

Polymer Communication

# Temperature dependence of dynamics of solutions of triblock copolymer in a selective solvent

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## Abstract

The temperature dependence of dynamic properties of solutions of a triblock copolymer with polystyrene outer blocks and a middle block of fully hydrogenated polybutadiene ( $M_w = 7.0 \times 10^4 \text{ g mol}^{-1}$ , mass fraction of PS 0.28) was studied in a selective solvent for the middle block, *n*-heptane. In dilute solutions, a gradual decomposition of the flower-like micelles was observed on heating. A more complex behavior was observed in semidilute solutions of the copolymer where three dynamic processes can be reliably extracted from the correlation functions. The fast mode corresponds to the collective diffusion mode of physically interconnected micelles, the broad middle mode is probably due to the tracer diffusion of polydispersed clusters (animal-like structures) formed by random association of the triblock copolymer and the slow mode is probably related to the diffusion of aggregates of insoluble polystyrene impurities. The crossover from relaxational to diffusive behavior was found for samples with  $c > 5.5\%$  (w/v). The scattered light intensity measurements revealed a phase transition for the solution with the concentration 4% (w/v) at a temperature of  $79 \pm 2^\circ\text{C}$ , which was related to the phase separation of polystyrene homopolymer present in a small amount in the copolymer used. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Triblock copolymer; Selective solvent; Semidilute solutions

## 1. Introduction

In a recent paper [1], we have reported the concentration dependence of the static and dynamic light scattering from dilute and semidilute solutions of a triblock copolymer with polystyrene outer blocks and a middle block of fully hydrogenated polybutadiene (PS-PHB-PS,  $M_w = 7.0 \times 10^4 \text{ g mol}^{-1}$ , mass fraction of PS 0.28) in a selective solvent for the middle block, *n*-heptane. Measurements of self-diffusion by pulsed-field-gradient NMR were also conducted. We have found that the dynamic mode for a dilute copolymer solution with  $c = 0.49\%$  (w/v) is diffusive and corresponds to the translation diffusion of micelles with flower-like structure [2]. The weight-average molecular weight of micelles,  $M_w = 2.26 \times 10^6$  (aggregate number of 32), and hydrodynamic radius of micelles,  $R_h = 23.8 \text{ nm}$ , were evaluated from static (SLS) and dynamic light scattering data (QELS) [3]. Small-angle X-ray scattering (SAXS) measurements [4] provided the core radius,

$R_{\text{core}} = 6.4 \text{ nm}$ , and molecular weight of the core,  $M_{\text{core}} = 6.3 \times 10^5$ .

At a higher concentration ( $1.1 \leq c \leq 2.6\%$  (w/v)), a slow dynamic mode can be distinguished. This is related to the diffusion of polydispersed clusters (animals [2]) formed by the random association of triblock copolymer molecules (bridging of insoluble domains). A complex dynamic behavior was observed in the semidilute region ( $4.0 \leq c \leq 6.9\%$  (w/v)). Three dynamic processes were observed. Both the fast and slow dynamic modes were found to be diffusive modes. The middle dynamic mode, between the two diffusive modes, was relaxational in character for samples with  $c = 5.5$  and  $6.9\%$  (w/v). The fast mode was interpreted as a collective diffusion mode from the physically interconnected nodes. The middle relaxation mode is probably due to the local movement of nodes trapped in the network of a physical gel. The slow mode was related to aggregates of insoluble polystyrene impurities. A similar system, poly(styrene-*block*-isoprene-*block*-styrene) in *n*-heptane, was thoroughly investigated by Lairez et al. by QELS, SAXS, SANS and viscosimetry [2,5,6].

In this paper we report the temperature dependence of the dynamic properties over the range of  $25$ – $100^\circ\text{C}$ . The

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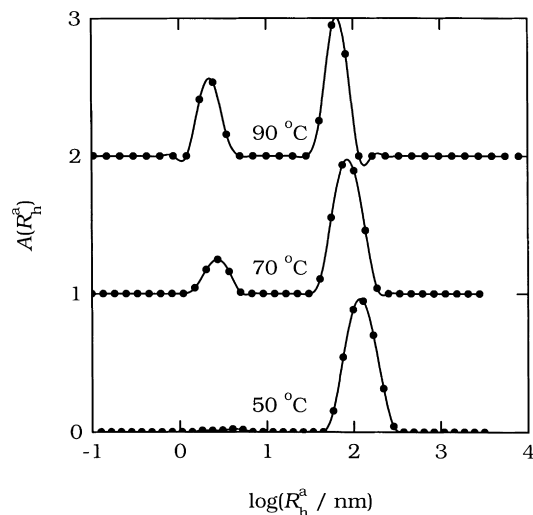


Fig. 1. Distribution of relaxation times,  $A(R_h^a)$  for three temperatures as indicated ( $c = 0.49\%$  (w/v),  $\theta = 90^\circ$ ).

measurements were performed on the same dilute and semi-dilute solutions used in the previous studies [1,3,4].

## 2. Experimental

A PS-PHB-PS triblock copolymer (Shell products, Kraton G-1650), was fractionated and the middle fraction corresponding to 15 wt.% of the original sample, was used in this study. The molecular weight of the sample was  $M_w = 7.0 \times 10^4$ , polydispersity  $M_w/M_n = 1.05$  and mass fraction of styrene was 0.28 [3]. The fractionation of the copolymer improved the copolymer polydispersity and decreased the content of PS homopolymer down to the detection limit of GPC [7].

Polarized quasielastic light scattering (QELS) measurements were made in the angular range of  $30\text{--}120^\circ$  using a light scattering apparatus equipped with an Ar ion laser ( $\lambda = 514.5$  nm) and an ALV 5000, multi-tau autocorrelator covering approximately 11 decades in the delay time  $t$ . The correlation functions were analyzed with the REPES program [8,9], to determine the inverse Laplace transformation of the measured intensity autocorrelation function  $g^{(2)}(t) = 1 + C|g^{(1)}(t)|^2$ , where  $C$  is an instrumental constant. The REPES program is similar to the widely used program CONTIN [10], except that CONTIN inverts the field autocorrelation function,  $g^{(1)}(t)$ , whereas REPES inverts the intensity autocorrelation function,  $g^{(2)}(t)$ . Since the REPES analysis has a tendency to split broad distributions into two or more contributions (overfitting), the electric field autocorrelation functions,  $g^{(1)}(t)$ , were also fitted to a sum of one or two single exponentials and a stretched exponential function.

Static light scattering measurements were performed with an instrument equipped with a vertically polarized He-Ne laser ( $\lambda = 632.8$  nm) in the angular range  $30\text{--}130^\circ$ . The scattered intensity  $I_s$  was corrected for the change in scatter-

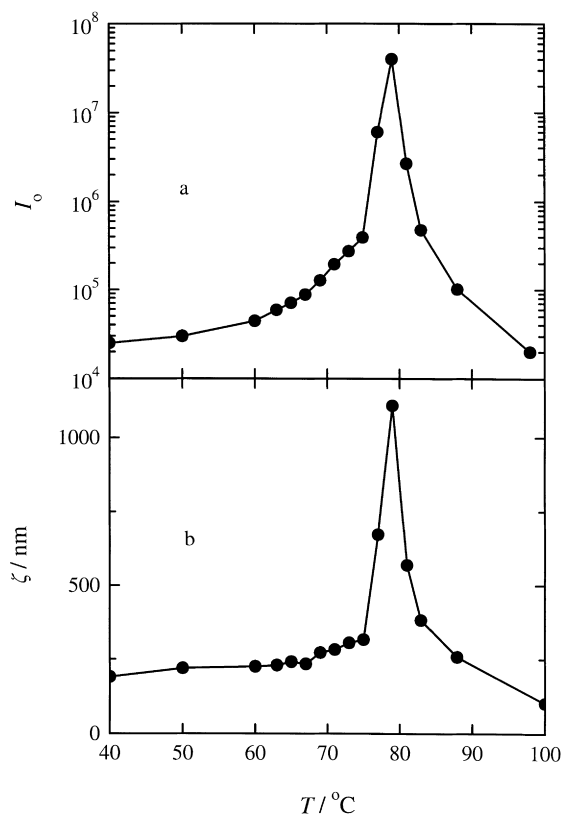


Fig. 2. (a) Temperature dependence of the zero angle scattering intensity,  $I_0$ , normalized by the scattering intensity of benzene. (b) Temperature dependence of the correlation length of a random heterogeneity  $\zeta$ . All the data in (a) and (b) are for the copolymer solution with  $c = 4\%$  (w/v).

ing volume and normalized by the scattering intensity of benzene.

## 3. Results and discussion

In dilute solutions the micelles gradually decomposed on heating and the contribution of the unimer (molecularly dissolved copolymer) to the scattered light increases as shown in Fig. 1, where the distribution of the apparent hydrodynamic radius,  $R_h^a$ , measured at  $c = 0.49\%$  (w/v) and the scattering angle  $\theta = 90^\circ$  is shown for three temperatures. The results are corrected for temperature and *n*-heptane viscosity changes. The small scatterers which correspond to the unimer, are virtually invisible at  $50^\circ\text{C}$ . With increasing temperature,  $T$ , the relative contribution of the unimer increases, until at  $90^\circ\text{C}$  its contribution is comparable to that of the micelles (larger scatterers). The apparent hydrodynamic radius of micelles,  $R_{hm}^a$ , slightly decreases with increasing temperature.  $R_{hm}^a$  at  $T \geq 50^\circ\text{C}$  is higher than  $R_h = 23.8$  nm of micelles obtained by extrapolation of the cooperative diffusion coefficient to infinite dilution at room temperature [3]. This increase in  $R_{hm}^a$  with concentration and temperature is due to attractive particle interactions [3] and, possibly, also to swelling of micelles. The

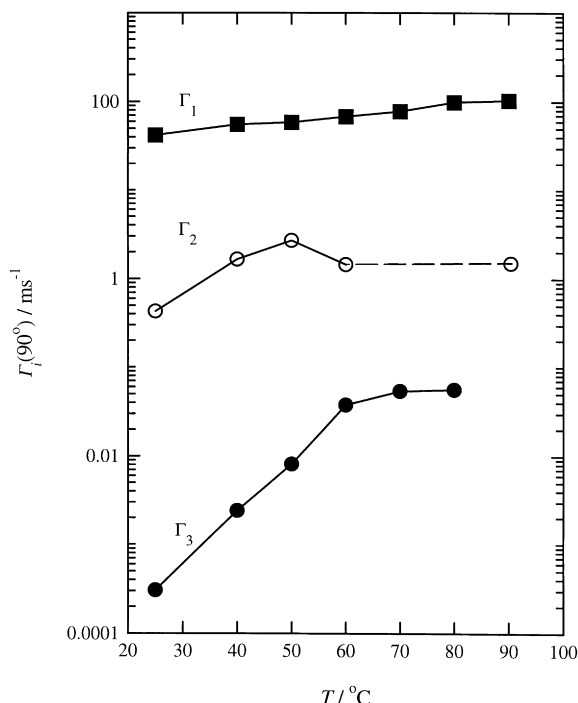


Fig. 3. Temperature dependence of  $\log \Gamma_i (i = 1-3)$  for copolymer solution with  $c = 4\%$  (w/v).

decomposition of micelles on heating obeys the model of closed association [11]. This model is characterized by an equilibrium between unimer and spherical micelles with a sharp mass and size distribution. In analogy to the critical micelle concentration, the critical micelle temperature (CMT) can be defined, as the temperature above which, at a given copolymer concentration, no micelles are present in solution. The CMT in the particular solution is well above the boiling temperature of *n*-heptane at temperatures higher than 100°C. CMT was also observed in solutions of the same triblock copolymer in 1,4-dioxane (selective solvent for PS) and 1,4-dioxane (70 vol.%)*n*-heptane (30 vol.%) mixtures [11] as well as in micellar solutions of the PS–PHB diblock copolymers, in decane (selective solvent for PHB) and 1,4-dioxane [12].

A considerably more complex phase separation behavior was observed in semidilute solutions of the copolymer, particularly at a concentration of 4% (w/v). The scattered light intensity measurements reveal a phase transition at a temperature of 79 ± 2°C, which manifests itself by a pronounced increase in the scattered light, particularly at low values of the scattering vector, *q*. The angle dependence could not be satisfactorily fitted by the Ornstein–Zernicke Lorentzian function, but, instead, it could be well fitted to the function  $I_s(q) = I_0 / (1 + \zeta^2 q^2)^2$  of the Debye–Bueche theory for a random heterogeneous system [13], where  $I_s$  is the scattering intensity,  $I_0$  is the zero angle scattering intensity,  $\zeta$  is the correlation length of random heterogeneities and *q* is the scattering vector. The temperature dependences of  $I_0$  and  $\zeta$  are shown in Fig. 2a and b, respectively.

A possible explanation is the following: the observed phase transition may be related to the phase separation of PS homopolymer which is still present in a small amount in the copolymer used [7]. PS is partly soluble in *n*-heptane at higher temperatures and phase-separated at low temperatures [2]. The PS phase separation in such a mixture is likely to be influenced by interactions with the triblock copolymer. Thus, PS-rich droplets can be stabilized by the copolymer, forming emulsion-like particles. The existence of such large particles in ternary solutions of a homopolymer (A) and diblock copolymer (AB) in a selective solvent for block B has been reported previously [14,15].

Three dynamic processes can be reliably extracted from the correlation function of the sample with  $c = 4\%$  (w/v) by using the REPES analysis. The temperature dependence of the mean decay rates,  $\Gamma_i$ , ( $i = 1-3$ ) of these modes is shown in Fig. 3. The slow mode was only observed at temperatures below 80°C. The middle mode cannot be reliably evaluated in the phase separation region because the slow mode is dominating the light scattering. Both the short-time and long-time decay modes ( $\Gamma_1$  and  $\Gamma_3$ ) can be well described with single exponential correlation functions while the middle mode ( $\Gamma_2$ ) is rather broad. All dynamic modes were found to be diffusive,  $\Gamma_i \propto q^2$ . As seen in Fig. 3,  $\Gamma_1$ , corresponding to the collective diffusion mode of physically interconnected micelles, has no temperature dependence beyond the usual temperature dependence of the collective diffusion constant. The broad middle mode is probably due to the tracer diffusion of polydispersed clusters (animals) formed by the random association of triblock copolymer molecules (bridging of insoluble domains via PHB blocks) [1]. As discussed earlier [1], the slow mode is probably related to the diffusion of aggregates of insoluble polystyrene impurities, which arise in the copolymer synthesis and are left behind after fractionation. Its strong temperature dependence reflects the viscosity of the solution in the vicinity of the gel point. This is further supported by the temperature behavior of the relative scattering amplitude ratio of the slow and fast modes (not shown), which shows an anomalous behavior between 70 and 80°C. This anomaly is enhanced at low *q* values.

In contrast to the sample with  $c = 4\%$  (w/v), the middle dynamic mode for samples with  $c = 5.5$  and 6.9% (w/v) is relaxational in character ( $\Gamma_2$  is independent of  $q^2$ ) at temperatures below 35°C [1]. The diffusive behavior of  $\Gamma_2$  ( $\Gamma_2$  is a linear function of  $q^2$ ) was observed at temperatures above 35°C. The crossover from relaxational to diffusive behavior is demonstrated in Fig. 4a where the log–log plot of  $\Gamma_i$  vs  $q^2$  is shown for sample with  $c = 6.9\%$  (w/v) at 35°C.  $\Gamma_2$  is independent of  $q^2$  only at higher  $q^2$  values and shows the linear  $q^2$ -dependence at low  $q^2$  values. A similar behavior was also observed for the sample with  $c = 5.5\%$  (w/v) but at a lower temperature (30°C). Such a crossover from relaxational to diffusive behavior has been observed in earlier studies of probe particle dynamics in gels [16,17]. Our QELS results in the gel/latex system

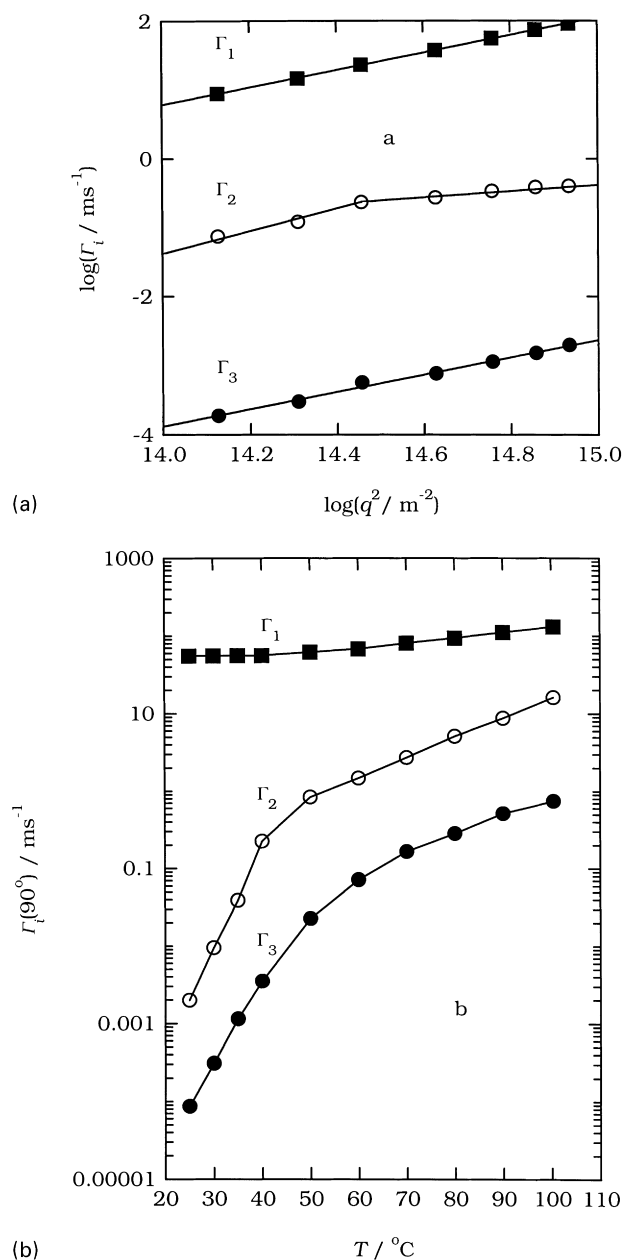


Fig. 4. (a)  $\log \Gamma_i (i = 1 - 3)$  vs  $\log(q^2)$  for copolymer solution with  $c = 6.9\%$  (w/v) at  $35^\circ\text{C}$ . (b) temperature dependence of  $\log \Gamma_i (i = 1 - 3)$  for copolymer solution with  $c = 6.9\%$  (w/v).

have shown that the crossover from diffusional to relaxational behavior depends on the length scale over which the movement was probed ( $1/q$ ) and the mesh size ( $l$ ) of network. If  $l \leq 1/q$ , then QELS probes larger scales than  $l$  and a translational diffusion may be observed. If  $l \gg 1/q$ , then QELS is essentially probing only the local movement of the particles inside the pores and, therefore,  $\Gamma$  is independent of  $q^2$ . The crossover between almost relaxational and free diffusion dynamics occurs at about  $ql \sim 1$  [18]. In analogy with probe diffusion in gels, we suggest that the middle relaxation mode represents a local movement of insoluble domains trapped inside a liquid-like ordered

structure of semidilute copolymer solutions [1,4,19]. When the ordered structure is partially destroyed, e.g. by heating, the local dynamics is changed into translational diffusion and the relaxation behavior changes to diffusive. Consequently, the ordered structure (6.9% (w/v)) should be stable up to  $35^\circ\text{C}$ . Indeed, all parameters characterizing the liquid-like structure (core radius, hard-sphere interaction radius and hard-sphere volume fraction) obtained on the same sample by X-ray analysis are independent of temperature up to  $35^\circ\text{C}$  and then melting of ordered structure and cores is observed on heating [19]. Since at  $35^\circ\text{C}$  the hard-sphere interaction radius is about 18.8 nm, it is plausible that  $l \approx 37.6$  nm. Then the crossover should be observed about  $q \sim 1/37.6 \text{ nm}^{-1}$  which corresponds to the scattering angle  $\theta = 103^\circ$  inside the measuring range used ( $\theta = 30\text{--}130^\circ$ ).

The temperature dependencies of  $\Gamma_i$  for the copolymer solution with  $c = 6.9\%$  (w/v) are shown in Fig. 4b. While the fast mode follows the viscosity changes of *n*-heptane, the middle and slow modes reflect the viscosity of solution and show a destruction of the liquid-like ordered structure at about  $40^\circ\text{C}$ .

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