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Polymer 46 (2005) 6605–6613

polymer

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Structures and rheological properties of reactive solutions of block copolymers. Part I. Diblock copolymers in a liquid epoxy monomer

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Abstract

P(S-*b*-MMA) and P(B-*b*-MMA) diblock copolymers (BCP) have been solubilized in a liquid epoxy. The obtained solutions have been characterized by rheology and small angle X-ray scattering (SAXS). As in the solid state, BCP can self-organize in solution to form well-ordered micellar structures. The two blocks respective roles have been clearly identified: at room temperature the PS or the PB block microsegregates while the PMMA block for which epoxy constitutes a good solvent, acts as a stabilizer of the microphase separation. The geometries and thermal stabilities of the ordered structures depend strongly on the molar masses and the chemical nature of the BCP blocks. For instance, the total molar mass of the BCP has to be high enough to obtain a periodic structure. On the contrary, if this molar mass is too high, too long relaxation times prevent the system from reaching its equilibrium. For the P(S-*b*-MMA) copolymer solution, a transition temperature from an order to a disorder state (T_{ODT}) is observed. The origin of this transition has been attributed to a solubilization of the PS domains around T_{ODT}. Macroscopically, this transition can be defined as a solid-like to a liquid-like transition. In the case of the P(B-*b*-MMA) copolymer solution, no order–disorder transition has been observed: it can be explained by the fact that the PB blocks are not soluble in epoxy at any temperature, up to $T=200$ °C.

Keywords: Block copolymers; Reactive solvent; SAXS

1. Introduction

The self assembling ability of block copolymers (BCP) has received considerable attention over the last decades [1–4]. When cooled down from the melt, BCP undergo an order–disorder transition (ODT) for a well-defined temperature and form spatially periodic microdomains structures induced by microphase separation. The connectivity between the BCP blocks is responsible for this behaviour by preventing the usual macroscopic phase separation observed in homopolymer blends. In the weak segregation regime, above the T_{ODT}, Leibler [5] presented a scattering theory for the phase behaviour of diblock copolymers in the framework of a random phase approximation. Within mean-field theory, two parameters which are the chain composition f and the product χN of Flory–Huggins interaction parameter χ with the total degree of polymerization N dictate BCP phase behaviour. The knowledge of the T_{ODT} can be very useful in many applications.

Elastic scattering techniques (SAXS, SANS) have been used extensively to study the structural changes occurring in BCP samples since, they provide an in situ characterization during the phase transitions. Secondary peaks, showing long range order, disappear as T_{ODT} is approached, and the first peak intensity drops to a weak intensity level relevant to the broad scattering maximum from disordered melts. It is also well established that a microphase separation affects the rheological behaviours [6–9]. The long relaxation modes, as observed in the dynamic moduli at low frequencies, drop significantly when heating through the T_{ODT}. Another indication of the ODT is the frequency dependence of the moduli which changes from non-terminal solid-like behaviour in the ordered state ($G' \sim G'' \sim \omega^{0.5}$) to terminal,

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doi:10.1016/j.polymer.2005.05.014

liquid-like behaviour in the disordered state ($G' \sim \omega^2$ and $G'' \sim \omega^1$).

Because the variation of χ with temperature is very small, this transition can only be observed on BCP having a very low molar mass. As in the solid state, the BCP can self-associate in solution [10] but the segregation power is significantly decreased and gives rise to easily observable ODTs [11]. In most cases, BCP are in a selective solvent that means that only one block is swelled while the insoluble one is microsegregated. An extensive literature, both theoretical and experimental, exists on the unusual rheological properties exhibited by BCP in selective solvents [4,12–19]. At low temperatures and high BCP concentrations, the solution exhibits solid-like behaviour while at temperatures higher than T_{ODT}, it exhibits a liquid-like behaviour.

Earlier works [20,21] on block copolymers dissolved in reactive solvents like styrene have been revalorised recently using thermoset (TS) precursors like epoxy systems [22–34]. With an appropriate design of the BCP architecture, these block copolymers self-assemble to form ordered or disordered morphologies before reaction in the solution of the thermoset precursors. The role of the thermoset curing is to lock in the morphology that is initially present or formed in the earlier stages of the reaction. Finally after reaction, BCP are self-associated into spherical micelles, wormlike micelles or vesicles and these nanostructures can increase the fracture resistance of epoxy networks [29–34]. Most of the studied networks are based on diglycidyl ether of bisphenol A, DGEBA cured with different hardeners. Several types of BCP have been used, reactive and non-reactive AB, ABA and ABC. To prevent macroscopic phase separation of the BCP during reaction, the common characteristic is to have one block that is miscible in the growing thermoset at any stage of the reaction or just expulsed in a local scale. This is the case for example of poly(methyl methacrylate), PMMA [29] or poly(ethylene oxide), PEO [22] in some DGEBA-diamine systems.

Knowing the selectivity of the liquid DGEBA for the PMMA [35] compared to the polystyrene [36] and the polybutadiene [37] homopolymers, an addition of diblock copolymers like poly(styrene-*b*-methyl methacrylate), SM or poly(butadiene-*b*-methyl methacrylate), BM is expected to lead at low temperature to, respectively, PS and PB microsegregated domains. These systems are supposed to be ordered at some a concentration and to present an ODT. Our aim is to study these two latter aspects. Based on a PMMA block, (i) the length of the PMMA block, (ii) the total molar mass of the BCP and (iii) the state of the microsegregated domains (liquid when the PB is microsegregated, vitreous in the case of PS) will be varied. Small angle X-ray scattering (SAXS) and rheology will be used to characterize the ODT. Only moderate concentrated solutions containing 30 wt% of diblocks will be studied.

This study on diblock copolymers in liquid DGEBA will be useful to understand the behaviour of triblock copolymers, SBM in the same reactive and selective solvent. This latter study will constitute the second part of this work. This is why our aim is not to discuss exhaustively the complex behaviour of diblock copolymers in a selective solvent (for example, possibilities of order–order transitions have not been investigated), but rather to describe the several microstructural events occurring in the solutions as a function of the temperature.

2. Experimental

2.1. Materials

The thermoset precursor is a liquid epoxy acting as a selective solvent: diglycidyl ether of bisphenol A (DGEBA $n = 0.15$) supplied by Huntsman as Araldite LY 556.

The block copolymers are a diblock poly(styrene-*b*-methyl methacrylate), SM and a diblock poly(butadiene-*b*-methyl methacrylate), BM whose characteristics are given in Table 1. The adopted nomenclature is similar to the one used in our previous publications [29–31], S or $B_t^x M_v$ with t and v corresponding to the mass percent of blocks and x to the PS or PB block number average molar mass in kg/mol. All the blends contain 30 wt% of block copolymers. The antioxydant Irganox was provided by Ciba. Chloroform (99.9%, supplied by SDS) was used as received without any purification.

2.2. Sample preparation

The samples were prepared by dissolving DGEBA and the block copolymers in chloroform. The chloroform was evaporated during 1 week at ambient pressure and temperature, then one night in a vacuum oven at 50 °C. An additional thermal ageing at 150–160 °C is performed in order to remove the residual solvent. When the block copolymers contain a PB block, a stabilizing agent (Irganox) is added (2 wt% of the total mass of the block copolymer). When it is indicated, the samples have been annealed at high temperature for 24 h and cooled down at room temperature at 0.2 °C/min. For solutions containing SM or BM diblock, the annealing temperature was set to 120 °C which is always higher than the upper T_g to facilitate molecular mobility and nanostructural development.

2.3. Experimental techniques

Rheological analyses were conducted on a TA stress-controlled rheometer (AR1000) equipped with 40 mm diameter parallel plates. The sample thickness was set to 0.8 mm. The linear viscoelastic domain has been determined at the highest frequency and the lowest temperature. When frequency sweep experiments are conducted, the temperature is raised from 20 to 180 °C by step of 10 °C. Measurements are started after a 30 min stabilization step.

Table 1
Characteristics of the block copolymers

Name	$\bar{M}_n$ (kg/mol)	I_p	Supplier
$S^{50}_{48}M_{52}$	PS: 50, PMMA: 54	1.04	Polymer source
$S^{47}_{25}M_{75}$	PS: 47.4, PMMA: 140.4	1.11	Polymer source
$S^{17}_{59}M_{41}$	PS: 17, PMMA: 12	1.20	Arkema
$B^{43}_{39}M_{61}$	PB: 43.1 (PB1,2: 6.4%), PMMA: 67.2	1.36	Arkema

When the frequency is set at 1 rad/s, the temperature ramp is 0.5 °C/min.

SAXS analyses were carried out on the BM2-D2AM beamline at the European Synchrotron Radiation Facility (Grenoble, France). For all experiments, the temperature is raised by step of 10 °C and again a stabilization of 30 min is ensured before starting measurements. The experiments consist in measuring scattering images, in point collimation conditions, by means of a 2D-CCD camera (from Ropper Scientific). The raw images are corrected from the response of the detector in absence of beam (dark images), and the response of the detector to the homogeneous illumination of a fluorescent sample (flat field). The empty cell is subtracted by means of a monitoring of the incident and transmitted intensity, and the distortion of the fiber optic taper was also corrected. At last, the radial averages around the incident beam center were calculated, and the scattering of an AgBe powder is used in order to build the scattering diagrams $I(q)$, where q is the scattering vector length, $q=4\pi\ \sin(\theta)/\lambda$, and 2θ is the scattering angle. All these corrections were performed by a software, BM2IMG, developed on the beamline in connection with local contacts and users.

Differential scanning calorimetry (DSC) analyses were conducted on a Mettler TA3000 apparatus under an argon atmosphere. Dynamic runs at constant heating rates were performed in order to measure the glass transition temperature, T_g (midpoint value). The experiments were carried out in a temperature range from −80 to 200 °C at a heating rate of 10 °C/min.

3. Results

3.1. Phase behaviour of a symmetric SM diblock copolymer ($S^{50}_{48}M_{52}$) in DGEBA

For the bulk diblock copolymers, the T_g's are 93 °C for the PS block and 102 °C for the PMMA block. At room temperature, the solution DGEBA/$S^{50}_{48}M_{52}$ is fully transparent and does not seem to flow when a tilt test is performed. According to DSC measurements, only one T_g is observed, the one of the matrix at −10 °C. Knowing the T_g of the DGEBA (−18 °C) and of the PMMA (102 °C), the T_g of an homogeneous blend of the PMMA block and the epoxy can be estimated using the Fox equation [38]. The calculated T_g is around −3 °C which is slightly higher than the measured one. This means that the system is not a perfect 'wet brush' system and/or the PMMA segments are non-uniformly distributed in the matrix [39]. These two hypotheses can explain the overestimation of the calculated T_g. In addition, still assuming the absence of DGEBA in the PS domains at room temperature, their volume fraction in the blend can also be estimated to be around 15%. According to the literature, the morphology of the blend at room temperature may be regularly packed spheres or cylinders.

SAXS data are recorded at 25 °C on DGEBA/$S^{50}_{48}M_{52}$ blends which have undergone different thermal histories (Fig. 1). At room temperature, when the solution has been previously cooled down quickly, the first order peak stays broad and there is no well defined second order peak (Fig. 1(a), 25 °C). Even if the solution is fully transparent, the morphology of the solution corresponds most likely to a non-equilibrium state. After a thermal ageing at 120 °C, and a very slow cooling ramp (0.2 °C/min), the scattering pattern displays a series of well defined secondary peaks indicating the presence of a highly ordered structure (Fig. 1(b), 25 °C). The relative positions of the higher-order peaks at, respectively, $q=\sqrt{3}q^*$, $q=\sqrt{4}q^*$, $q=\sqrt{7}q^*$, $q=\sqrt{9}q^*$ are consistent with a hexagonally-packed cylinders structure. The characteristic distance given by $d=2\pi/q^*$ is

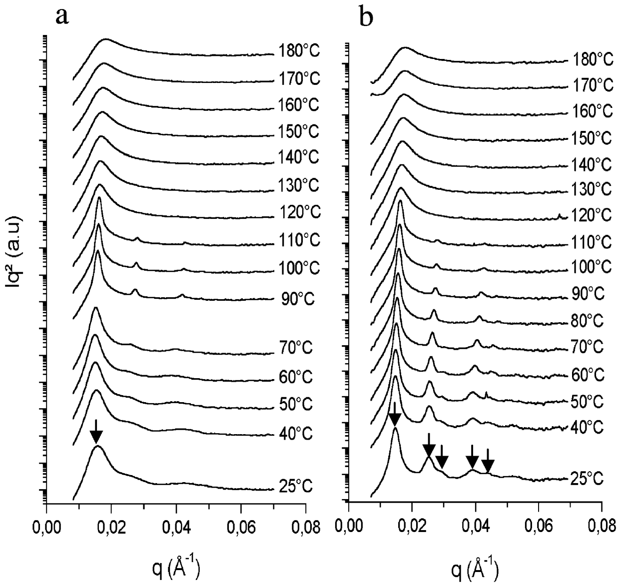

Fig. 1. Temperature dependence of the SAXS patterns (intensity vs. wave factor, q) for the solution DGEBA/$S^{50}_{48}M_{52}$ (a) non-annealed system, (b) annealed system. Arrows denote the characteristic reflection used to identify the ordered state of symmetries. The individual curves have been shifted for clarity.

43 nm and corresponds to the distance between two cylinders.

The temperature dependences of the SAXS profiles for the non-annealed and the annealed solutions have been recorded from room temperature to 180 °C. A sharpening of peaks is observed for the non-annealed sample when the temperature is raised from 60 to 70 °C (Fig. 1(a)). The structure is equilibrating and ordering. Increasing temperature can have a double effect, which would be explained latter. At 90 °C, the system is well-ordered and the relative positions of the peaks are indicative of hexagonally-packed cylinders as it was observed for an annealed sample at 25 °C (Fig. 1(b)). This means that the structure of an equilibrated system at 90 °C is recovered. This result supports the choice of an annealing temperature higher than 100 °C. Whether it is annealed or not, when the temperature is raised to 120 °C, the high order peaks disappear completely and the principal peak broadens considerably, indicating an ODT. The ODT temperature does not seem to be affected by a preliminary thermal ageing according to these SAXS results.

The effects of the structural transition observed by SAXS were also studied by using the rheology in the linear viscoelastic regime, since this technique is also extensively used to study the ODT [40–42]. The elastic modulus G' is plotted vs. the loss modulus G'' at different temperatures for the DGEBA/$S_{48}^{50}M_{52}$ blend (Fig. 2). Han et al. [41] have suggested that the threshold temperature for which log G' vs. log G'' becomes linear with a slope of 2 independent of temperature, was the signature of a disordered system. In our system, four regimes are observed. Below 60 °C, the curves are superimposed and a low frequency elastic plateau is exhibited. Between 60 °C and 110–120 °C, an intermediate regime is observed and can correspond to a softening of the lattice. As said previously, increasing temperature can have a double effect: (i) the migration of DGEBA in the PS-core is more and more likely to occur and may plasticize the PS domains and (ii) the temperature is reaching a value close to the T_g of the microsegregated PS-rich domains. In this temperature range, the system is very sensitive to the strain. Between 110 and 140 °C, a viscoelastic regime with a Maxwellian behaviour (slope of 2) is exhibited but the curves do not superimpose. This means that the system contains persistent micelles or heterogeneities. Above 140 °C, all the curves are perfectly superimposed with a slope of 2 indicating that the solution is homogeneous. However, T_{ODT} measured by SAXS is located below 140 °C. This means that just above T_{ODT}, there might be persistent micelles or concentration fluctuations. The system is homogeneous at $T_{\mathrm{ODT}}+25$ °C.

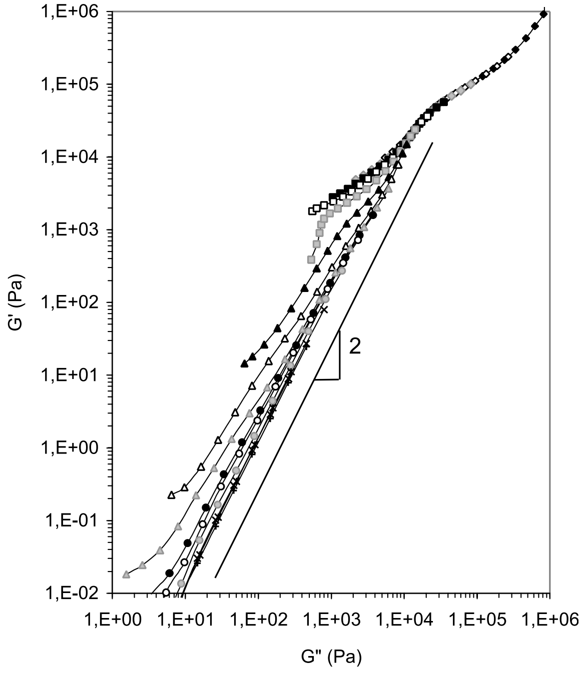

Fig. 2. G' vs. G'' for the solution DGEBA/$S_{48}^{50}M_{52}$ at different temperatures and frequencies from 0.01 to 100 rad/s. (♦) 20 °C, (◇) 30 °C, (♦) 40 °C, (■) 50 °C, (□) 60 °C, (■) 70 °C, (▲) 80 °C, (△) 90 °C, (▲) 100 °C, (●) 110 °C, (○) 120 °C, (●) 130 °C, (×)140 °C, (+) 150 °C, (*) 160 °C.

The T_{ODT} can also be determined by plotting G' and G'' vs. temperature at 1 rad/s (Fig. 3). The sample has been annealed at high temperature and the experiment has been started at room temperature. This latter temperature is located just after the vitreous transition zone of the matrix and it may explain the fact that G' and G'' values are very close at this temperature. Between 70 and 100 °C a slight increase of G' is detectable; this increase can be attributed to the swelling of the micelles due to the gradual swelling of the PS core by the solvent. This event may lead to an increase of the physical interactions between micelles. T_{ODT} can also be defined as the temperature for which G' starts dropping or for which G' and G'' curves cross each other. By this method, T_{ODT} is found to be close to 100 °C. It is clear that T_{ODT} measured by SAXS is 15 °C higher than T_{ODT} measured by the rheological criterion $G'=G''$; the temperature extracted by rheology is underestimated compared to the true equilibrium T_{ODT} [7,43]. This difference could be the consequence of the softening of the lattice, which may

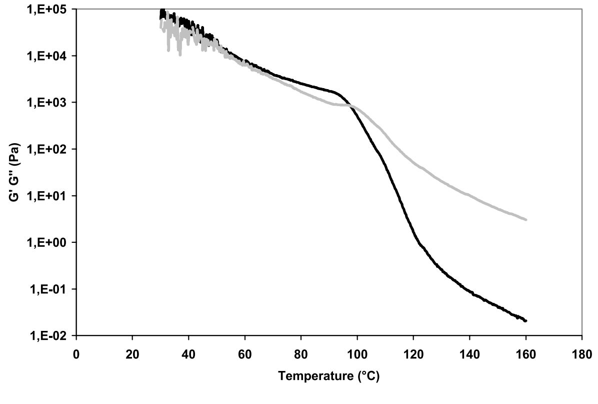

Fig. 3. Temperature dependence of G' (—) and G'' (—) at 1 rad/s for the solution DGEBA/$S_{48}^{50}M_{52}$. The heating rate is 0.5 °C/min and the imposed stress equal 2 Pa.

break prematurely by the imposed stress, even if this stress is as low as 2 Pa.

As we explained previously, the solution does not flow at room temperature when a tilt test is performed. At such a temperature the PS domains are vitreous and are supposed to affect the PMMA blocks relaxation in the solvent by increasing their relaxation times. Indeed, the PMMA chain is partly locked by a covalent link with the PS vitreous domain. The physical interactions life times are then longer than the experimental time and the solution behaves like a ‘gel’. A first explanation of this solid-like behaviour could be to assume that PMMA chains are entangled in its selective solvent DGEBA. But if one considers a solution of homoPMMA in the DGEBA with a volume fraction of the order of 18%, the critical molar mass of the PMMA, $(M_c)_{sol}$ necessary to create entanglements can then be estimated to be 300 kg/mol [43]. This value is six times higher than the molar mass of the PMMA block in the $S_{48}^{50}M_{52}$. Therefore, it is reasonable to admit that PMMA chains are not entangled in such a DGEBA solution. The PMMA chains may just interact with each other but without creating an entangled regime. The contribution to the elasticity in the ordered solution is, as explained in previous studies [8,9], the solicitation of the PS cylinders. This contribution is most likely due to their orientation relative to the shear axis.

On the contrary, when the temperature is reaching the T_g of the PS-rich domains which are swelled by the solvent in this temperature range, the mobility of the chains increases strongly and the physical interactions life times are then shorter than the experimental time. This difference in relaxation times may explain an apparent gel–sol transition around 100 °C. This temperature is 15 °C below the T_{ODT}, which confirms that this pseudo gel–sol transition is not the true equilibrium ODT. This temperature is still very important for processing because above 100 °C the solution has a low viscosity and it flows; the epoxy/BCP systems are semi-concentrated solutions: moduli drops at the ODT are expected to be higher in the case of solutions than in the case of bulk polymers.

3.2. Phase behaviour of a highly asymmetric SM diblock ($S_{25}^{50}M_{75}$) in DGEBA

In this part, the effect of a very long PMMA block will be discussed. The PS block of $S_{25}^{50}M_{75}$ is the same as the one of $S_{48}^{50}M_{52}$ while the PMMA block is three times longer (but still four times lower than the minimum molar mass of the PMMA required to create entanglements). The solution DGEBA/$S_{25}^{50}M_{75}$ is fully transparent and the T_g of the matrix has been measured and found around −9 °C which again and for the same reasons as previously is lower than the estimated one (+3 °C). The volume fraction of the PS core at room temperature is of the order of 8%. Here again, according to the literature, the morphology may be spheres or cylinders. As for the DGEBA/$S_{48}^{50}M_{52}$ system, the solution does not flow when it is tilted.

SAXS data have been recorded for an annealed DGEBA/$S_{25}^{50}M_{75}$ blend (Fig. 4). The system is clearly not perfectly ordered as the secondary peaks are still ill-defined. Due to the high molar mass of the PMMA block, the relaxation times of the chains are very long and it could take a long time to the BCP to reach an ordered state. At high temperatures, the profiles show a continuous disappearance of the secondary peaks but without significant broadening of the first order peak. It is reasonable to say that there is no more structural evolution up to 180 °C and that some micelles are persisting. These aggregates are obviously more stable than the ones observed for the symmetrical BCP.

The absence of a well-defined ODT in this system is clear when plotting G' and G'' vs. temperature at 1 rad/s (Fig. 5). Below 100 °C, G' is higher than G''; G' starts to decrease slowly around 80 °C; G' and G'' curves cross each other at 120 °C but it is not followed by a significant drop of G'. As it is shown by SAXS, the relaxation times of copolymer chains are very long and the 30 min equilibration step between two measurements (0.5 °C/min, 1 rad/s) is not long enough. The origin of this behaviour may also be found in the swelling of the micelles in this temperature range which leads to strong physical interactions between closely packed micelles. Both explanations may explain the gradual decrease of G', both are also correlated with the high molar mass of the BCP. Even in the disorder state and up to 180 °C, the solution keeps a high viscosity that may be close to the one of the ordered system.

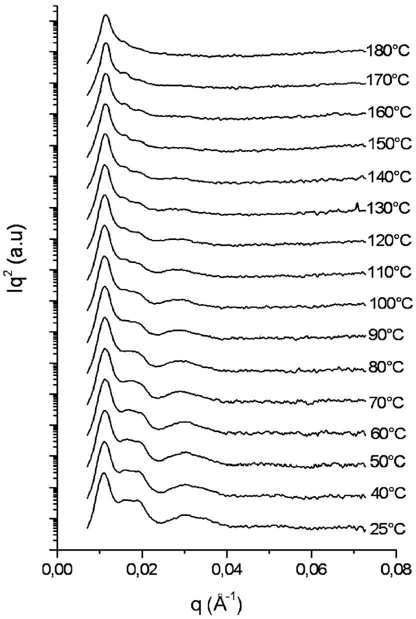

Fig. 4. SAXS patterns at room temperature (intensity vs. wave factor, q) for the annealed solution DGEBA/$S_{25}^{50}M_{75}$.

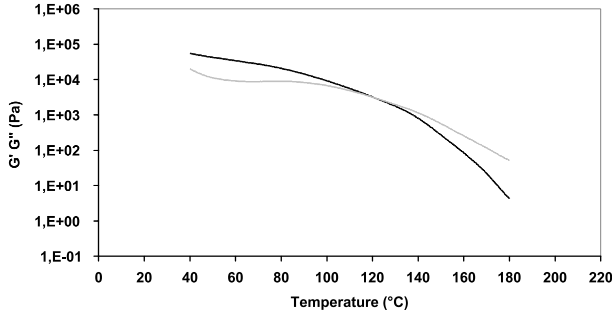

Fig. 5. Temperature dependence of G' (—) and G'' (—) at 1 rad/s for the solution DGEBA/$S_{25}^{50}M_{75}$. The heating rate is 0.5 °C/min.

3.3. Phase behaviour of a very low molar mass SM diblock ($S_{59}^{17}M_{41}$) in DGEBA

In this part, the effect of a very low total molar mass of the diblock will be discussed. As for the other solutions, the system DGEBA/$S_{59}^{17}M_{41}$ is fully transparent at room temperature. The T_g is -13 °C which is again lower compared with the estimated one (-5 °C). The volume fraction of the PS can be estimated to be of the order of 18.5% vol. By performing a tilt test on this solution, it has been concluded that it starts to flow after a very long period of time.

SAXS patterns have been recorded for a non-annealed and an annealed DGEBA/$S_{39}^{43}M_{61}$ blends at 25 °C (Fig. 6(a) and (b)). The thermal annealing of the system does not seem to strongly affect the organization. The first order peak is slightly sharpened and the position of the secondary peak is slightly modified. Its position related to q^* is close to $\sqrt{6}q^*$. The structure could be an arrangement of spheres on a cubic-centred or face-centred cubic lattice, but some facts like the absence of the usual secondary peaks ($\sqrt{4}$, $\sqrt{9}$) are indicative of a disorder state. The thermal ageing undergone by this low molar mass BCP solution cannot be responsible for this lack of organization as the same treatment was able to perfectly organize the higher mass DGEBA/$S_{48}^{50}M_{52}$ solution.

The plot of G' and G'' vs. temperature at 1 rad/s indicates that the solution does not present any elasticity at low temperature (Fig. 7). Using a very short PS block has two effects: the first one is a slight decrease of the T_g of the block and the second more significant effect is an increase of the miscibility window [44]. The consequence is a decrease of the solvent selectivity. Instead of a G' plateau, a continuous decrease of G' and G'' is observed as the temperature is increased. G' and G'' curves do not really cross each other. In conclusion, the very low molar mass of the BCP does not create a high enough segregation power in a 30 wt% BCP solution and an ordered structure cannot be induced.

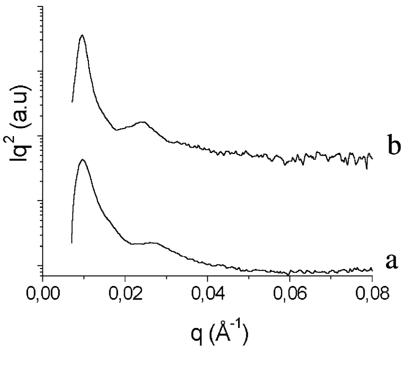

Fig. 6. Temperature dependence of the SAXS patterns (intensity vs. wave factor, q) for the solution DGEBA/$S_{59}^{17}M_{41}$.

3.4. Phase behaviour of a slightly asymmetric BM diblock ($B_{39}^{43}M_{61}$) in DGEBA

Shifting from an epoxy-SM solution towards an epoxy-BM solution does not represent a significant change in the solvent selectivity. The DGEBA still constitutes a good solvent of the PMMA. Nevertheless, the difference is twofold: (i) unlike PS, PB is never miscible in DGEBA and the microsegregated domains are a priori insensitive to the temperature, and (ii) the T_g of the PB block is located around -60 °C and consequently the mobility of the copolymer chains at 25 °C (T_g+85 °C) are well higher than the SM one. By comparison, this mobility would be equivalent to the one of a SM at 180 °C. The $B_{39}^{43}M_{61}$ architecture is quite similar to the $S_{48}^{50}M_{52}$ structure with a PB block slightly shorter (7 kg/mol shorter) and a PMMA block slightly longer (14 kg/mol longer). At 30% bw in DGEBA, the volumic fraction of PB is estimated to be of the order of 14%. The morphology is supposed to be spherical or cylindrical. The measured value of the T_g of the matrix is -13 °C while the calculated one is 0 °C. No flow is observed by tilting the solution.

The SAXS profiles from non-annealed and annealed solutions are quite similar (Fig. 8). For the annealed system, a first order peak at $q=0.012$ Å^{-1} is observed close to a shoulder present at $q=0.02$ Å^{-1} (Fig. 8(b)). The SAXS patterns do not indicate a well-ordered structure even if the solution is fully transparent. Hanley et al. [11] connect this type of SAXS profiles to the micelles morphologies. For the $S_{48}^{50}M_{52}$ BCP, it has been observed that above the T_g of the PS-rich microsegregated domains, the mobility was high

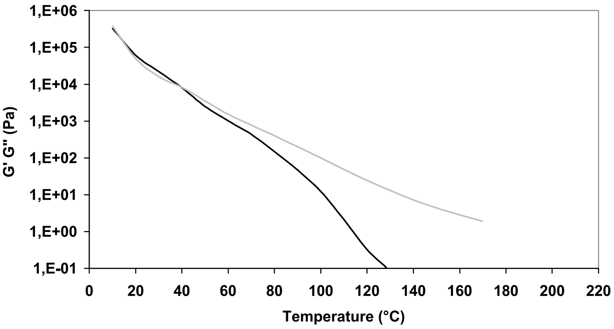

Fig. 7. Temperature dependence of G' (—) and G'' (—) at 1 rad/s for the solution DGEBA/$S_{59}^{17}M_{41}$. The heating rate is 0.5 °C/min.

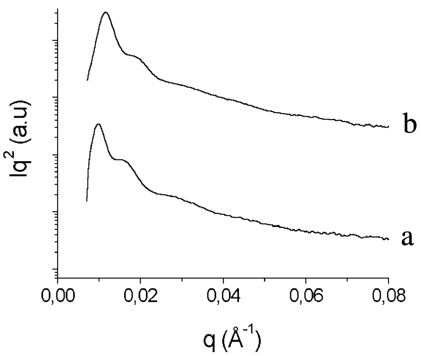

Fig. 8. SAXS patterns at room temperature (intensity vs. wave factor, q) for the solution DGEBA/$B_{39}^{43}M_{61}$. (a) Non-annealed system, (b) annealed system.

enough to allow a reorganization of the solution. In our present situation, even at 25 °C, we are far above the T_g of the PB microdomains and the solution is supposed to be totally equilibrated.

The temperature dependences of the SAXS profiles for the non-annealed and the annealed solutions (not presented here) have been recorded from 25 to 180 °C and no evolution has been observed. No ODT can be noted in this temperature range. Moreover, no drop of G' and G'' can be observed during a temperature ramp at 0.5 °C/min at 1 rad/s. These results indicate that the system stays microsegregated no matter how high the temperature is. This unique and crucial difference with the $S_{48}^{50}M_{52}$ can be explained by the nature of the PB microsegregated domains which are not miscible in the solvent on the explored temperature range. This is confirmed by plotting G' and G'' measured at 1 rad/s vs. temperature (Fig. 9). At 200 °C, G' is still higher than G'' and this system is still ordered. It can be seen that below 80 °C, G' is well higher than G''. From 80 to 200 °C, G' and G'' are fairly close in an ordered phase.

The absence of structural evolution in this solution allows to apply the concept of time-temperature superimposition and to plot the master curve of the solution at 20 °C (Fig. 10). For extremely long relaxation times, a terminal viscoelastic regime ($G' \sim \omega^2$ and $G'' \sim \omega$) is observed. The PMMA blocks, which are swollen by the DGEBA, do not prevent the solution from flowing. This curve illustrates the complexity of the notion of physical gel: if the classical tilt test is performed at high temperature on this solution, the experimentalist would conclude that the solution does not flow. But this is only a time-dependent phenomenon. Between 10^{-7} and 10^{-4} rad/s, a second relaxation is observed and can be attributed to the microsegregated domains of PB [7]. These extremely long relaxation times might explain the ill-defined SAXS pattern at 25 °C (Fig. 8). As previously, $(M_c)_{sol}$ can be estimated to be of the order of 250 kg/mol for a pure solution of PMMA at 20.7 vol% in DGEBA (corresponding to 30 wt% of $B_{39}^{43}M_{61}$). The molar mass of the PMMA block is well below this value and PMMA cannot be entangled. Thus, the contribution of the PB domains to the elasticity must be significant. It could be surprising to consider that the presence of non-interacting elastomeric domains can enhance the elasticity of the solution. It is important to recall that it is the value of the rubbery plateau (G_N^0) which is discussed here and not a Young modulus. According to the master curve (Fig. 10), the G_N^0 of the solution can be estimated to be of the order of 2.10^4 Pa. The G_N^0 of the homoPB is known to be of the order of 7.10^5 Pa which is higher than the value of the G_N^0 of the solution. Thus, the PB microsegregated domains can have a reinforcing effect.

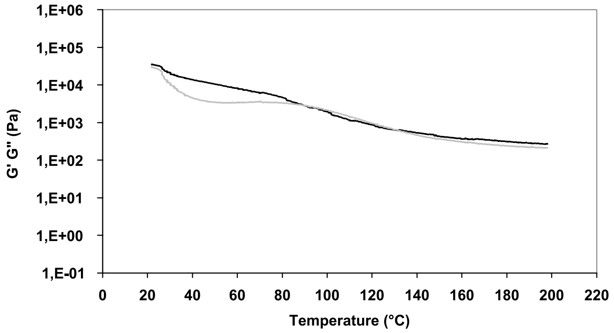

Fig. 9. Temperature dependence of G' (▬) and G'' (▬) at 1 rad/s for the solution DGEBA/$B_{39}^{43}M_{61}$. The heating rate is 0.5 °C/min.

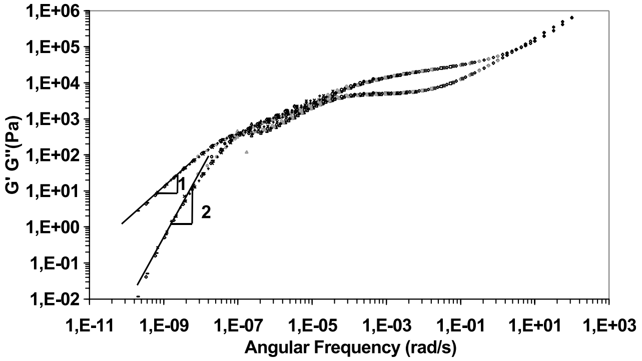

Fig. 10. Master curve at 20 °C for the solution DGEBA/$B_{39}^{43}M_{61}$ ($\ln(a_T) = (12,846/T) - 46$).

4. Conclusion

The objective of this first part of our work dedicated to the structures and rheological properties of reactive solutions of BCP was to understand the rheological phenomena associated with ODT in the case of simple systems like diblock copolymers in liquid epoxy solution. The respective roles of the blocks constituting the BCP have been elucidated. The PMMA block stabilizes the microphase separation while the PS or PB blocks are microsegregated and allow the solution to keep its transparency.

From the four studied 70/30 w/w DGEBA/diblock solutions, two of them are particularly interesting. The first one is the solution of DGEBA containing 30% of $S_{48}^{50}M_{52}$ because of its clear ODT measured by SAXS between

110 and 120 °C. The second very interesting system is the DGEBA/$B_{39}^{43}M_{61}$ that does not present any ODT.

For $S_{48}^{50}M_{52}$ copolymer, the dramatic drops of the elastic and loss moduli at a temperature in the vicinity but lower than the T_{ODT} measured by SAXS, is attributed to the solubilization of the PS-rich domains. This solubilization suddenly increases the relaxation of the PMMA chains. The related relaxation times become closer to the one of a homopolymer in solution. It has also been concluded that the ODT is not always a transition from an ordered to a disordered and homogeneous solution. Experimentally, the homogeneity has been observed 25 °C above the T_{ODT} for this system containing 30% bw of $S_{48}^{50}M_{52}$.

In the case of the BM copolymer, the PB block stays microsegregated whatever the temperature is. The relaxation times of the chains are not affected significantly in the temperature range 20–180 °C, and no ODT is observed. By using the time–temperature superimposition principle, it has also been checked that the terminal behaviour of this DGEBA/BM solution was reached for very long relaxation time: this result is consistent with the physical nature of the interactions responsible for the BCP self-association.

In addition, as observed on SM diblocks, the total molar mass of the BCP is an important parameter. A solution of DGEBA containing 30% of $S_{48}^{50}M_{52}$ is organized in a hexagonally-packed cylinders structure. But if the total molar mass of the diblock is too low, the segregation power of the system is not high enough to induce a well-ordered structure at this concentration. The diblock micelles are not organized, the interparticular distance being too large for these micelles to interact and the solution does not exhibit any elasticity. On the contrary, if the molar mass of the diblock is well higher (200 kg/mol) and the BCP highly asymmetric, the system cannot be easily brought back to its equilibrium because of longer relaxation times, and micelles seem to be stable at high temperature (180 °C). Two reasons may explain such a result: (i) the curve of the interface of block copolymer and (ii) the decrease of the miscibility window when increasing the molar mass of the PMMA.

The temperature dependence of moduli, G' and G'' at 1 rad/s for the DGEBA/SM solutions is a useful tool to determine the range of temperature for which the solutions can be easily processed.

Acknowledgements

Arkema (ex-Atofina) is gratefully acknowledged for financial support. The authors would like to thank A. Bonnet, P. Cassagnau and J. Gimenez for helpful discussions. C. Rochas and J. F. Berar are also acknowledged for perfect settings of the beam at ESRF.

References

[1] Lodge T. Macromol Chem Phys 2003;204:265–73.

[2] Park C, Yoon J, Thomas EL. Polymer 2003;44:6725–60.

[3] Alexandridis P, Lindman B, editors. Amphiphilic block copolymers: self assembly and applications. New York: Elsevier; 2000.

[4] Bhatia SR, Mourchid A, Joanicot M. Curr Opin Colloid Interf Sci 2001;6:471–8.

[5] Leibler L. Macromolecules 1980;13:1603–17.

[6] Rosedale JH, Bates FS. Macromolecules 1990;23:2329–38.

[7] Pakula T, Floudas G. In: Balta Calleja FJ, Roslaniec Z, editors. Block copolymers. New York: Marcel Dekker; 2000. p. 123–77 [Chapter 6].

[8] Kossuth MB, Morse DC, Bates FS. J Rheol 1999;43:167–76.

[9] Sebastian JM, Lai C, Graessley WW, Register RA, Marchand GR. Macromolecules 2002;35:2700–6.

[10] Alexandridis P, Spontak RJ. Curr Opin Colloid Interf Sci 1999;4: 130–9.

[11] Hanley KJ, Lodge TP, Huang CI. Macromolecules 2000;33:5918–31.

[12] Lodge TM, Xu X, Ryu CY, Hamley IW, Fairclough JPA, Ryan AJ, et al. Macromolecules 1996;29:5955–64.

[13] Kleppinger R, Mischenko N, Reynaers HL, Koch MHJ. J Polym Sci Part B: Polym Phys 1999;37:1833–40.

[14] Vega DA, Sebastian JM, Loo YH, Register RA. J Polym Sci Part B: Polym Phys 2001;39:2183–97.

[15] Lai C, Russel WB, Register RA. Macromolecules 2002;35:841–9.

[16] Nie H, Bansil R, Ludwig K, Steinhart M, Konak C, Bang J. Macromolecules 2003;36:8097–106.

[17] Theunissen E, Overbergh N, Reynaers H, Antoun S, Jérôme R, Mortensen K. Polymer 2004;45:1857–65.

[18] Inomata K, Nakanishi D, Banno A, Nakanishi E, Abe Y, Kurihara R, et al. Polymer 2003;44:5303–10.

[19] Hamley IW, Daniel C, Mingvanish W, Mai S-M, Booth C, Messe L, et al. Langmuir 2000;16:2508–14.

[20] Finaz G, Skoulios A, Sadron C. C R Acad Sci Paris 1961;253:265–9.

[21] Sadron C, Gallot B. Makromol Chem 1973;164:301–32.

[22] Hillmyer MA, Lipic PM, Hadjuk DA, Almdal K, Bates FS. J Am Chem Soc 1997;119:2749–50.

[23] Lipic PM, Bates FS, Hillmyer MA. J Am Chem Soc 1998;120: 8963–70.

[24] Höfflin F, Könczöl L, Döll W, Morawiec J, Mülhaupt R. J Appl Polym Sci 2000;76:623–34.

[25] Mijovic J, Shen M, Sy JW, Mondragon I. Macromolecules 2000;33: 5235–44.

[26] Grubbs RB, Dean JM, Broz ME, Bates FS. Macromolecules 2000;33: 9522–34.

[27] Kosonen H, Ruokolainen J, Nyholm P, Ikkala O. Macromolecules 2001;34:3046–9.

[28] Dean JM, Lipic PM, Grubbs RB, Cook RF, Bates FS. J Polym Sci Part B: Polym Phys 2001;39:2996–3010.

[29] Ritzenthaler S, Court F, David L, Girard-Reydet E, Leibler L, Pascault JP. Macromolecules 2002;35:6245–54.

[30] Ritzenthaler S, Court F, Girard-Reydet E, Leibler L, Pascault JP. Macromolecules 2003;36:118–26.

[31] Girard-Reydet E, Pascault JP, Bonnet A, Court F, Leibler L. Macromol Symp 2003;198:309–22.

[32] Rebizant V, Abetz V, Tournilhac F, Court F, Leibler L. Macromolecules 2003;36:9889–96.

[33] Dean JM, Verghese NE, Pham Ha Q, Bates FS. Macromolecules 2003;36:9267–70.

[34] Rebizant V, Venet AS, Tournilhac F, Girard-Reydet E, Navarro C, Pascault JP, et al. Macromolecules 2004;37:8017–27.

[35] Ritzenthaler S, Girard-Reydet E, Pascault JP. Polymer 2000;41: 6375–86.

[36] Bonnet A, Pascault JP, Sautereau H, Taha M, Camberlin Y. Macromolecules 1999;32:8517–23.

[37] Chen D, Pascault JP, Bertsch RJ, Drake RS, Siebert AR. J Appl Polym Sci 1994;51:1959–70.
[38] Fox TG. Bull Am Phys Soc 1956;1:123–31.
[39] Auschra C, Stadler R, Voigt-Martin IG. Polymer 1993;34:2094–110.
[40] Bates FS. Macromolecules 1984;17:2607–13.
[41] Han CD, Kim J. J Polym Sci Part B: Polym Phys 1987;25:1741–64.
[42] Wang X, Dormidontova EE, Lodge T. Macromolecules 2002;35:9687–97.
[43] Floudas G, Pakula T, Velis G, Sioula S, Hadjichristidis N. J Chem Phys 1998;108:6498–507.
[44] Soule ER, Fine T, Borrajo J, Pascault JP, Williams RJJ. Submitted for publication.