

MOBILITY OF POLYMERS IN NANOMETER SLITS: KINETICS OF POLYMER MELT INTERCALATION IN LAYERED SILICATES

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Introduction

Recently, polymer nanocomposites have attracted a lot of research interest, not only because they exhibit new and improved properties comparing to their bulk counterparts(1), but also because they represent unique model systems to study the statics and dynamics of polymers confined over distances ranging from the statistical segment length to the radius of gyration of the chains. In particular, increased interest has been concentrated on polymer intercalated systems employing 2:1 mica-type phyllo-silicates, such as smectites and hectorites (2).

By following the temporal evolution of X-ray diffraction patterns during polymer melt intercalation into the galleries of layered silicates the non-equilibrium dynamics of polymer chains in a 2 nm slit has been studied. In this paper we will present and discuss the intercalation kinetics of polystyrene as a function of molecular weight, polymer/surface interaction, chain ends and polymer architecture (i.e. random, block and star).

Furthermore, structural details obtained from neutron and x-ray scattering will be presented and discussed.

Experimental

Monodispersed polystyrene over a wide range of molecular weights with different end group modification was used. The functionality of the hydroxy/carboxy terminated polystyrene was determined by titration with potassium hydroxide solution against phenolphthalein. In the case of the dihydroxy terminated polystyrene, it was determined by UV-measurement after treated with Rhodamine 6G.

Block and star copolymers were synthesized by living anionic polymerization methods (3). Their order-disorder transition temperature was determined by SAXS when applicable (4).

By ion-exchanging with alkyl ammonium, pristine silicates could be rendered organophilic and thus could be intercalated with non-polar polymers.

Polymer and silicate powder were mechanically mixed and then pressed into pellets. The pellets were then annealed in a vacuum oven at a temperature above the softening temperature of the polymer and the kinetics data was obtained following a previous reported procedure (5).

X-ray diffraction was performed using a θ - θ Scintag Diffractometer with Cu K α radiation at Cornell.

Results and Discussion

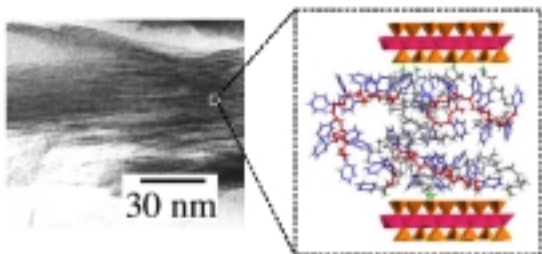


Figure 1. TEM bright field image and a snapshot from computer modeling studies of the experimental system.

Figure 1 shows a TEM bright field image and a snapshot from computer simulation. The intercalated polystyrene is located between two parallel

inorganic crystalline planes modified by end grafted alkyl-ammonium surfactants. The width of the inorganic layers is 9.7Å, whereas the width of the confined polystyrene film is around 20Å.

A wide range of molecular weights of polystyrene standards were intercalated into three of the organically modified silicates (C18-, C16-, and C14-FH). As shown in Figure 2, the degree of polymerization N spans a range between 2 and 52 entanglement lengths and the corresponding D scales as $D \sim N^{-1}$

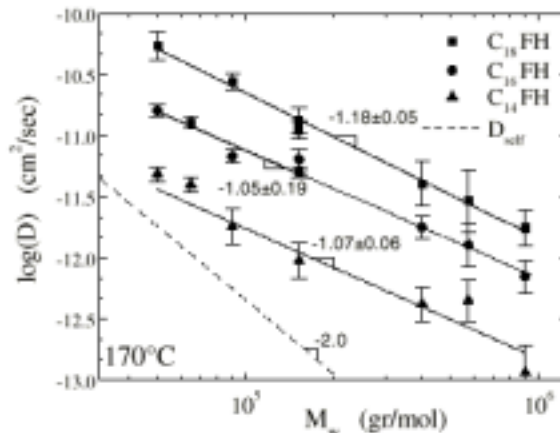
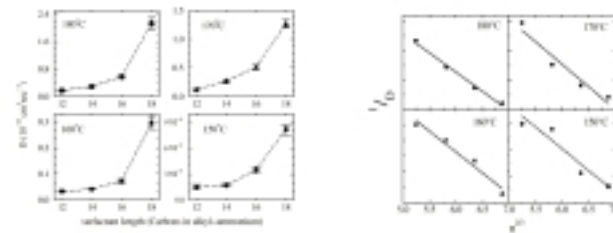


Figure 2. The molecular weight dependence of the diffusion coefficient on the polymer M_w .

It also shows that the intercalating polymers are moving with a much faster effective diffusivity than either the bulk tracer diffusion (6) or the same polymer in a thin film (7). The fast kinetics is attributed to the thermodynamic driving force for intercalation. The $D \sim N^{-1}$ scaling can be explained from the polymer reptation theory in two dimensions.

Polymer-surface interactions can be controlled through two means. One way is by changing the length of the surfactants. Typical dependence of the polymer diffusion coefficient as a function of the surfactant length for various temperatures is shown in Figure 3(a). The same data is plotted as inverse D versus length of the surfactant to the 2/3 power in Figure 3(b). A constant β , which depends only on the grafting density and the alkyl ammoniums, could



be obtained from the mean square fitting to the experimental data, and in very good agreement with result from molecular simulations.

Figure 3. The diffusion coefficient versus the length of the alkyl-chain of the surfactants.

The other way is to modify the polymer, for example, employing different functional group terminated polystyrene. Carboxyl, dihydroxyl, dicarboxyl and methyl terminated polystyrene were also used in addition to H-terminated polystyrene. The effective diffusion coefficients of these polymers with several organically modified fluorohectorites at 150°C are reported in Table 1. Due to the much higher friction coefficient between silicate surface and functional end group, the motion of modified polystyrene inside silicate galleries is greatly slowed down comparing with unmodified polystyrene.

Table 1. Diffusion coefficients [10^{-14} cm²/sec] at 150°C for different PS-X/Fy mixtures

	PS	PS-2OCH ₃	PS-2OH	PS-COOH	PS-2COOH
F14	116±4	48.4±2.8	7.02±0.59	3.90±0.37	2.53±0.22
F16	206±13	72.6±3.8	13.3±0.7	5.33±0.31	3.58±0.44
F18	789±71	266±20	61.9±1.9	22.4±0.9	13.8±1.2
F18s	445±27	-	-	-	10.8±0.8
F18t	2240±130	-	-	-	30.4±1.5
F18q	61.3±3.2	-	18.9±1.3	19.1±1.5	9.26±0.78

Another interesting issue is the intercalation of copolymers and polymers with an architecture other than linear structure. A block copolymer of polystyrene/polyisoprene was intercalated into C18-FH at temperature both under and above its order-disorder transition temperature. Intercalation could be achieved in the ordered state, as well as in the disordered state.

Conclusions

In general, intercalation of high polymers is faster than the corresponding polymer self-diffusion. In addition, the diffusion coefficient scales as N^{-1} .

The mobility of polymer inside the organically modified 2nm slits depends strongly on the interaction between the polymer and the surface inside the galleries. This interaction can be engineered by either varying surface modification or the polymer. The motion of polymer can be enhanced by reducing the polymer-surface friction coefficient or the surface exposed to the polymer.

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