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Observation of internal relaxation modes during early state of spinodal decomposition in the isotopic polymer mixture d-PS/PS with SANS

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Abstract

Early state of spinodal decomposition in a symmetric isotrope mixture d-PS/PS has been studied with SANS at two temperatures well below T_c . Nonexponential time behaviour was found according to internal relaxation modes of the polymer. The data could satisfactorily be described by an ansatz from Akcasu which includes internal relaxation modes approximately and is an extension of the Cahn-Hilliard-Cook theory for polymer blends. The interaction range for the Onsager coefficient was found increasing with time and larger than the radius of gyration.

1 Introduction and Theoretical Background

Polymer blends are ideal systems for the study of phase transition because they are liquids with relaxation-time constants long enough for experimental studies. A theoretical and experimental survey about this subject can be found in References [1-4]. Our interest in this subject is the study of early state of spinodal decomposition for which the Cahn-Hilliard-Cook theory [2] is valid.

$$S_T(Q, t) = S_T(Q) + [S_{T0}(Q) - S_T(Q)]L^2(Rt) \quad (1)$$

S_T and S_{T0} are the static structure factors at the respective temperatures T_0 and T in the one and two phase regime. L is the normalized dynamic structure factor [5] which is $L = \exp(-R(Q)t)$ for C-H-C theory. The relaxation rate R is given by [2]

$$R = Q^2 D_c = Q^2 \Lambda(Q) \cdot S^{-1}(Q) \quad (2)$$

with the collective diffusion constant D_c and the Onsager coefficient Λ [6]

$$\Lambda(x) = \Lambda_0 \{ [1 - \exp(-x)]/x \} \quad (3)$$

and $x = Q^2 R_0^2$. There is a 'fundamental' time constant $\tau_0 = 6R_g^2/D_0$ [7] in polymers which roughly determines the time the polymer needs to diffuse over a distance equal to its own size. R_g is the radius of gyration and D_0 the self diffusion constant of the polymer with $D_c = D_0(1 - \Gamma_f/\Gamma_c)$. Γ_f

and Γ_c are the Flory-Huggins parameters at T and T_c . In a recent publication [8] we presented studies of early state of spinodal decomposition in d-PS/PVME systems for times up to about 200 s with τ_0 between 2 and 10 s. In this system we always found at $t > \tau_0$ an exponential time behaviour of the relaxation modes in agreement with the C-H-C prediction. However, the extrapolation to $t = 0$ gave some indication of nonexponential behaviour for $t < \tau_0$ [9]. Relaxation experiments within the one phase regime [10] of the isotope mixture d-PS/PS with $V_w \simeq 0.9 \cdot 10^6 \text{ cm}^3/\text{mol}$ gave nonexponential time behaviour for $t < \tau_0$, which we could describe by a phenomenological Kohlrausch ansatz with a Q dependent stretched exponent. In this publication we will present SANS studies of a symmetric d-PS/PS blend with $V_w \simeq 1.4 \cdot 10^6 \text{ cm}^3/\text{mol}$ and a critical composition of $\phi_c = 0.5$ in order to study the phase decomposition for times less than τ_0 in more detail. The data will be analyzed by

$$L(Q, t) = \frac{1}{2}(1 + A)\exp(-R_1 t) + \frac{1}{2}(1 - A)\exp(-R_2 t) \quad (4)$$

as derived by Akcasu [5]. R_1 and R_2 describe the relaxation rates of the diffusional and internal modes respectively. R_1 is given by the expression in eq. (2). R_2 and A are discussed in [5].

2 Experiment

The characteristic data for the sample are collected in table I.

table I: Characteristic data of symmetric d-PS/PS blend with $\phi = 0.5$. V_w has been determined by GPC, R_g was calculated from V_w and the segment length. T_c has been interpolated from the equilibrium structure factor at various temperatures. Γ is given in [$10^{-6} \text{ mol}/\text{cm}^3$].

$V_w [10^6 \text{ cm}^3/\text{mol}]$	Γ_c	$\Gamma_f(150^\circ\text{C})$	$\Gamma_f(170^\circ\text{C})$	$R_g [\text{\AA}]$	$T_c [^\circ\text{C}]$
1.42	1.41	2.42	2.12	417	227

The small angle neutron experiments were performed at the KWS II at the research center in Geesthacht. The measurement time for each spectrum was between 1 and 2 hours in order to get statistical errors within 1 %. The data analysis has been performed in a standard way [10]. The samples were in an evacuated sample container when heat-treated in an oil bath and quenched in ice water to room temperature which is about 70 K below the glass transition temperature. Before the experiment the samples were homogenized 13 K above T_c at 240°C , because the sample was prepared within the two phase regime. However, the samples were not yet in the equilibrium state at $T = 240^\circ\text{C}$ as we found out after the experiment. We studied the early state of spinodal decomposition at 170°C and 150°C e.g. 57 and 77 K below T_c .

3 Results

Figure 1a shows the time dependent normalized structure factor $\sigma(Q, t) = S_T(Q, t)/S_{T0}(Q)$ versus Q at $T = 170^\circ\text{C}$ for times between 2 and 70 hours. The interference peak characteristic for spinodal decomposition is clearly seen. A shift of Q_m from values at $Q_m \simeq 4 \cdot 10^{-3}$ to $2 \cdot 10^{-3} \text{ \AA}^{-1}$ and an increase of $S(Q_m)$ from 1.7 to 4.5 with respect to $S(Q)$ at $t = 0$ is observed. In Figure 1b and 2a $\ln L$ is plotted versus time for various Q values (eq. (1)) for the respective $T = 170^\circ\text{C}$ and $T = 150^\circ\text{C}$. The positive and negative slope of $\ln L$ is due to unstable and stable fluctuation modes, respectively. The phase decomposition at $T = 170^\circ\text{C}$ (Figure 1b) shows quite clearly a nonexponential time behaviour while at $T = 150^\circ\text{C}$ (Figure 2a) an exponential behaviour is found in the studied time interval. The analysis of the results at $T = 170^\circ\text{C}$ with the ansatz from Akcasu

in eq. (1) and eq. (4) gives an excellent agreement as demonstrated by the solid lines in Figure 1a. It was found that the interaction range R_0 of the Onsager coefficient in eq. (3) is linear dependent on time and increases from a value of $R_0 \simeq 420\text{\AA}$ to a value of about $670\text{\AA}$.

The data for $\ln L$ in Figure 2a shows a linear behaviour. Because the diffusion constant at $T = 150^\circ\text{C}$ is roughly one order of magnitude less than that at $T = 170^\circ\text{C}$ the nondiffusive behaviour may be observable at later times. The data in Figure 2a were analyzed by calculations of the first cumulant, namely by $\partial(\ln L)/\partial t$ in the limit $t = 0$ from which the Onsager coefficient in Figure 2b was derived (eq. (2)). $\Lambda(Q)$ strongly depends on Q which could be satisfactorily fitted by eq. (3) as shown by the solid line. From the extrapolated $\Lambda(Q = 0)$ the diffusion constants, τ_0 and from the Q dependence an interaction range of the Onsager coefficient is obtained.

table II: Diffusion constants, fundamental time constant and interaction range of the Onsager coefficient.

$T[^\circ\text{C}]$	$D_0[10^{-16}\text{cm}^2/\text{s}]$	$D_c[10^{-16}\text{cm}^2/\text{s}]$	$\tau_0[\text{h}]$	$R_0[\text{\AA}]$
170	4.3	- 2.12	70	420 - 670
150	0.63	- 0.45	460	$\simeq 550$

Fig. 1a: Normalized time dependent structure factor showing spinodal decomposition after 2h ($\blacktriangle$), 4h ($\circ$), 8h ($\blacksquare$), 22h ($\triangle$), and 70h ($\blacklozenge$) at $T = 170^\circ\text{C}$. Solid lines represent fits with the Akcasu model. Fig. 1b: Normalized dynamic structure factor L versus time at $Q = 1.65$ ($\blacklozenge$), 2.36 ($\circ$), 2.6 ($\square$), 3.31 ($\blacktriangle$), 3.55 ($\diamond$), 3.78 ($\bullet$), 4.02 (∇), 4.96 ($\blacksquare$) in $[10^{-3} \text{\AA}^{-1}]$. Dashed line is a guide for the eye.

4 Conclusions

Early state of spinodal decomposition was studied with SANS in a symmetric isotope mixture of d-PS/PS at two temperatures well below T_c . At $T = 170^\circ\text{C}$ a clear nonexponential time behaviour was observed. The observed linear behaviour at $T = 150^\circ\text{C}$ may be caused by the much slower diffusion constant and the visibility of the very initial decomposition process. The analysis of the experimental data gave the diffusion constants, the fundamental time constant τ_0 and the interaction range R_0 of the Onsager coefficient. Their values are collected in table II. A transition from nonexponential to exponential time behaviour could not be observed. The time interval for

Fig. 2a: Same as in Figure 1b for spinodal decomposition at $T = 150^\circ\text{C}$ for $Q = 1.9$ [-•-], 2.84 [-o-], 3.07 [-◇-], 4.02 [-△-], 4.25 [-x-], 4.5 [-◆-], 4.73 [-▽-], and 5 [-□-] in $10^{-3}\text{\AA}^{-1}$.

Fig. 2b: Onsager coefficient obtained from the 1. cumulant in Figure 2a. The data were fitted with the ansatz from Pincus in eq. (3).

early state of spinodal decomposition at $T = 170^\circ\text{C}$ is about the same as τ_0 and therefore an exponential time behaviour is not observable. A further result is the observed time dependence of the interaction range of the Onsager coefficient which increases with time and is larger than R_g . A theoretical explanation for this result is still missing.

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