

RELAXATION IN DOMAINS: STRUCTURE AND SEGMENTAL DYNAMICS OF LC/I DIBLOCK COPOLYMERS

B. Stühn*, S. Joukov, R. Staneva, R. Ivanova, W. Gronski** and S. Geppert**

Ilmenau Technical University, Techn. Physik II, D-98693 Ilmenau, Germany

***Universität Freiburg, Inst. f. Makromolekulare Chemie, D-79104 Freiburg, Germany*

Abstract A series of block copolymers consisting of an isotropic (polystyrene) block and a side-chain liquid crystalline block (LC) have been studied using small-angle X-ray scattering and dielectric spectroscopy. The triblock copolymer (PS-LC-PS) displays an order-to-order transition (OOT) together with the isotropic/nematic transition of the LC phase. The series of diblock copolymers show no clear OOT but the phase diagram differs from that of non-LC block copolymers. The segmental dynamics as measured with dielectric spectroscopy is dominated by the α and δ relaxation of the LC block. Both display a WLF like temperature dependence. The relaxation times are influenced by the constraints of the nanoscale domains. They are decreased for the LC confined in the domain as compared to the LC in the continuous matrix.

Keywords Dielectric relaxation, Segmental dynamics, Confinement, LC/I block copolymers

INTRODUCTION

The segmental dynamics of polymers comprises wide scales in length and time as it is composed of a large number of modes. A particularly interesting feature is the glass transition which is seen in a strong slowing down of relaxations when approaching a characteristic temperature. The process relevant to this phenomenon is called the α -process. Recent experiments on glass formers confined in nano pores and investigations of ultrathin films of polymers have lead to exciting and in some respects contradicting results. It was found that the α -process is strongly influenced by the confinement and in particular by its size. Several papers reported a decrease of the α relaxation time^[1], but also the opposite behaviour was observed^[2]. The reason for this apparent contradiction is seen in the contribution of specific interaction between the glass former and the confining walls to its relaxational dynamics. The existence of a characteristic length related to the glass transition is of course put forward on the basis of these results.

In the present study we investigate the segmental dynamics of block copolymers consisting of an isotropic (polystyrene) and a liquid crystalline block. With these systems we are able to create domains with length scales defined by the molecular size of the block. The domain structure is the result of the microphase separation transition, which for sufficiently low molecular weight may be observed by variation of temperature. Domains may be varied in size by the molecular weight of the block copolymer and their form is controlled by the volume fraction of the blocks. It is thus possible to study the dynamics of the polymers confined in nano domains using various methods. In this contribution we focus on dielectric spectroscopy which has the advantage of covering a wide range of frequencies and temperatures. The glass transition of the system as well as faster relaxation processes may be determined and we investigate the dependence of these relaxations on the confinement provided by the domains.

* Corresponding author: B. Stühn; E-mail: bernd.stuehn@physik.tu-ilmenau.de

Invited lecture presented at the International Symposium on Polymer Physics, 2002, Qingdao, China

Received August 31, 2002

An important prerequisite for such a study is the detailed knowledge of the domain structure. We therefore use small angle X-ray scattering (SAXS) to determine the domain form and size as well as its change with temperature.

EXPERIMENTAL

The samples used in this study are diblock copolymers of polystyrene (PS) and a liquid crystalline (LC) block. This block consists of cyanobiphenyl mesogens coupled to a poly(1,2-butadiene) main chain through valeric acid spacers. Details of the synthesis of these polymers are given in Ref. [3]. The series of diblock copolymers is discussed in detail in Ref. [4]. One triblock copolymer is also included in this series. Its composition is PS-LC-PS.

Data for the molecular weight and wt% were calculated stoichiometrically on the basis of the measured composition of the precursor polymers and 100% conversion. Data for the vol% were calculated using the density of the PS block (1.04 g/cm^3) and of the LC block (1.25 g/cm^3).

Detailed properties of this polymer are given in Ref. [5]. The molecular weight distribution was determined with size exclusion chromatography using the precursor polymers. Conversion of the reaction for the addition of the mesogen was controlled with FTIR and $^1\text{H-NMR}$. Nearly 100% conversion was found. The molecular weight distribution of the anionically synthesized precursor polymers is very narrow with $M_w/M_n < 1.1$ and it does not change during the conversion reactions.

The naming of the polymers is PSLC xy with x giving the PS volume fraction and y the LC volume fraction. Table 1 provides an overview of the samples used and compiles their properties. The LC homopolymer is denoted as PSLC0/100.

Table 1. Composition and molecular weight of the polymers used

	MW	PS (wt%)	LC (wt%)	PS (vol%)	LC (vol%)
PSLC 0/100		0	100	0	100
PSLC 7/93	77.000	5.7	94.3	6.8	93.2
PSLC 14/86	53.700	11.5	88.5	13.5	86.5
PSLC 19/81	104300	16	84	19	81
PSLC 30/70	98700	26	74	30	70
PSLC 39/61	55.000	34.5	65.5	38.8	61.2
PSLC 59/41	38.300	54.5	45.6	58.9	41.1
PSLC 77/23	62.800	73.4	26.6	76.8	23.2
PSLC 85/15	86.500	82.5	17.5	85	15
PSLC 97/3	125.000	96.9	3.1	97.4	2.6
Triblock	84000	12	88	13	87

The SAXS experiments were carried out with a Kratky compact small angle system equipped with a scintillation counter. $\text{CuK}\alpha$ radiation from a sealed X-ray tube was filtered with a Ni foil. The sample was kept in vacuum during the measurement. Temperature was controlled with a precision better than $\pm 0.1^\circ$. The samples were solid bars with 2 mm thickness. The SAXS profiles were measured in heating and cooling runs in steps of 10° or 20° . Following each temperature change the sample was allowed to equilibrate for 30 min. Standard data treatment involves subtraction of experimental background, desmearing and normalization to the incoming flux using Paar's moving slit device.

For the dielectric spectroscopy we employed two experimental set-ups. In the frequency range 10^{-2} Hz – 10^6 Hz we use a Solartron Schlumberger 1260 frequency response analyser. For higher frequency (10^6 Hz – 10^8 Hz) a RF HP4191A impedance analyser was used. The samples are thin films of 0.05–0.1 mm kept between gold plated electrodes. Sample temperature is controlled by a nitrogen gas jet with a stability better than $\pm 0.05^\circ$. Also the dielectric data were collected at fixed temperature in heating and cooling cycles with temperature steps of 2 – 5° . After each temperature change the sample was allowed to equilibrate.

RESULTS AND DISCUSSION

The thermal properties of our samples are described by two glass transition temperatures obtained in DSC measurements. They relate to the PS ($T_g^{\text{PS}} \approx 106^\circ\text{C}$) and LC ($T_g^{\text{LC}} \approx 34^\circ\text{C}$) domains, respectively. The existence of two T_g 's is already evidence for the strong separation between both blocks on the nanometer scale. Above the T_g^{PS} for the block copolymers we find an endothermal peak in the DSC diagram as a result of the nematic to isotropic phase transition at T_{ni} . This transition is found between 120°C for PSLC0/100 and 122°C for the triblock copolymer.

With increasing volume fraction of PS the block copolymer domain structure is expected to change from that of a nematic matrix containing PS spheres to the opposite situation of spherical domains containing the mesogens embedded in a PS matrix. This expectation is based on the phase diagram of block copolymers consisting of two amorphous blocks like PS and polyisoprene. It does not take into account the energy involved in the disturbance of the nematic field by the presence of either inclusions on the nanometer scale or domain walls. Clear evidence for the impact of this energy on the domain form was found for the triblock copolymer. Details may be found in Ref. [5]. The SAXS profiles below and above the nematic-isotropic phase transition differ qualitatively and are described on the basis of the two dimensional hexagonal lattice with cylindrical domains for the low temperature and a bcc lattice with spherical domains for the high temperature. The total scattering intensity at each scattering vector q is given by three contributions^[6]:

$$I(q) = I_{\text{Bragg}}(q) + I_{\text{diff}}(q) + I_{\kappa} \quad (1)$$

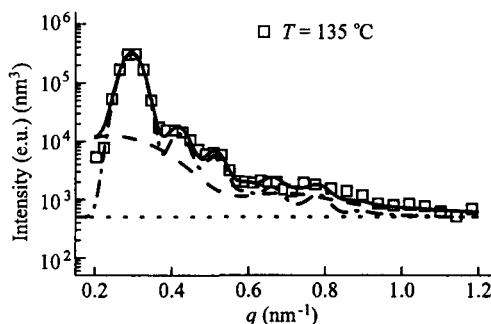


Fig. 1 SAXS profile of the triblock copolymer in its isotropic state
Broken lines are the components of the fitted curve according to Eq. (1)

Bragg scattering allows the determination of lattice constants and therefore of the distances between domains. The domain size, however, is only given by the intensity of the reflections. In view of the small number of reflections this quantity would carry a large error. The diffuse scattering, however, is also modulated in q with the form factor of the domains and serves as an additional source of information. In Fig. 1 we show an example of a measurement on the triblock copolymer in the isotropic state. Several maxima are observed which may be indexed on the basis of a bcc lattice. The total intensity for each scattering vector q is calculated by Eq. (1) using the form factor of a sphere for the domains. In a least squares procedure we then fit Eq. (1) to the data and obtain the full curve as a result. It obviously describes the data very well and we are thus able to derive the sphere radius and the domain distance for each temperature. In the isotropic state the system may therefore be envisaged as a continuous matrix of LC polymer with embedded spherical domains of PS. The radius of the spheres is 7.5 nm and they are arranged on a bcc lattice with a lattice constant of 30 nm. Lowering temperature drives the system close to the transition from the isotropic to the nematic state. The spherical domains severely distort the nematic field. As a consequence at the phase transition they are deformed along the 111 axis to form cylindrical domains on a hexagonal lattice. In the SAXS experiment this shows as an abrupt change of the scattering pattern at the phase transition. The cylindrically formed domains obviously provide a smaller disturbance to the nematic field.

The system therefore displays the combination of an order-order-transition in its domain structure and the liquid crystalline phase transition within the domains.

We now turn to the domain structure of the diblock copolymers. The SAXS experiments again show a pattern of distinct peaks indicating a microphase separated structure. From the peak positions we can determine the lattice type and again use Eq. (1) to fit the appropriate models to the data. However, we do not find a strong variation of domain structure with temperature at T_{ni} . Only one sample, PSLC7/93, displays a variation of the cylinder distance of more than 10% at T_{ni} but is well described by the hcp model in the full temperature range. We therefore summarize the domain structure in Fig. 2 providing the type of domain form and structure for each block copolymer.

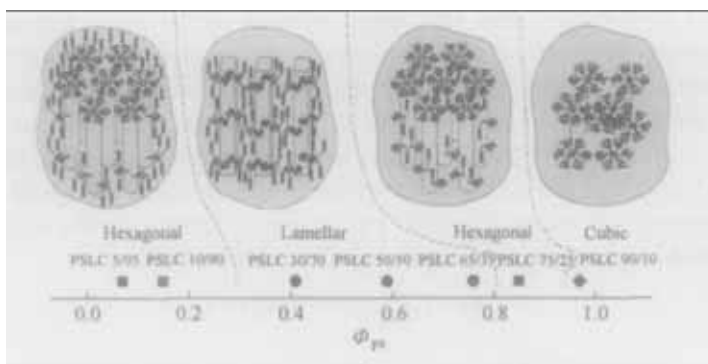


Fig. 2 Schematic representation of the domain structure of the PSLC diblock copolymers. Small cylinders depict the mesogens of the LC block.

Compared to the phase diagram of diblock copolymers with amorphous blocks the lamellar regime in the phase diagram is obviously enlarged. For strongly asymmetric composition we find the hexagonal structure to be preferred over the bcc structure. Only one sample (PSLC9010 denoting PSLC97/3) displays a scattering pattern compatible with a bcc structure. However, the lattice is not well ordered. The series of diblock copolymers reflects the same interaction between orientational order of the mesogens and domain order as was seen in the OOT of the triblock copolymer in its phase diagram. However, we do not find an OOT in these systems at T_{ni} .

The dielectric relaxation behaviour of the diblock copolymers is rather complex as it consists of several relaxation regimes. We have therefore employed a combination of two experimental techniques in order to cover a wide frequency range at each temperature. Moreover we study the relaxations in a temperature range between -80°C and 150°C . In this contribution we focus on the collective relaxations which are called the α - and δ -process. They are observed in a rather wide temperature range which includes T_{ni} . As an example we show the data of one block copolymer in Fig. 3. The figure displays the loss part of the dielectric function $\varepsilon''(f)$.

Besides the collective relaxations we observe an additional strong relaxation regime at low frequency which is attributed to the Maxwell-Wagner (MW) effect. It is found for those samples that consist of the LC phase in domains. The strong increase of the dielectric loss at low frequency is caused by the contribution of dc conductivity. In order to determine the dominant relaxation time for each process at a given temperature we fit the data with the phenomenological Havriliak/Negami function taking into account the contribution of the MW relaxation as an additional term:

$$\varepsilon^*(\omega) - \varepsilon_{\infty} = \sum_k \frac{\Delta\varepsilon_k}{(1 + (i\omega\tau_k)^{\alpha_k})^{\gamma_k}} - \frac{i\sigma}{\varepsilon_0\omega^s} \quad (2)$$

As a result of this evaluation we arrive at the temperature variation of the relaxation times for the α - and δ -process. Both processes display a WLF like dependence on temperature. They both become increasingly slow when approaching the glass transition temperature. There is no clear discontinuity at T_{ni} . However, in the isotropic state both processes are so close on the frequency scale, that it is difficult to separate them into different

relaxation.

Concerning the microscopic dynamics underlying the δ and α processes in side chain LC polymers there appears to be no unique picture at present. The α process is commonly attributed to the segmental dynamics of the whole polymer chain and is the signature of the glass transition. Various models have been proposed for the δ process. The most extensively discussed model for the low frequency δ relaxation assumes that it is caused by cooperative rotation of the side groups^[7]. The large relaxation strength and its dependence on the longitudinal component of the side groups' dipole moment confirm this model.

Of particular importance for this investigation is the variation of relaxation times with the change of the confinement. We therefore compare the measurements on all samples at the same temperature in Fig. 4. The relaxation times are normalized to the maximum values of $\tau_\alpha = 0.18$ s and $\tau_\beta = 2.51$ s.

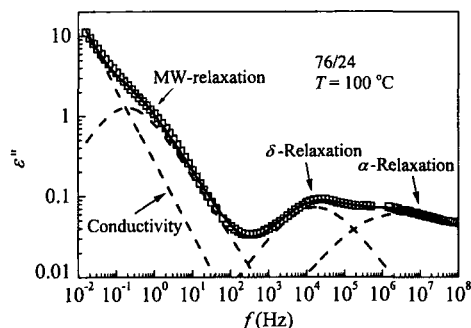


Fig. 3 Loss part of the dielectric function for sample 76/24

The curve is made up of the contributions of several relaxations.

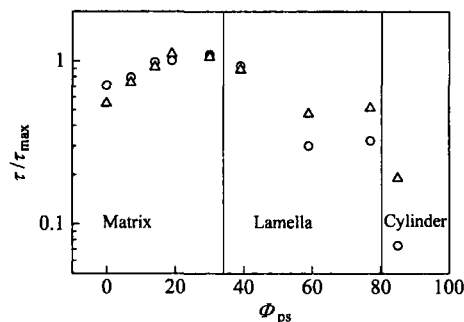


Fig. 4 Relaxations times of α (circles) and δ (triangles) process at $T = 40^\circ\text{C}$
Experimental errors are within symbol size.

It is clearly seen in Fig. 4 that with increasing content of polystyrene we observe an initial increase of the relaxation time. This is due to the effect of the coupling of the LC block to the glassy polystyrene domain. For these low PS contents the LC is in the continuous matrix. Further increase of the PS volume fraction leads us into the lamellar and subsequently the hexagonal structure with the LC contained in domains. The domains obviously reverse the effect of the slowing down and decrease the relaxation times of δ and α processes significantly.

Close inspection of the line shape leads to the conclusion that the α process remains unchanged whereas the δ process displays a strong, symmetric broadening. We speculate that the larger size of the molecular unit also leads to an increased cooperativity of the δ process as compared to the α process which then leads to the increased width of the relaxation time distribution. The variation of relaxation times with domain form in the block copolymers is the result of two competing effect. The LC block is coupled to the glassy PS domain and the relaxation times are therefore extended compared to the LC homopolymer. Opposed to this is the influence of the confinement causing a reduction of the relaxation times. The situation is therefore more complex than that of simple glass formers in pores or free standing polymer films.

REFERENCES

- Schüller, J., Richert, R. and Fischer, E.W., Phys. Rev. B, 1995, 52: 15232–15238;
Gorbatschow, W., Arndt, M., Stannarius, R. and Kremer, F., Europhys. Lett., 1996, 35: 719–724;
Huwe, A., Kremer, F., Behrens, P. and Schwieger, W., Phys. Rev. Lett., 1999, 82: 2338–2341;
Arndt M., Stannarius, R., Groothues, H., Hempel, E. and Kremer, F., Phys. Rev. Lett., 1997, 79: 2077–2080;
Pissis, P., Kyritsis, A., Daoukaki, D., Barut, G., Pelster R. and Nimtz, G., J. Phys.: Condens. Matter, 1998, 10: 6205–6227;

- Fukao, K. and Miyamoto, Y., *Europhys. Lett.*, 1999, 46: 649–654;
Fukao, K. and Miyamoto, Y., *Phys. Rev.*, E 2000, 61: 1743–1754
- 2 Schüller, J., Melnichenko, Y.B., Richert, R. and Fischer, E.W., *Phys. Rev. Lett.*, 1994, 73: 2224–2227;
Huwe, A., Arndt, M., Kremer, F., Haggemüller, C. and Behrens, P., *J. Chem. Phys.*, 1997, 107: 9699–9701;
Petychakis, L., Floudas, G. and Fleischer, G., *Europhys. Lett.*, 1997, 40: 685–690
Jeon, S. and Granick, S., *Macromolecules*, 2001, 34: 8490–8495;
 - 3 Sängler, J. and Gronski, W., *Macromol. Chem. Phys.*, 1998, 199, 555–561
 - 4 Zhukov, S., Geppert, S., Stühn, B., Staneva R., Ivanova R. and Gronski W., *Macromolecules*, 2002, 35(22): 8521–8530
 - 5 Sängler, J., Gronski, W., Maas, S., Stühn, B. and Heck, B., *Macromolecules*, 1997, 30: 6783–6787
 - 6 Schwab, M. and Stühn, B., *Colloid Polym. Sci.*, 1997, 275: 341–351
 - 7 Zentel, R., Strobl, G. and Ringsdorf, H., *Macromolecules*, 1985, 18: 960