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Detection of the glass relaxation process of the PS-phase in block copolymers

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Abstract

The relaxation behavior of the glass process of the polystyrene (PS) phase in three different types of block copolymers has been investigated. Four triblock copolymers are used, namely, two styrene–butadiene–styrene (S–B–S), styrene–styrene butadiene–styrene (S–SB–S) and styrene–ethylene butylene–styrene (S–EB–S). The materials were crosslinked by means of dicumylperoxide (DCUP) with concentrations up to 10 phr, i.e. 10 g of DCUP per 100 g of the polymer. Dynamic mechanical measurements have been done for the complex shear compliance in wide temperature and frequency windows, 30–150 °C and 10^{-3}–10 Hz, respectively. Complete master curves have been constructed for all samples and analyzed using Cole–Cole function. It is observed that crosslinking reduces the relaxation strength of the low frequency process much more than that of the high frequency process. Therefore, the glass relaxation process of the PS-phase can be easily detected in the crosslinked samples. The relaxation frequency of the maximum of the glass relaxation process of the PS-phase is found to be independent of the crosslinking concentration. The relaxation behavior of block copolymers with respect to crosslinking is compared to styrene butadiene rubber (SBR) statistical copolymer. A method to detect the glass transition temperature (T_g) of the investigated block copolymers is suggested. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Block copolymers; Statistical copolymers; Glass relaxation process

1. Introduction

Because of the ability of block copolymers to form spontaneously ordered nanometer-sized microstructures [1–3] and their versatility in a variety of established [4] and emerging commercial applications [5,6], they remain the subject of intense research interest. The equilibrium morphologies in block copolymers are highly dependent on the relative composition of the blocks [7,8]. The temperature window in which block copolymers are suitable in commercial applications as modified glassy materials, for example, high impact polystyrene (PS), HIPS, or as thermoplastic rubber is the temperature range between the glass transition temperatures of the soft and hard blocks [9]. Block copolymers like Shell products (for instance, styrene–butadiene–styrene (S–B–S)) have been around for over 20 years and have many commercial applications, for instance, thermoplastic elastomers [10,11], pressure sensitive hot-melt adhesives [12] and viscosity stabilizers for oils [13].

A great deal of effort has been devoted to investigate the morphology of block copolymers in dependence of many factors, for instance, the effect of molecular weight [9–14], cast solvent [9,14,15], effect of composition [16,17] and solvent evaporation and post evaporation annealing [9,14,15]. In addition to the morphological studies done on block copolymers, investigation of their dynamic mechanical properties have gained attention in literature [4,18–22]. In block copolymers, for instance, S–B–S and styrene–isoprene–styrene (S–I–S) triblock copolymers it is difficult to detect the glass transition, T_g, of the PS-phase [19–23], especially when the content of PS is low (<30% by weight) [19–23], while the glass transition is smeared out [19–23]. Other block copolymers like styrene–styrene butadiene–styrene (S–SB–S) suffer also from this problem [21,22], while the glass transition of the PS-phase cannot be determined at all [21,22]. In addition, the dielectric thermal analysis cannot detect the glass relaxation process of the PS-phase in block copolymers. This is attributed to the fact that PS (nonpolar) has a very small dielectric loss (ε'') [24]. Moreover, in block copolymers, the peak maximum is expected to be lower due to the low PS content.

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Table 1
Characterization of the block copolymer samples

Material name	Styrene block content (wt%)	Type of the mid block	M_n PS block (kg/mol)	M_n (mid block) (kg/mol)	Total M_n[a] (kg/mol)	Pd[a,b] $= M_w/M_n$
S–B–S 1102	28.5	Butadiene	10.3	51.5	72.1	1.22
S–B–S 1101	31.0	Butadiene	14.1	62.8	91.0	1.30
S–SB–S	32.0	Styrene–butadiene (1:1)	16.8	71.5	105.1	1.21
S–EB–S	13.0	Ethylene–butylene	3.7	46.6	57.0	1.30

[a] Determined by gel permission chromatography (GPC) against PS homopolymer fractions. The eluent used is tetrahydrofuran (THF).

[b] PD is the polydispersity.

Therefore, the glass relaxation process of the PS-phase in block copolymers is less evident and as a result no available precise activation curves could be achieved for the glass process of the PS-phase in these block copolymers.

Accordingly, the present work aims to investigate the glass relaxation process of the PS-phase in different types of block copolymers and also to construct precise activation curves. In order to achieve this goal, four different candidates of block copolymers have been chosen which are shown in Table 1. In addition a styrene butadiene rubber (SBR), random copolymer is investigated to compare its glass relaxation process with those of the block copolymers.

2. Experimental section

2.1. Materials

Two S–B–S triblock copolymer samples having the trade names Kraton D1101 and Kraton D1102, respectively (named in this work as S–B–S 1101 and S–B–S 1102), and Kraton G1657 S–EB–S are kindly supplied from Shell Chemical Company, Eschborn, Germany. A triblock copolymer sample of S–SB–S having the trade name Styroflex BX6105 is kindly supplied from BASF AG, Germany. Table 1 gives a summary of the characterization of these samples. All of them are linear block copolymers. In addition, a SBR statistical copolymer has the trade name M1585. The number average molecular weight is 140 kg/mol. This sample was kindly supplied from Chemische Werke Hüls, Marl, Germany. The styrene content of the sample is 31.2%.

2.2. Sample preparation

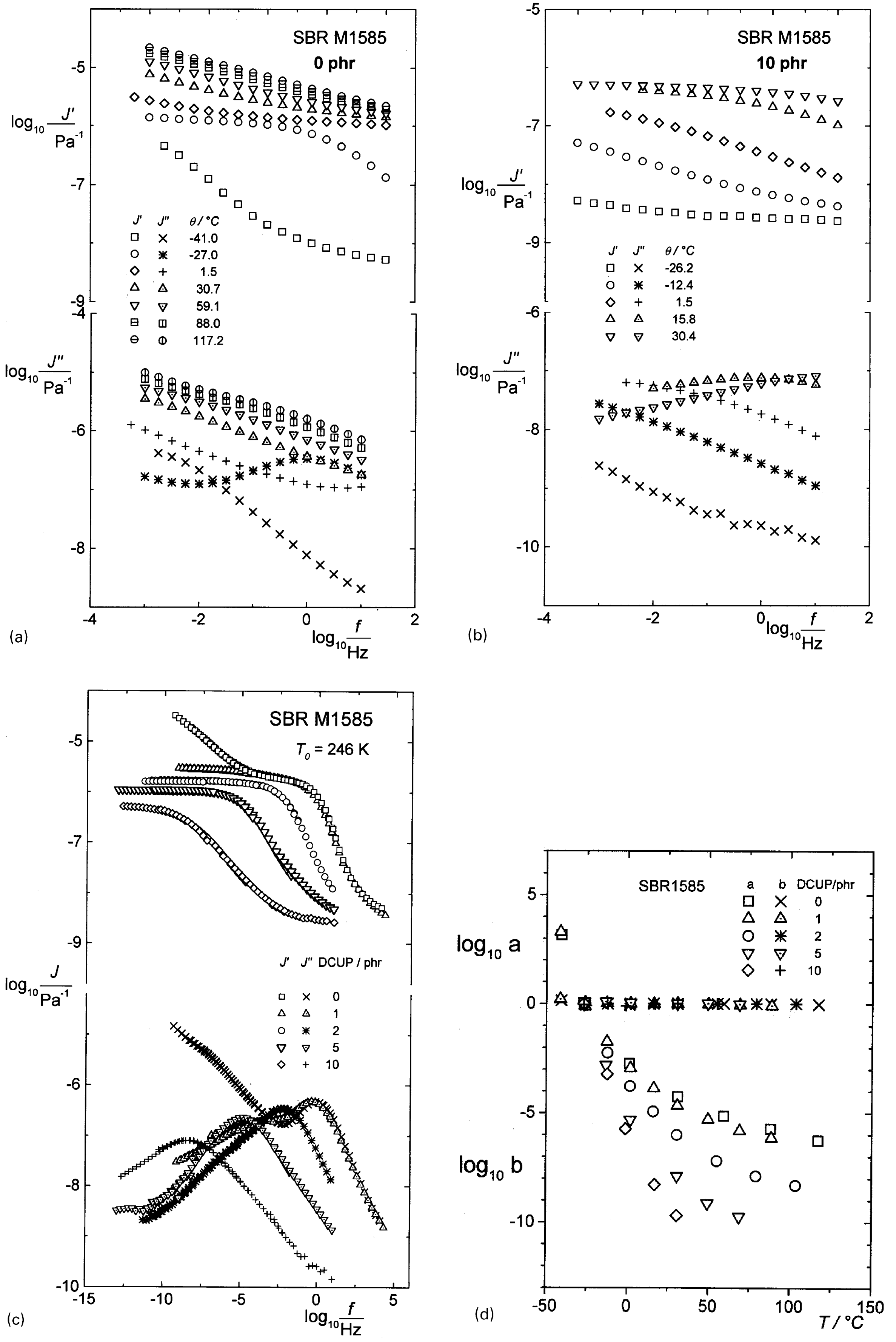
Block copolymers have been dissolved with dicumylperoxide (DCUP) in methylene chloride as a common solvent for both. The solvent was evaporated and the resultant cast films have been hot compressed at 150 °C for 1 h in order to get a plate with a thickness of ≈1.5 mm. This time period and temperature is enough to achieve complete crosslinking of DCUP [25]. The concentration of DCUP ranges from 0 to 10 phr (phr means 1 g of DCUP per 100 g of the polymer). The block copolymer samples have been cut in the form of disks of thickness 1.5 mm and diameter of 5 mm.

2.3. Methods

The dynamic mechanical measurements of the dynamic shear storage and loss compliance J' and J'', as functions of frequency at various temperatures for each of the block copolymer samples have been carried out using a dynamic mechanical thermal analyzer with double sandwich sample holder [26]. The instrument is self-designed at the Department of Physics, Ulm University, Ulm, Germany. The frequency window of the instrument is from 10^{-4} to 10 Hz, while its temperature range is from −130 to 230 °C. The accuracy in determination of the loss factor is $\pm 10^{-3}$ and that of the absolute values of the complex compliance is ±5%. The temperature control was satisfactory to be within 1 °C. More information about the instrument are found elsewhere [26].

For transmission electron microscopic measurements, samples were cut under liquid nitrogen at about −120 °C to obtain ultrathin films having thicknesses of the order of 50 nm. The samples then were subjected to the vapor of osmium tetraoxide solution (4% by weight) for 24 h. Transmission Electron Microscope type EM 301, from Philips, is used. The magnification factor applied is 100,000.

Fig. 1. (a) Isothermal measurements of the real and imaginary parts of the complex shear compliance of uncrosslinked SBR M1585 sample at different temperatures. (b) Isothermal measurements of the real and imaginary parts of the complex shear compliance of crosslinked SBR M1585 random copolymer (10 phr) at different temperatures. (c) Shear compliance master curves of SBR M1585 random copolymer samples crosslinked by DCUP. (d) Variation of both of the logarithmic values of the horizontal (a) and the vertical (b) shift factors against temperature for SBR M1585 random copolymer at different crosslinking concentrations.


SBR M1585
0 phr
$\log_{10}\frac{J'}{Pa^{-1}}$
$\log_{10}\frac{J''}{Pa^{-1}}$
J' J'' θ/°C
-41.0
-27.0
1.5
30.7
59.1
88.0
117.2
$\log_{10}\frac{f}{Hz}$
(a)
SBR M1585
10 phr
J' J'' θ/°C
-26.2
-12.4
1.5
15.8
30.4
(b)
SBR M1585
T_0 = 246 K
$\log_{10}\frac{J}{Pa^{-1}}$
J' J'' DCUP / phr
0
1
2
5
10
(c)
SBR1585
a b DCUP/phr
0
1
2
5
10
$\log_{10}$ a
$\log_{10}$ b
T / °C
(d)

3. Results and discussion

3.1. *Effect of crosslinking on SBR random copolymer*

Fig. 1(a) and (b) shows representative examples of the isothermal measurements of the real and imaginary parts of the complex shear compliance carried out at different frequencies and temperatures for uncrosslinked and heavily crosslinked (by 10 phr DCUP) SBR random copolymer, respectively. These figures show the presence of relaxation processes in the temperature and frequency ranges of measurements. In order to compare the relaxation spectra observed for samples with different DCUP content, it would be helpful to construct master curves. Accordingly, master curves are constructed using the well known time–temperature superposition principle [27], where a reference temperature is arbitrary chosen and then higher temperature and lower temperatures isotherms are shifted to lower and higher frequencies, respectively, in order to get the best superposition.

It is known that at sufficiently high temperatures (low frequencies), uncrosslinked polymer behaves like Newtonian liquids. At this temperature and frequency ranges which is called the viscous flow region, the shear compliance is related to the complex viscosity according to the following relation [27]:

$$J^* = \frac{1}{\mathrm{i}\omega\eta^*} \tag{1}$$

where J^* is the complex shear compliance and η^* is the complex viscosity. At the viscous flow region, the real part of the complex shear compliance of a given polymer (representing the elastic component of the system) can be neglected and the complex shear compliance can be expressed by its imaginary part only, then [27]

$$J'' = \frac{1}{\omega\eta(T)} \tag{2}$$

where J'' is the imaginary part of the complex shear compliance and η is the viscosity of the polymer at a given temperature (T). According to Eq. (2), a logarithmic plot of J'' over ω will be a straight line of slope of -1.

The compliance at the viscous flow in homopolymers and random copolymers is suppressed to a great extent much more than the glass relaxation when they are crosslinked chemically or by radiation [28–31]. A typical example showing the effect of crosslinking on the different relaxation processes in random copolymers or homopolymers is represented in Fig. 1(c). Fig. 1(c) represents the master curves for SBR random copolymer at different concentrations of crosslinking agent, DCUP. All of the master curves are reduced at 246 K. Therefore, it should be noticed here that the logarithmic values of -15 of the frequency scale is only due to the selection of the reference temperature, which is selected as the temperature of the isotherm that shows a relaxation process to get reliable master curves. Fig. 1(d) shows the horizontal (frequency) and the vertical (compliance) shift factors for various SBR samples with different DCUP contents. Of course, the uncertainty in the position of the maximum of J'' increases with increasing difference to the reference temperature. This uncertainty depends on the application of this diagram and therefore it is not possible to indicate error bars here. It is clear from Fig. 1(d) that the vertical shift is almost equal to zero indicating the reliability of the master curves shown in Fig. 1(c). Also, it is clear that the shape of the observed processes does not change by temperature. Furthermore, it is worth noting that the glass process and the shear band process in amorphous homopolymers and random copolymers have the same temperature dependence [28,29,31]. We can observe that, the imaginary part of the complex shear compliance of the uncrosslinked SBR sample is reduced by about 2.5 decades (at the terminal flow region) when the concentration of DCUP reaches 1 phr. On the other hand, neither the height nor the position of the glass relaxation process is affected due to this crosslinking concentration (1 phr). The glass relaxation process starts to shift to lower frequencies at crosslinking concentrations of 2 phr and more (Fig. 1(c)). Moreover, the relaxation strength of the glass relaxation process starts to reduce at crosslinking concentrations of 2 phr and more. Fig. 2 shows the frequency of the loss compliance peaks deduced from Fig. 1(c) and (d).

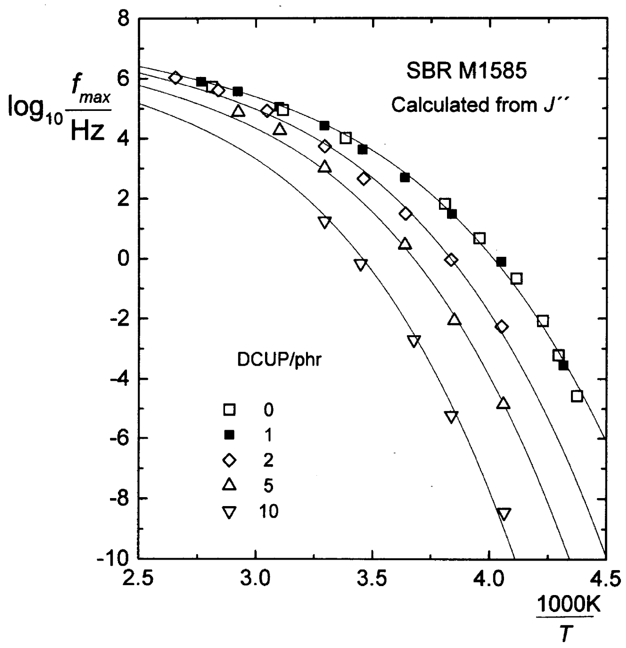


Fig. 2. Activation curves calculated from J'' for SBR M1585 series crosslinked by DCUP. Solid lines are the fitting curves according to Eq. (5).

3.2. *Effect of crosslinking on S–B–S block copolymers*

Master curves of both the real and imaginary parts of shear compliance carried out at different crosslinking densities, by means of DCUP, for S–B–S 1102 triblock

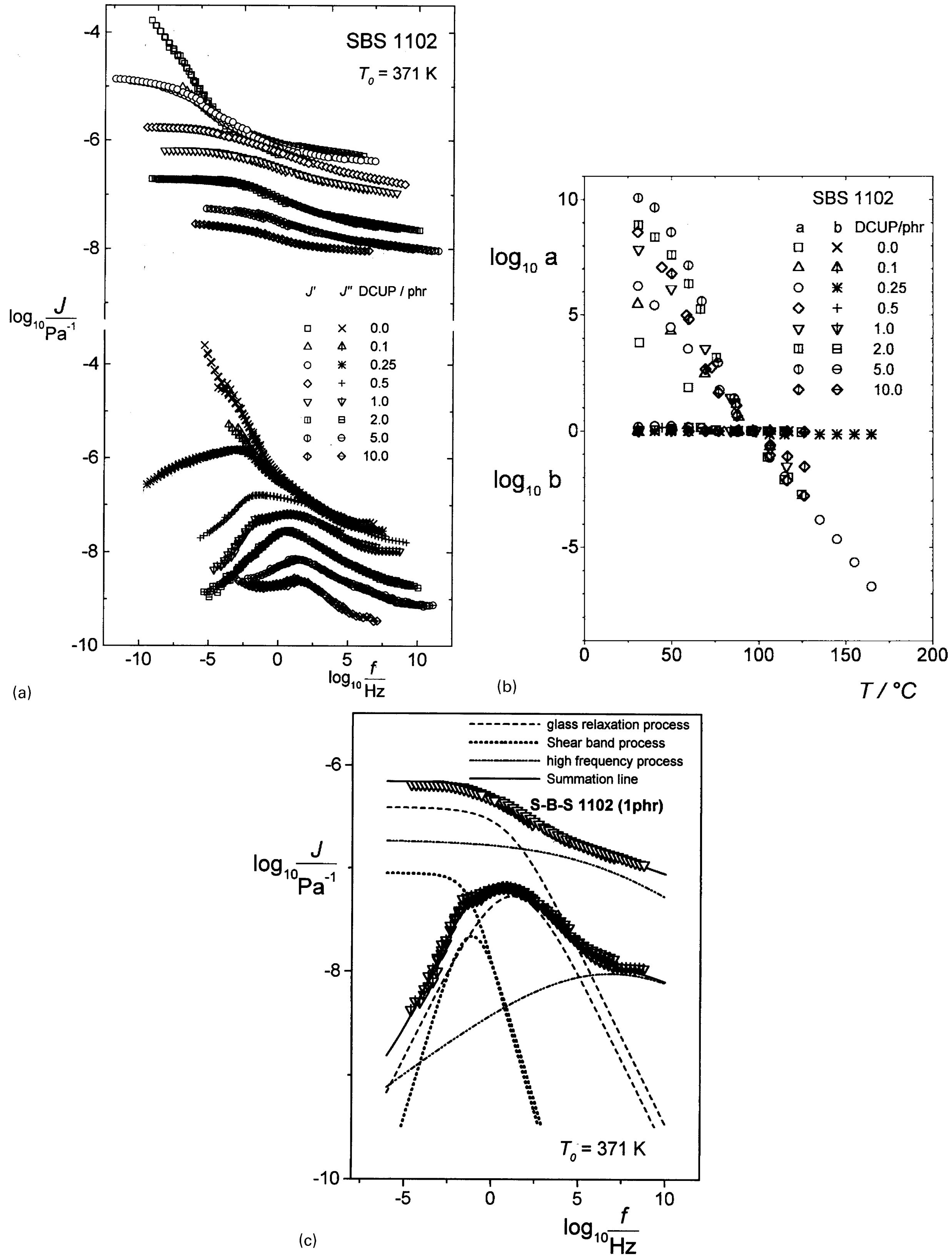


Fig. 3. (a) Shear compliance master curves of DCUP crosslinked S–B–S 1102 block copolymer samples. (b) Variation of both of the logarithmic values of the horizontal (a) and the vertical (b) shift factors against temperature for S–B–S 1102 triblock copolymer at different crosslinking concentrations. (c) An example of the analysis of master curves.

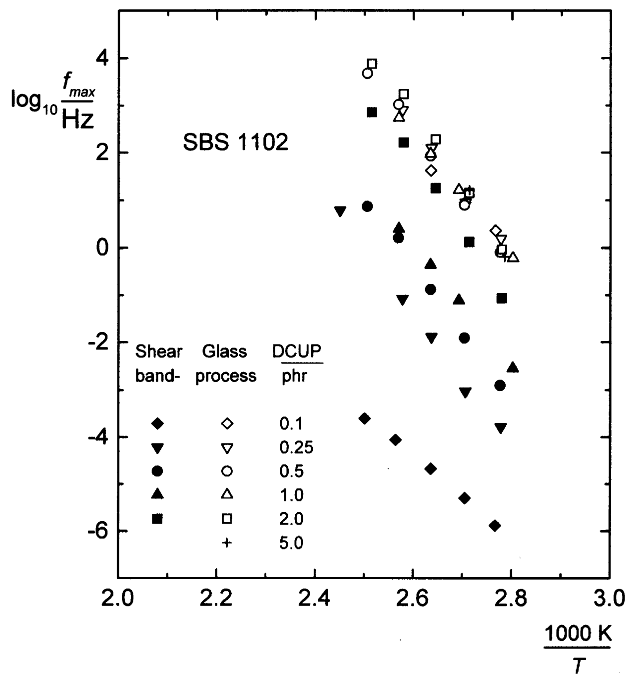


Fig. 4. Activation curves of the different processes observed in S–B–S 1102 triblock copolymer sample crosslinked by DCUP.

copolymer sample are revealed in Fig. 3(a). Fig. 3(b) shows the horizontal (frequency), (a) and the vertical, (b) shift factors used in constructing the master curves shown in Fig. 3(a). It is clear that the vertical shift is very small indicating the reliability of the master curves. It should be noticed here that we are dealing at this temperature range only with the relaxation of the PS-phase. In Fig. 3(a) no maximum in the loss compliance curves corresponding to the glass relaxation process of the PS-phase is observed in the uncrosslinked sample. Two relaxation processes are observed in the crosslinked samples (for instance, master curves of the samples at crosslinking concentration of 0.25, 0.5 and 1.0 phr). An example is given in Fig. 3(c), where a third relaxation process (small) is visible at the high frequency limit. Of course, all of these processes are present in the uncrosslinked sample; but they overlap with the viscous flow region. The relaxation process appearing at about 10 Hz is interpreted as the glass relaxation process of the PS-phase in S–B–S 1102. The second process at lower frequencies is attributed to the shear band process. The shear band process is observed before in homopolymers and random copolymers and thoroughly discussed in the frame of the meander model of Pechhold [28–31]. The shear band process shows a special behavior towards crosslinking, its relaxation strength is suppressed and its frequency of the maximum shifts to higher frequency values on increasing the concentration of crosslinking.

The frequency of the maximum, $f_{\max}$, of the glass relaxation process of the PS-phase in S–B–S 1102 is almost constant and independent of the concentration of DCUP (Figs. 3(a), 4, and 5(a)). All of the master curves in Fig. 3(a) are analyzed using Cole–Cole function to find the contribution of the different relaxation processes (example of analysis is given in Fig. 3(c)). Fig. 3(c) shows a representative example of the analysis of the master curves. The master curves are analyzed using Cole–Cole function for three processes. The analysis is based on the

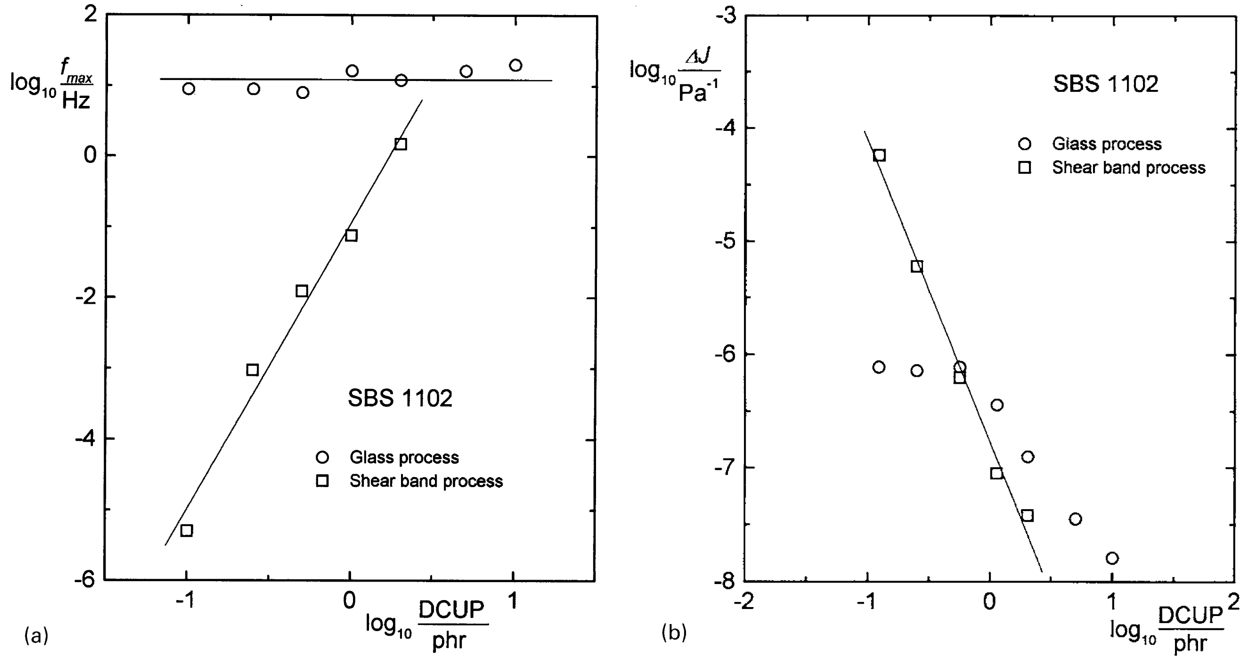


Fig. 5. (a) Variation of relaxation frequency (maximum of J'') of the glass process and the shear band process of S–B–S 1102 as a function of DCUP concentration. (b) Variation of relaxation strength of the glass process and the shear band process of S–B–S 1102 as a function of DCUP concentration.

previous results obtained by Pechhold et al. [29,31,32], as they assumed that polymeric chains are anisotropic on a molecular level. Pechhold assumed different shear motions of molecular layers and named it glass relaxation, shear band relaxation and flow relaxation. They calculated relaxation time and strength for each process separately [29,31,32] based on statistical thermodynamical treatment. They used the formula of Reuss for the calculation of the shear modulus of heterogeneous materials. Reuss assumed that the stress is uniform in the sample this means a series connection of domains. It is worth noting that from the literature it is known that Reuss method is more adequate for soft material than Voigt method. Evaluation of the shift factors and the values of $\log f_{\max}$ of all of the master curves in Fig. 3(a) leads to the activation curves corresponding to the glass relaxation process of the PS-phase and the shear band process (Fig. 4). The activation behavior of the glass process of the PS-phase is almost independent of the concentration of the crosslinking agent, DCUP (Fig. 4). On the other hand, the shear band process is systematically shifted to high frequency values as the concentration of DCUP increases (Figs. 4 and 5(a)) and its relaxation strength reduces systematically on increasing the concentration of DCUP (Fig. 5(b)). This is a typical behavior of the shear band process in homopolymers or random copolymers towards crosslinking [28–31]. It should be noticed here that the thermal history of the samples could influence the size and the anisotropy of the domains of the uncrosslinked sample. Therefore, all samples were prepared at 150 °C by the same procedure, where crosslinking does not change the structure of the domains. Accordingly, we believe that the thermal history has no influence on the conclusion. The glass process of the PS-phase has the same relaxation time for all samples irrespective with the crosslinking concentration.

The effect of crosslinking on S–B–S 1101 triblock copolymer sample having slightly higher molecular weight than S–B–S 1102 sample (Table 1) is shown in Fig. 6(a). It is clear that the crosslinked samples show better master curves than the uncrosslinked samples (Fig. 6(a)). In addition, the glass relaxation process of the PS-phase is well defined in the crosslinked samples (1, 2 phr) and it is easy to evaluate the value of $\log f_{\max}$ and the activation behavior of the glass relaxation process of the PS-phase in the crosslinked samples. Therefore, we can conclude that crosslinking has not affected the activation behavior of the glass relaxation process of the PS-phase at least up to 2 phr.

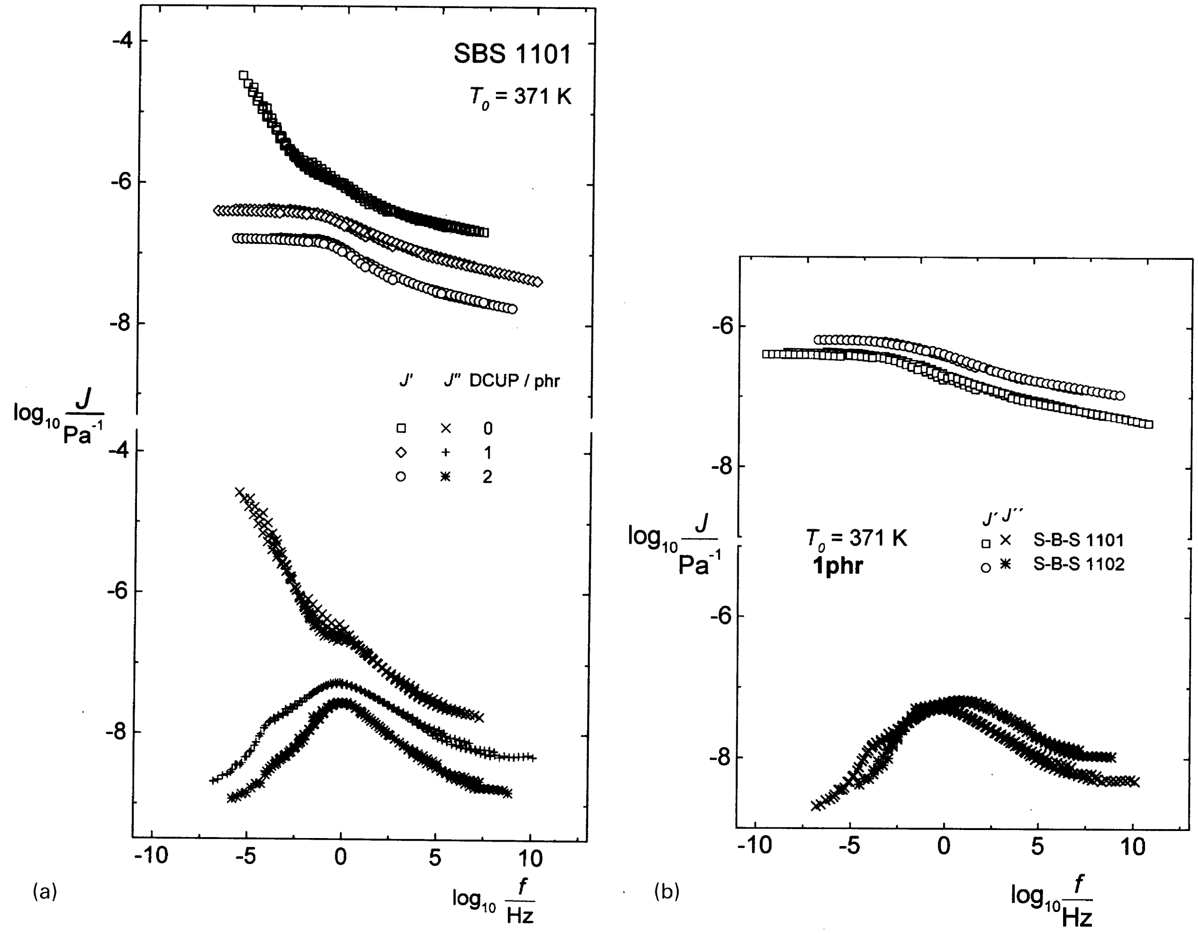


Fig. 6. (a) Shear compliance master curves of DCUP crosslinked S–B–S 1101 block copolymer samples. (b) Master curves obtained for S–B–S 1101 and S–B–S 1102 crosslinked to 1 phr.

Therefore, it is possible to compare the behavior of the glass relaxation process of the PS-phase in different S–B–S block copolymers. Fig. 6(b) shows master curves for S–B–S 1101 and S–B–S 1102 crosslinked to the same extent (1 phr). It is surprising to observe that, although, the difference in the PS block length in these block copolymers is not large (Table 1), there is a large difference in the value of log $f_{\max}$ about 1.2 decades (~factor 16) at 98 °C. To explain why the glass relaxation process of the PS-phase is faster in S–B–S 1102 than S–B–S 1101, the activation curves of the glass relaxation process should be quantitatively studied. This will be done later in Section 3.5.

3.3. The effect of crosslinking on S–SB–S and S–EB–S

The effect of crosslinking of DCUP on the relaxation behavior of S–SB–S triblock copolymer is shown in Fig. 7. The typical behavior of S–B–S triblock copolymers is also observed here. The low frequency terminal region is affected dramatically upon crosslinking. The value of log $f_{\max}$ of the glass relaxation process can be obtained for the crosslinked samples in a precise manner, and is almost independent of crosslinking up to 5 phr of DCUP (Figs. 7 and 8) and the shear band process is reduced systematically and shifted to higher frequencies as the concentration of DCUP increases.

An interesting example to show the potency of the method of crosslinking to detect the relaxation process of the PS-phase in different block copolymers even at small PS content, is styrene–ethylene butylene–styrene (S–EB–S), triblock copolymer having a PS content of 13%. The glass relaxation process of this block copolymer cannot be detected at all in the uncrosslinked sample (Fig. 9). Crosslinking of this sample leads to a well defined glass relaxation process for the PS-phase (Fig. 9). The activation curve of the glass relaxation process of the PS-phase in S–EB–S is presented in Fig. 10.

3.4. Calculation of the glass temperature T_g

Stoll et al. [32,33] suggested an empirical formula through which the glass temperature (determined by conventional DSC cooling or heating curves) can be related to the corresponding relaxation time for enthalpy relaxation

$$q\tau_{\mathrm{veq}} = 15\ \mathrm{K} \tag{3}$$

where q is the calorimetric cooling rate and τ_{veq} is the enthalpy relaxation time at T_g. Using Eq. (3) and the well known relation between relaxation time and maximum frequency in dynamic experiments [32]:

$$2\pi f_v \tau_{\mathrm{veq}} = 1 \tag{4}$$

a relaxation frequency (frequency of maximum for the imaginary part in modulated DSC experiments) may be predicted at the glass temperature (T_g) which has been

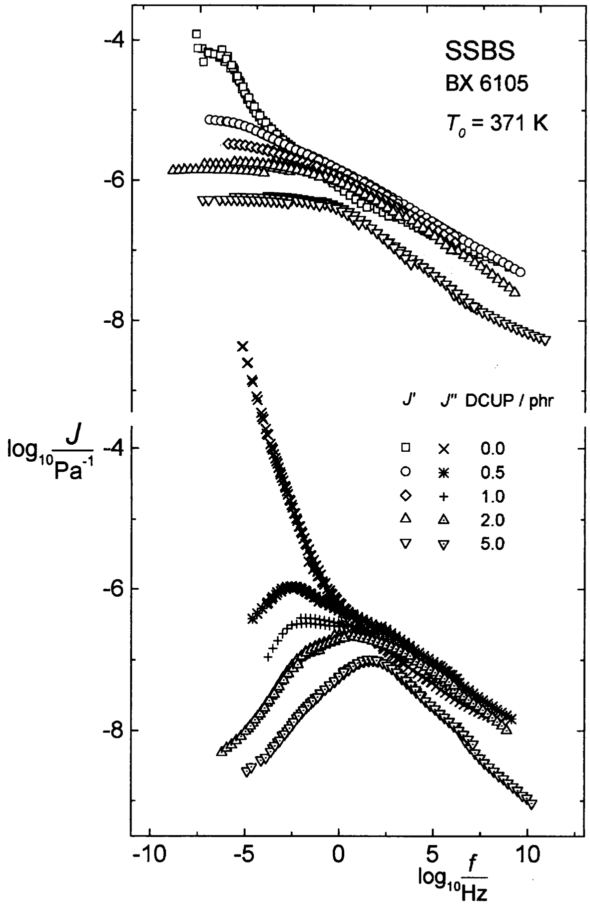


Fig. 7. Shear compliance master curves of DCUP crosslinked S–SB–S block copolymer samples.

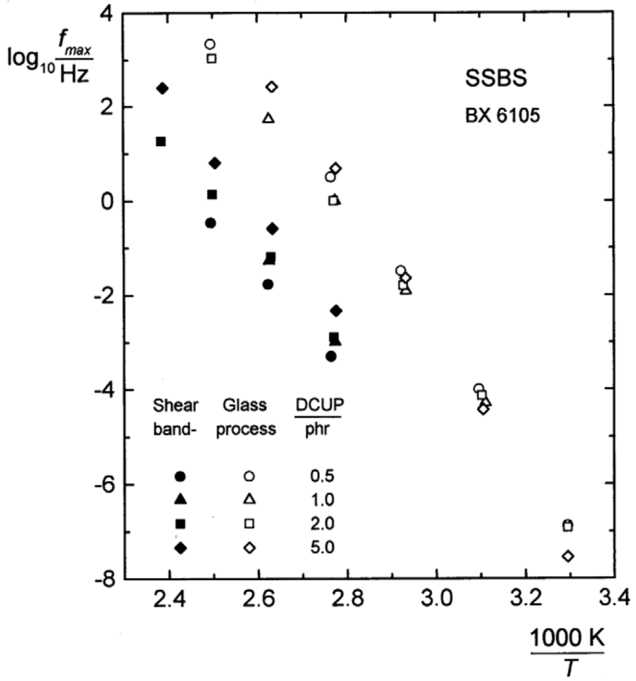


Fig. 8. Activation curves of the different processes observed in S–SB–S triblock copolymer sample crosslinked by DCUP.

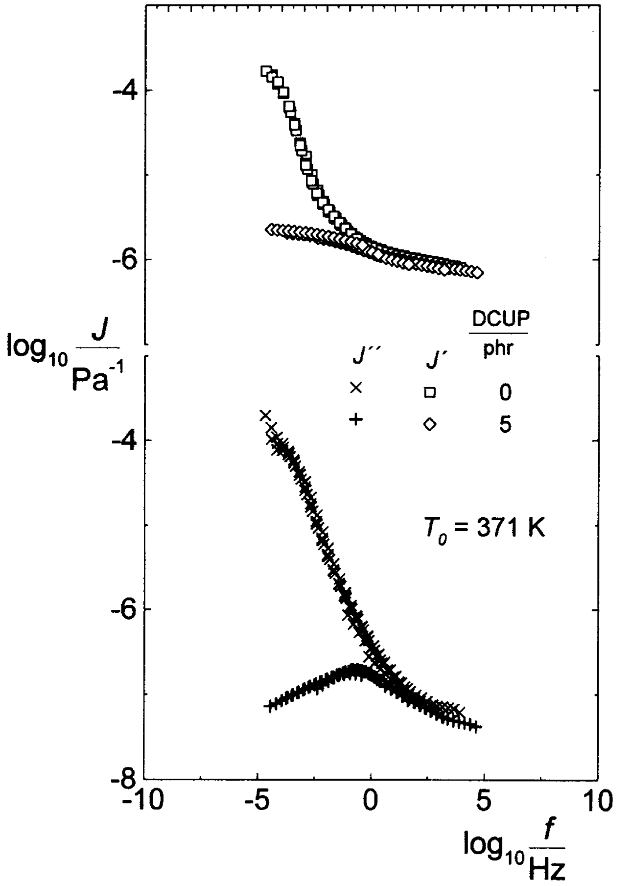


Fig. 9. Shear compliance master curves of DCUP crosslinked S–EB–S block copolymer samples.

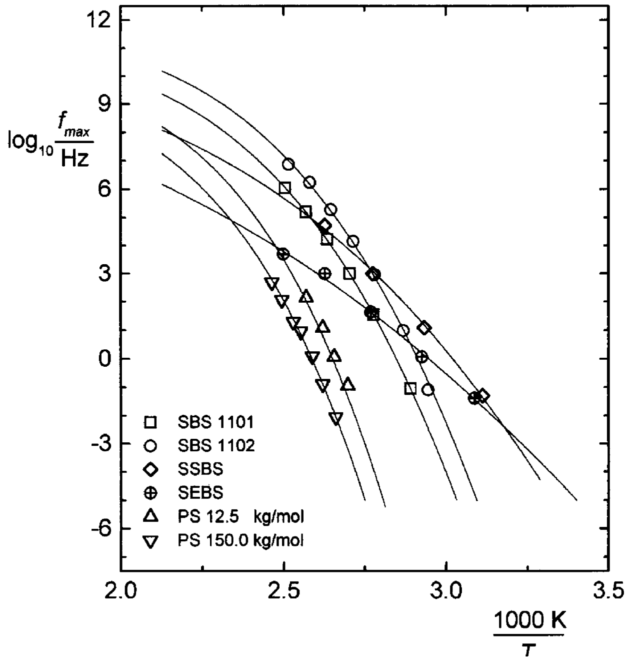


Fig. 10. Comparison between the activation curves of the PS-phase in different block copolymers with those of PS homopolymers. Solid lines are the fitting curves according to Eq. (3).

Table 2
Comparison between the values of T_g obtained from DSC measurements and those delivered from the activation curves in Fig. 10

Material	M_n of the PS block (kg/mol)	T_g (°C) from DSC at cooling rate 10 K/min	T_g (°C) from the activation curves
S–B–S 1101	14.1	–	68.6
S–B–S 1102	10.3	–	61.4
S–SB–S	16.8	–	40.0
S–EB–S	3.7	–	38.8
PS (homopolymer)[a]	4.0	78.0[b]	76.5[b]
PS (homopolymer)[a]	12.5	94.1	92.1
PS (homopolymer)[a]	150.0	101.5	103.4

[a] PS fractions having polydispersity equals to 1.04.
[b] Taken from Ref. [33].

evaluated from conventional DSC measurements. The relation between conventional DSC, modulated DSC, dielectric and dynamic mechanical measurements has been investigated for several polymeric and low molecular weight glasses by Schick et al. [34,35]. Eqs. (3) and (4) have also been checked for polymethylmethacrylate (PMMA) [36]. Stoll et al. [33] and Weyer et al. [35] reported that the dielectric and enthalpy relaxation times are nearly equal and that the mechanical relaxation times of shear modulus, respectively, shear compliance differ from them by a constant factor [28,32]: i.e. the activation curves of the mechanical and dielectric results as well as modulated DSC (TMDSC) are parallel to each other. The activation curves for different PS homopolymer fractions obtained from the dielectric loss are found to be about one decade higher (on the frequency axis) than those obtained from DSC [33] or TMDSC [35]. The activation curves from G'' usually is one decade higher than the dielectric [28,30,31]. That one from compliance (J'') is lower than G'' by 3–5 decades. In other words, for each activation curve obtained from the compliance we can estimate the position of the activation curve belonging to the enthalpy relaxation. Accordingly, the activation curves obtained from compliance for all samples have been shifted three decades to higher frequency values, in order to represent the curves of the enthalpy relaxation. Then, T_g of the PS-phase is estimated by using Eq. (4) with a cooling rate of 10 K/min, which is typical for DSC experiments. These data are listed in Table 2.

3.5. Relation of T_g to the domain size

It is well established that the glass relaxation process is cooperative in nature [37–39] and there is a cooperative rearranging region, CRR, which is responsible for dynamics of the glass process [37–39]. Glass transitions in finite systems confined to nanopores [40–42] and thin films [43–45] have received a great interest and are investigated currently, because such systems can be regarded as model systems for studying the length scale of glass transitions. In these systems deviation from the properties of the bulk can

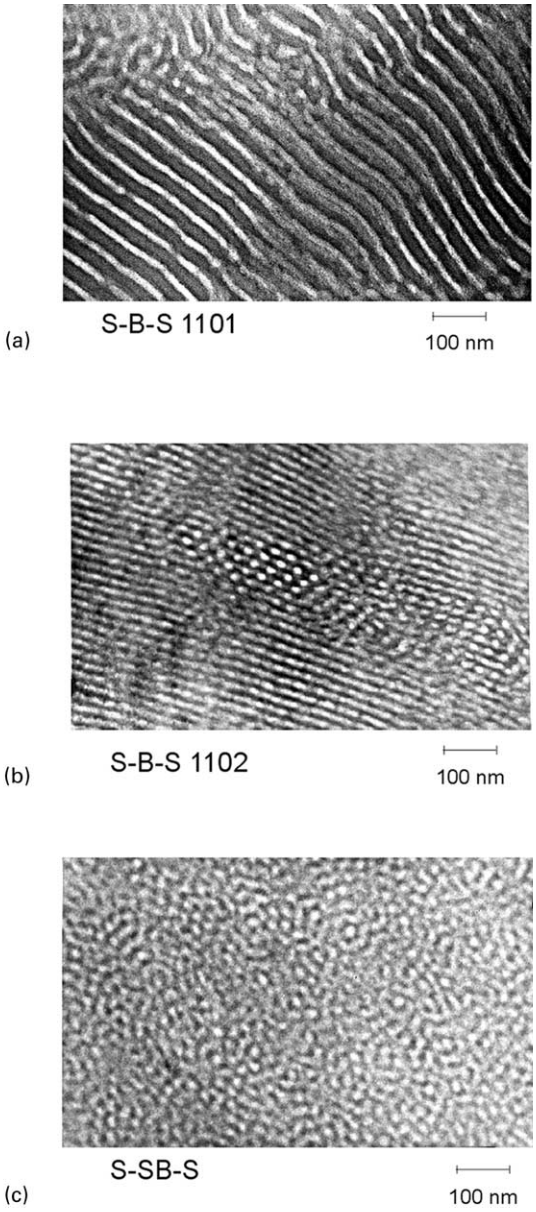


Fig. 11. Transmission electron microscopy (TEM) photos of (a) S–B–S 1101 (b) S–B–S 1102 and (c) S–SB–S.

be expected, if the system size is comparable to the characteristic length scale of the CRR. Several authors have reported that, ultrathin films [43–45] as well as systems confined to nanopores [40–42] show a lower T_g for smaller thickness [43–45] or reduction of the size of nanopores [40,42].

Block copolymers having cylindrical or lamellar morphologies would be considered as finite confined systems [46,47]: nanopores in case of cylindrical morphology and thin films in case of lamellar microdomains. Morphologically speaking, S–B–S 1102 is composed of PS cylinders imbedded in PB matrix (Fig. 11), i.e. the PS microdomains are confined by the PB matrix. S–B–S 1101 exhibits a mixture of PS cylinders and lamellas (more lamellas) embedded in PB matrix. This confinement applied on the PS-phase would be expected to decrease the T_g values of the PS-phase in S–B–S block copolymer samples as compared to those of the PS in bulk (Table 2). The size of the cooperative rearranging regions has been calculated for several systems by means of DSC and TMDSC [37,38,40]. Unfortunately, it is difficult to use a DSC scan for S–B–S 1101 and S–B–S 1102 block copolymers for this calculation, because the glass transition of the PS is smeared out and can hardly be detected. On the other hand, it is possible to calculate the size L of the structure unit which is responsible for the glass transition from the fit of the activation curves by means of meander model equation (given by Pechhold) [26,28–33,36] which reads:

$$f_{\max} = \frac{f_0}{\pi} \mathrm{e}^{\frac{-Q_\gamma}{kT}} \left[1 - \left(1 - \mathrm{e}^{\frac{-\varepsilon_s}{kT}} \right)^{\frac{L}{d}} \right]^{3\left(\frac{L}{d}\right)^2 \frac{d}{s}} \tag{5}$$

where L is the size of the cooperative reorienting structural unit, f_0 is the local vibrational frequency, d is the interchain distance (0.87 nm for PS) [31], s is the segment length (length of two styrene monomers which equals 0.44 nm) [31], ε_s is the dislocation energy and Q_γ is the local activation energy. More details about the meander model are found elsewhere [28–32,36]. Fitting of the activation curves of the glass relaxation process [28–32,36] of the PS-phase of S–B–S 1101 and S–B–S 1102 (Fig. 10) by means of Eq. (5) leads to the same value of L (14 nm). The value of L is almost the same as the average domain size of the PS-phase in both samples (14.5 nm in both S–B–S block copolymers) as shown in Fig. 11. In the meander model [28–32,36], the neighborhood of a superstructural unit influences the mean energy ε_s of a quasi-dislocation wall. This is because these walls are extended over more than one superstructural unit. Consequently, it should be expected that ε_s and the T_g of the PS-phase in S–B–S 1101 and S–B–S 1102 are lower than those of homopolymers of PS (in bulk) of the same molecular weight. This agrees with the experimental data in Table 2 and Fig. 10. It is observed in Figs. 6(b) and 10 that, the frequency of the maximum of the glass relaxation process of the PS-phase of S–B–S 1102 is higher than that of S–B–S 1101 by 1.2 decades of frequency. Also, the T_g value of the PS-phase is about 7 K lower in S–B–S 1102. This difference can be attributed to the fact that the molecular weight of the PS block in S–B–S 1102 is smaller than that of S–B–S 1101. Therefore, the number of end groups within the same superstrucrural unit ($L = 14$ nm) is greater in S–B–S 1102, which can cause a decrease of the values of ε_s (Table 3) a consequently reduction in T_g and increase in the frequency of the maximum will take place.

The T_g of the PS-phase in S–SB–S is lower than that of PS fractions having a similar molecular weight. On the other hand, the observed T_g of the PS-phase is lower than those of the PS-phases in S–B–S 1101 and S–B–S 1102, although

Table 3
Fitting results of the activation curves for the block copolymer samples and a PS fraction (Fig. 10) by means of Eq. (3)

Material	M_n of the PS block (kg/mol)	Size of PS microdomains from TEM (nm)	L (nm)	ε_s (kJ/mol)	Q_γ (kJ/mol)
S–B–S 1101	14.1	14.5	14	4.102	23.4
S–B–S 1102	10.3	14.5	14	4.046	16.2
S–SB–S BX 6105	16.8	17.5	9.2	3.250	35.0
S–EB–S 1657	3.7	–	6.3	2.780	49.2
PS (fraction)	12.5	–	16	4.695	32.5
PS (fraction)	150.0	–	16	4.758	40.65

the molecular weight of the PS block length is higher in S–SB–S (Table 1). This reduction of T_g of the PS-phase in S–SB–S cannot only be attributed to the confinement applied on the PS microdomains, while the domain size of the PS-phase in S–B–S samples is smaller than this in S–SB–S as observed (Table 3 and Fig. 11).

On the other hand, the fuzzy borders of the PS microdomains in S–SB–S (Fig. 11) indicate an extended interface typical for a system close to the order–disorder transition (ODT) [21,22]. The repulsive interaction between the PS and the SB phase is greatly diminished compared to a PS/PB system [21,22]. The T_g of the PS-phase presumably does not depend only on the molecular weight of the PS block or the applied confinement (domain size); but also on the amount of SB segments incorporated in the PS domains. This could reduce the mean energy of formation of a quasi-dislocation wall (ε_s) as tabulated in Table 3 which results in a reduction in T_g of the PS-phase (Table 2).

It is worth noting here that the value of the PS domain size, 17.5 nm (Fig. 11), in S–SB–S is almost twice the value of L (Table 3). This result means that the domains of PS-phase of S–SB–S (17.5 nm) are formed from association of two structural units ($\approx$ 9 nm).

On the other hand, the T_g of the PS-phase in S–EB–S has the lowest value (38.8 °C). This is expected, from the influence of molecular weight and from the confinement (the value of L calculated from Eq. (5) is 6.3 nm). Unfortunately, it was difficult to obtain TEM photos for S–EB–S sample; but it is expected that it should exhibit a spherical microdomain morphology and the PS microdomains should have a small size according to the small PS block length and the composition (13% PS).

4. Conclusions

The effect of crosslinking (by means of DCUP) on the relaxation behavior of block copolymers at high temperatures is investigated and compared to that of random copolymers. For this reason, four different candidates of block copolymers are chosen, namely, two S–B–S, S–SB–S and S–EB–S triblock copolymers. The results show that:

1. Crosslinking of block copolymers suppress both the viscous flow as well as the shear band process of them (similar effect is observed in SBR random copolymer). Consequently, it is possible to detect the glass relaxation process of the PS-phase precisely even at small PS content (13% in case of S–EB–S).
2. Crosslinking reduces the relaxation strength of the glass relaxation process (above certain concentration of DCUP as seen in Figs. 3(a), 5(b) and 7). On the other hand, the relaxation frequency of the maximum and/or the activation behavior of the glass relaxation process of the PS-phase are almost independent of the crosslinking concentration.
3. The activation curves of the PS-phase in block copolymers lie always at higher frequency values than those of PS homopolymer fractions of the same molecular weight.
4. It is possible from the activation curves to get the T_g values of the PS-phase in block copolymers. The determined T_g's in block copolymers are generally lower than the T_g values in PS homopolymer fractions of similar molecular weight.
5. This lowering of T_g of the PS-phase in block copolymers is attributed to the confinement applied on the PS in block copolymers by the matrix.
6. Block copolymers of the same type and the same L values exhibit a markedly difference in T_g values and activation behavior when the PS block lengths are slightly different (for instance, S–B–S 1101 and S–B–S 1102).
7. The interfacial interaction and the miscible fraction at the domain boundaries lower the values of ε_s, so that T_g decreases additionally (for instance, in case of S–SB–S).
8. The values of L determined from Eq. (5) can be correlated to the size of microdomains observed by TEM. The microdomains are consisted of association of superstructural units (for instance, two units in case of S–SB–S and one unit in case of S–B–S block copolymers).

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