument.

RESULTS AND DISCUSSION

Block Copolymers

The melt rheological behavior of a series of polyether-di-amide block copolymers was studied. The copolymers consisted of a polyether (**B**)-based soft segment and a diamide (**A**) HS. The chemical structure of the HS is presented in Fig. 1. The polymers could be broadly classified as **B** (mono), **AB** (di), **ABA** (tri), **BAB** (tri), and $(\mathbf{AB})_n$ (multi) block copolymers and a simplification of their polymer structure is given in Table 1. The difference between these copolymers was the number of HS in the chain, the concentration of the HS, the molecular weight of the HS, and whether the HS were situated within the chain or at the chain end (Table 1). The subscript in the polymer code indicates the diamide concentration in the copolymer (wt%).

Effect of Amide End Segments

The complex viscosity and complex modulus of the monoblock **B** and triblock **ABA7** copolymers were stud-

TABLE 1. List of PTMO-diamide block copolymers and their properties [26].

Polymer code ^a	Polymer structure ^b	Diamide segment		η_{inh} (dL/g)	Molecular weight (g/mol)	T_{flow} (°C) (by DMA)	
		Wt%	No. ^c				
Monoblock	B	B-(Y) ₉₀₀₀ -B	—	0	0.8	8,600	25 ^d
Diblock	AB₃	(Y) ₉₀₀₀ -TΦB	3	1	0.9	9,600	125
Triblock	BAB₃	(Y) ₄₉₀₀ -TΦT-(Y) ₄₉₀₀	3	1	1.0	10,700	110
Triblock	ABA₇	BΦT-(Y) ₉₀₀₀ -TΦB	7	2	0.9	9,600	160
Multiblock	(AB)_{n,7}	-[(Y) ₄₁₀₀ -TΦT]- <i>n</i>	7	6.3	2.6	27,800	175
Multiblock	(AB)_{n,4}	-[(Y) ₉₀₀₀ -TΦT]- <i>n</i>	4	3.3	2.9	31,000	125

^a Subscript is the wt% HS.

^b Y stands for the -PTMO₂₉₀₀-(T-PTMO₂₉₀₀)p-, B for a benzyl group.

^c Number of diamide segments in a chain.

^d As measure by DSC.

ied as functions of frequency (Fig. 2). These two copolymers had similar molecular weights (≈ 10000 g/mol) but differed with respect to their end groups: copolymer **B** had benzyl end groups and **ABA₇** had diamide (TΦB) end groups. Furthermore, copolymer **B** displayed a melting temperature of 25°C corresponding to the melting of the PTMO₂₉₀₀ segments, and the **ABA₇** triblock copolymers had an amide melting temperature of 160°C. As the structure of associates in the melt strongly depend on the temperature above the melt, the melt rheological experiments were carried out 40°C above the T_m of the copolymer, at 60° and 200°C, respectively. The complex viscosity of the monoblock **B** copolymer showed a clear Newtonian behavior, as was expected of a linear polymer of low molecular weight. At high frequencies, the triblock **ABA₇** copolymer demonstrated a high complex modulus and a low complex viscosity, the complex modulus and viscosity of the **B** and **ABA₇** were on the same order of magnitude. Although the test temperatures differed, the results suggested that the **B** and **ABA₇** copolymers with similar molecular weights behaved the same at high frequencies. Surprisingly, at low frequencies, the polymer **ABA₇** had a lower complex modulus and a much higher complex viscosity. Furthermore, the complex modulus of the **ABA₇** polymer showed a low slope, indicating that associations existed in the melt. The observed melt rheological behavior at low frequencies was thus believed to be the result of a gelling effect due to a clustering of the H-bonding diamide end segments. At low frequencies, these diamide segments were likely present in clusters that formed a network structure.

Temperature Effect on the (AB)_n (Multiblock) and ABA (Triblock) Copolymers

The effect of temperature on the complex modulus of the multiblock **(AB)_{n,7}** and triblock **ABA₇** copolymers is presented in Fig. 3. The temperature had an enormous influence on the complex modulus of the triblock copolymer; for **ABA₇**, it was found to decrease sharply when the temperature was raised from 200 to 223 °C (Fig. 3a).

In other words, the complex modulus decreased by a factor of two decades on increasing the temperature by 25°C. This effect is much stronger than that on the multi-

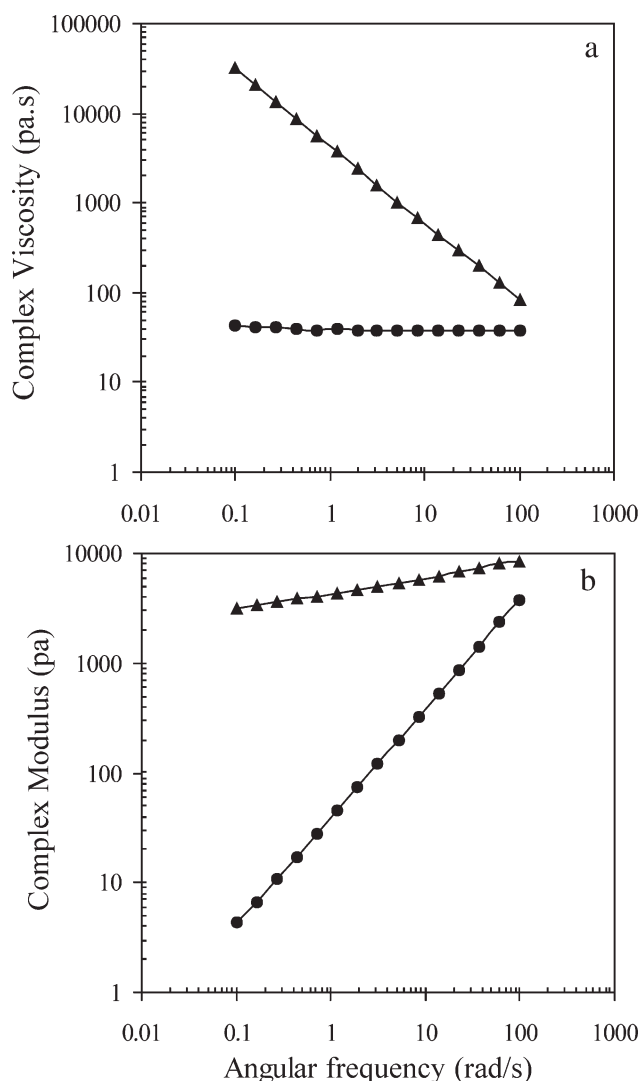


FIG. 2. (a) The complex viscosity and (b) the complex modulus as a function of frequency at 0.1% amplitude at 60°C above their T_m : ●, monoblock **B** ($\eta_{inh} = 0.8$, at 60°C); ▲, triblock **ABA₇** ($\eta_{inh} = 0.9$, at 200°C).

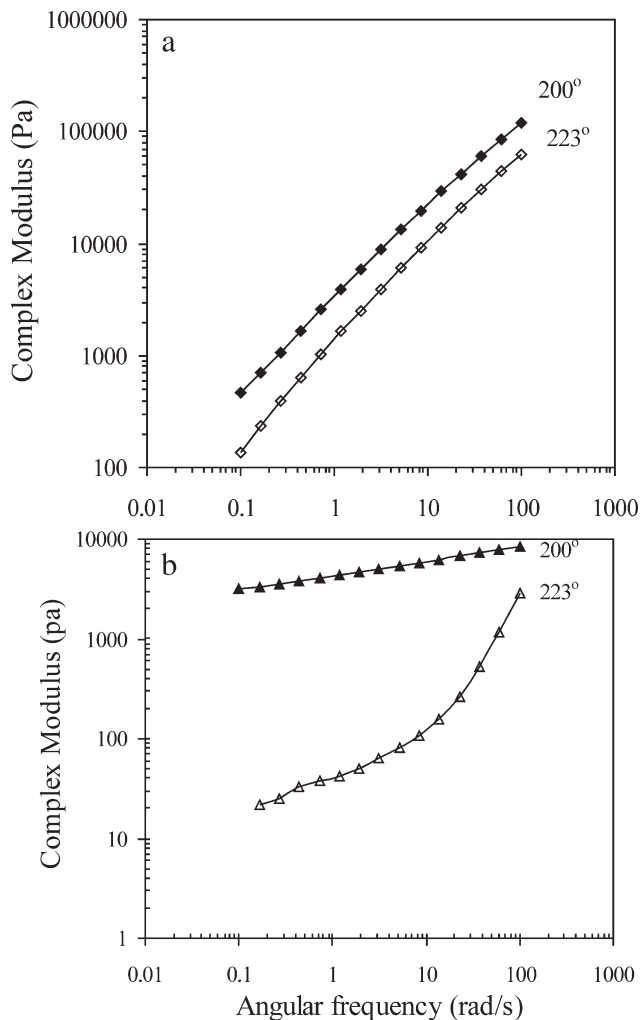


FIG. 3. The effect of the temperature on the complex modulus of copolymers containing 7 wt% 1/HS: (a) $(AB)_{n,7}$; (b) ABA_7 .

block copolymer (Fig. 3b). The aggregated structure in the melt of the ABA triblock copolymer was thus very susceptible to temperature and gradually broken up as the temperature difference between the test temperature and the melting temperature increased. As a result of this dissolu-

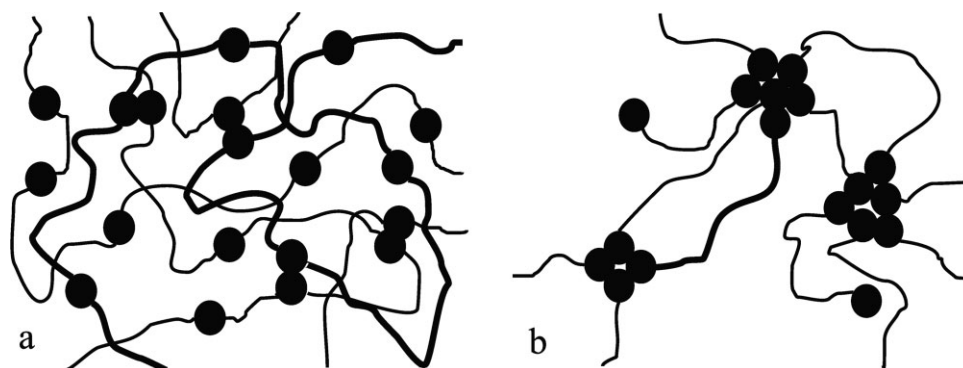


FIG. 5. Schematic diagrams of the structure in the melt of (a) a multiblock $((AB)_n)$ and (b) a triblock (ABA) copolymer.

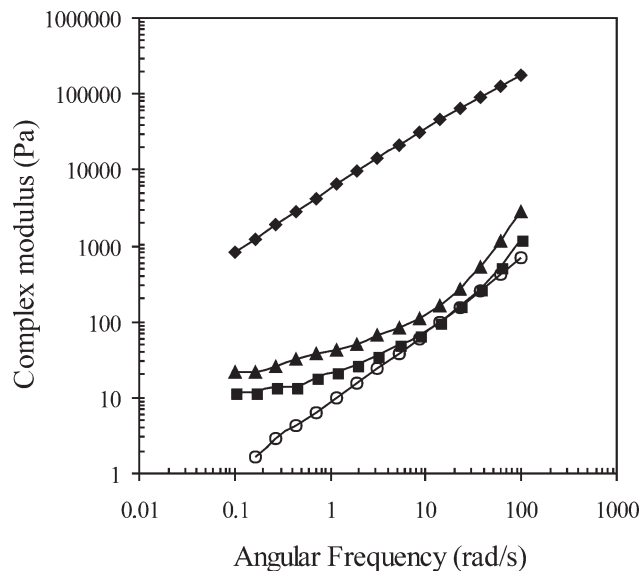


FIG. 4. The complex modulus as a function of frequency at 0.1% amplitude and at $\sim 60^\circ\text{C}$ above the T_m : \blacklozenge , multi $(AB)_{n,4}$ ($\eta_{inh} = 2.9$, at 170°C); \blacktriangle , triblock ABA_7 ($\eta_{inh} = 0.9$, at 223°C); \blacksquare , diblock AB_3 ($\eta_{inh} = 0.9$, at 190°C); \circ , triblock mid-hard segment BAB_3 ($\eta_{inh} = 1.0$, at 190°C).

tion of the aggregates with temperature and this being related to the melting temperature, the activation energy was lowered with decreasing temperature [26]. On the other hand, the complex modulus of the multiblock copolymer showed a small change when increasing the temperature from 200 to 223°C (Fig. 3a). This small decrease in the modulus (factor 2–3) was due to the increase in chain mobility on increasing the temperature. It should be noted that the HS content of these two polymers was the same (~ 7 wt%), but nonetheless, the polymers demonstrated completely different behaviors as a function of temperature.

Position of Hard Segment

The effect on the melt rheological behavior of the position and number of diamide segments in the copoly-

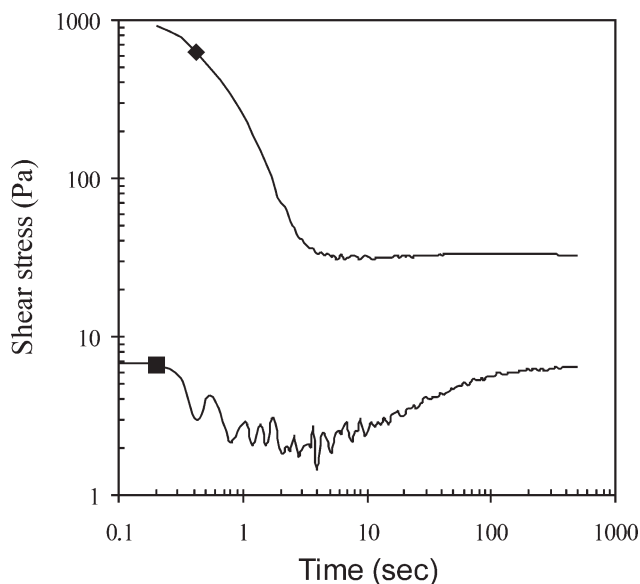


FIG. 6. The stress response as a function of time at a shear rate of 0.1 s^{-1} , following 150 s at a shear rate of 5 s^{-1} : ◆, multiblock $(\text{AB})_{n,3}$ ($\eta_{\text{inh}} = 2.9$ at 250°C); ■, diblock AB_3 ($\eta_{\text{inh}} = 0.9$ at 190°C).

mer chain was studied and the results are displayed in Fig. 4.

The di (AB_3), tri (ABA_7 , end HS) and tri (BAB_3 , mid-HS) copolymers all had approximately the same molecular weight, whereas that of the multi ($(\text{AB})_{n,4}$) block was higher (cf. Table 1). For BAB_3 and $(\text{AB})_{n,4}$, the diamide segments were situated in the chain, whereas for the AB_3 and ABA_7 materials, the diamide segments were at the chain ends. The number of diamide units in the chain for AB_3 and BAB_3 was one, whereas it was two for ABA_7 and approximately three for $(\text{AB})_{n,4}$. As the structure of associates in the melt strongly depend on the temperature above the melt, the test temperatures were in this case $\sim 60^\circ\text{C}$ above the T_m of the copolymers and ABA_7 was thus measured at 223°C . The BAB_3 and $(\text{AB})_{n,4}$ copolymers with the diamide units located in the chain showed a rheological behavior corresponding to that of a linear polymer. However, at low frequencies, the ABA_7 and AB_3 copolymers with the diamide segments situated at the chain ends displayed a low terminal slope typical of a

network polymer. The number of diamide segments in the copolymer and the concentration of diamide segments did not seem to have any effect on these results. The copolymer with a higher molecular weight, i.e., $(\text{AB})_{n,4}$, naturally had a much higher complex viscosity than the other materials. The copolymers with diamide mid-segments, i.e., the multiblock $(\text{AB})_n$ and the triblock BAB , demonstrated a normal polymer-melt rheological behavior and had thus without cluster formation (Fig. 5a). However, the copolymers with diamide end segments, i.e., the triblock ABA and the diblock AB copolymers, behaved as a gelled melt and the amide segments must still be associated in the melt in the form of clusters (Fig. 5b).

The fact that the amide end segments formed a gelled structure, whereas the very similar mid-segments did not was very puzzling. The amide end segments seemed to be less steric hindered to form clusters. For the AB diblock copolymer, an aggregate formation of the end segments was also found to take place. However, these diblocks with an aggregated structure were not expected to form networks.

Structure Build-Up in End Block Copolymers

To confirm the hypothesis that end-block copolymers associated in the melt, the time-dependent rheological behavior of the di- (AB_3) and multiblock $(\text{AB})_{n,4}$ copolymers were studied and are presented in Fig. 6.

In this experiment, the melts were first predeformed at a shear rate of 5 s^{-1} for 150 s to break down some of their structure/entanglements. Subsequently, the shear rate was lowered to 0.1 s^{-1} and the shear stress was monitored. Because the Physica rheometer is a stress-controlled rheometer, one is unable to measure the stress transients during a stepwise reduction in shear rates at times smaller than approximately 2–4 s. After approximately 4 s, the shear stress of the multiblock copolymer sample changed only slightly with time. It was thus believed that $(\text{AB})_{n,4}$ had reached its limiting shear stress at this lower strain rate. However, the shear stress of the diblock copolymer (AB_3) increased gradually in the following 300 s. After this time, it attained a constant value and the agglomeration reached a steady state. The

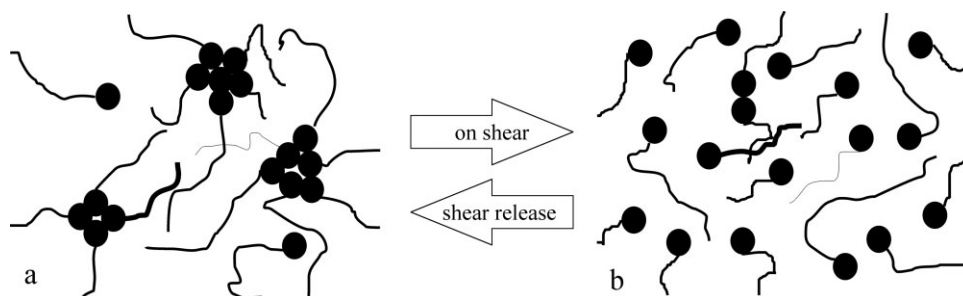


FIG. 7. A schematic representation of the aggregates in a diblock copolymer with diamide segments in the melt: (a) the breaking-up of the aggregates on shear (b) their reformation on shear release.

increase in shear stress after a stepwise reduction in shear rate was due to the rebuilding of the network structure at the low shear rate, thus illustrating a thixotropic nature of the melt [31]. A schematic diagram of the break-up and aggregation of the HS in the diblock copolymer is presented in Fig. 7.

CONCLUSIONS

The melt rheological behavior of segmented block copolymers with monodisperse diamide segments was studied. The diamide segments were able to H-bond with two neighboring diamide segments and constituted the HS in these copolymers. The composition of the block copolymer was varied with regard to the number of HS, the concentration of HS, the position of the HS, and the molecular weight of the copolymers. The melt rheological behavior of these materials was measured at a minimum of 40°C above the melting temperature of the copolymers. The monoblock **B**, triblock **BAB**, and multiblock **(AB)_n** copolymers all displayed the melt rheological behavior of a linear polymer. Apparently, the diamide mid-segments could not form stable clusters in the melt. The **AB** diblock copolymer and the **ABA** triblock copolymer with diamide end segments demonstrated a rheological behavior of a gelled melt. The shear rate-dependant structure of the amide end groups of the diblock copolymer in the melt was further confirmed by time-dependent rheological experiments. The network structure of the **AB** and **ABA** copolymers was believed to have been due to the clustering of the diamide end segments, and these clusters were stable near the melting temperature and at low shear rates. The copolymers with diamide end segments had a thixotropic behavior.

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