

Nanoscopic Studies on Polymer Molecules(STM-other surfaces)

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Nanoscopic Studies on Polymer Molecules

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A new field of study in the polymer science and engineering is being opened with the use of scanning tunneling microscope (STM), atomic force microscope (AFM), and scanning probe microscope (SPM). In this short review article several examples are given with comments. They are direct observation of poly(macromonomer), structure of a cross-linking domain of a gel, and observation of topochemically photopolymerizable conjugated aromatic compound. Moreover, nanorheological properties of polymer blends are shown as an example of the application of AFM force curve measurements. There are many possibilities of application of SPM to nanoscopic studies on polymer molecules.

KEYWORDS: STM, AFM, poly(macromonomer), gel, conjugated aromatic compound, electronic structure

1. Introduction

It is essential to have information on nanoscale structure of polymer molecules to understand physical properties of polymers. However, electron microscope or X-ray and/or light scattering methods have some drawbacks to study soft materials like polymers. We have been applying field ion microscope (FIM), scanning tunneling microscope (STM) and atomic force microscope (AFM) to study polymer molecules in nanoscopic order.

FIM was applied to observe phenyl rings attached to polystyrene chain with limited success [1]. STM was applied to observe a monolayer of polyimide [2], polyaniline chains in good or poor solvents [3], and molecular images of polymacromonomers [4]. Moreover, we could study crosslink structure of gellan gum [5] and structure of a main-chain type thermotropic liquid-crystalline homopolyester [6]. At present we are planning to use photo-polymerizable monomer to study the structure before and after polymerization [7, 8]. AFM was constructed in our laboratory to study nano-rheological properties of polymer blends [9].

In this invited lecture we will summarize some of our recent studies with typical results and point out problems special to polymer molecules.

2. Experimental

A Nanoscope II (Digital Instruments, Inc.) was mostly used to obtain STM images of polymer molecules at room temperature under atmospheric pressure. Highly oriented pyrolytic graphite (HOPG) was mostly used as a substrate. However, it should be mentioned that this substrate had to be used very carefully. As described in the literature [10], the use of HOPG can result in the generation of artifacts. Therefore, we paid special attention to artifacts and we believe that the STM images presented here contain no artifacts. The scanning

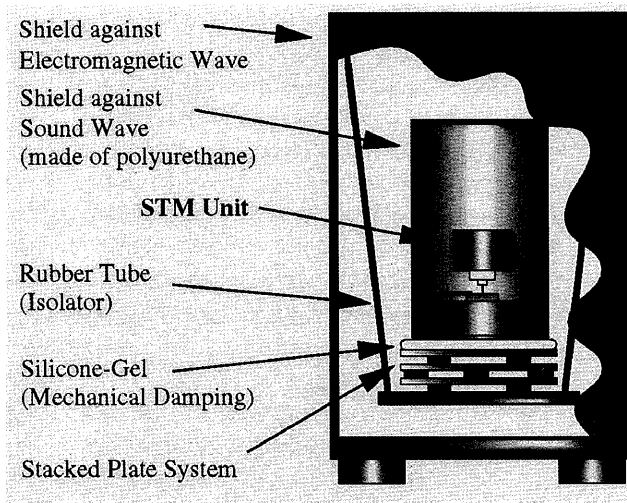


Figure 1. Vibration and noise reduction system of STM and AFM.

tips used were made of Pt-Ir (8 : 2) for most cases. For ultra-high-vacuum (UHV) STM, tips electrochemically etched from (111) oriented single crystal W wires were used.

Sample preparation is the most critical condition for the observation of polymer molecules in nanoscopic order and the details will be found in the references. The next condition is the setting of bias voltage and tunneling current. We have to look for the best condition for each polymer since there is no experimental data before our trial in most cases.

Vibration and noise reduction system for the STM unit was homemade as shown in Fig. 1 in a very compact form. The essential points are the use of rubber tube for hanging the STM unit, use of stacked plate system with stainless steel plate and rubber sheets, and the application of high damping silicone-gel. This system

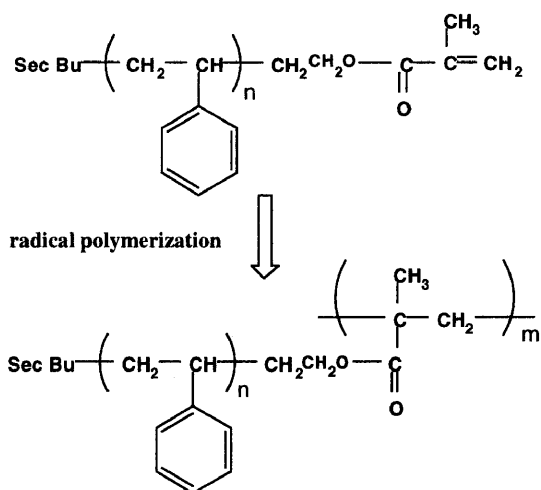


Figure 2. Poly(macromonomer)s of polystyrene.

was also used for the homemade AFM.

For the AFM experiments, triangular cantilevers with pyramidal shaped Si_3N_4 tips (Olympus, OMCL-TR 800 PS-1) were mostly used. The height of the pyramid was $2.9 \mu\text{m}$. The size and the thickness of the triangle was $100 \mu\text{m}$ and $0.8 \mu\text{m}$, respectively. The spring constant of the cantilever was 0.68 N/m . The displacement of the cantilever was detected by a laser light beam and a bisected photo-diode. In this case we used AFM to study force curve characteristics by changing the movement of the tip in a wide range from 1 nm/s to 10000 nm/s .

3. Results and Discussions

3.1 Direct observation of poly(macromonomer) [4]

Recently, macromonomers, *i.e.*, oligomers or polymers having a polymerizable functional group at one end, have been gaining much attention as useful building blocks for the development of new polymeric materials. Polymerization of macromonomers can produce well-defined regular multibranched polymers, where the branch length and the branch number are controlled by the molecular weight of the macromonomer and the polymerization conditions. Furthermore, every repeating unit of the backbone chain of the multibranched polymers, *i.e.*, poly(macromonomer)s, has one long branch, *i.e.*, side chain, at all times. Thus, the branching period is regular and the branch density is extremely high. The molecular shape and properties of the poly(macromonomer)s are expected to be very different from those of corresponding linear polymers.

Figure 2 shows a scheme of a polystyrene based poly(macromonomer) where polystyrene is a branch and the backbone chain is a polymethacrylate. A poly(macromonomer) sample having 20 branches ($m = 20$) with uniform length ($n = 26$), poly(MA-PSt 2900)-20 was prepared and it was dissolved in toluene to obtain approximately 10^{-3} wt\% solution. A few drops of the solution were placed onto an HOPG substrate and

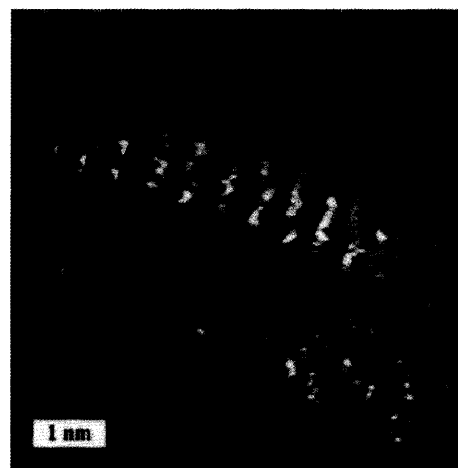


Figure 3. STM top view a single molecule of poly(MA-PSt 2900)-20 on HOPG⁴).

spin coating at 3000 rpm for 1 min was conducted immediately. After a few hours drying at room temperature, STM observation was carried out. Image acquisition in the constant height mode was done in air at room temperature with a scanning speed of 78 Hz.

Figure 3 shows a typical example of STM images taken for poly(MA-PSt 2900)-20 on an HOPG substrate [4]. The scan size was $5.36 \times 5.36 \text{ nm}^2$ and a tip bias voltage was -138.6 mV with a tunneling current of 2.30 nA . An HOPG pattern is clearly visible both upper right and lower left in the image. There are two islands of parallel line arrays, each composed of 10 short lines, although the images of the lower island is unclear. These lines are considered to be part of the 20 polystyrene side chains of poly(MA-PSt 2900)-20, because phenyl groups or double bonds flatly adsorbed on the HOPG surface are usually observed as bright spots in STM measurement in spite of the low bias voltage [3, 11]. From the figure, the interval between the side chains is 0.42 nm and the periodicity of one phenyl group in the side chain is 0.30 nm . The size of the interval may be explained by considering that the main chain of a poly(macromonomer) has TG^+TG^- conformation. From this type of observation we can study the nanoscopic structure of a single polymer chain.

3.2 Observation of the structure of a cross-linking domain of a gel [5]

Science and technology of gels have been progressing rapidly with many applications. However, little is known about the cross-linking domain of a gel although it is essential for the understanding of the very peculiar property of a gel. We have chosen a gellan gum which is a bacterial polysaccharide to apply STM to observe a cross-linking domain.

Figure 4 shows the repeating-unit of gellan gum and schematic representation of a model for the conformation and functional interaction between gellan molecules

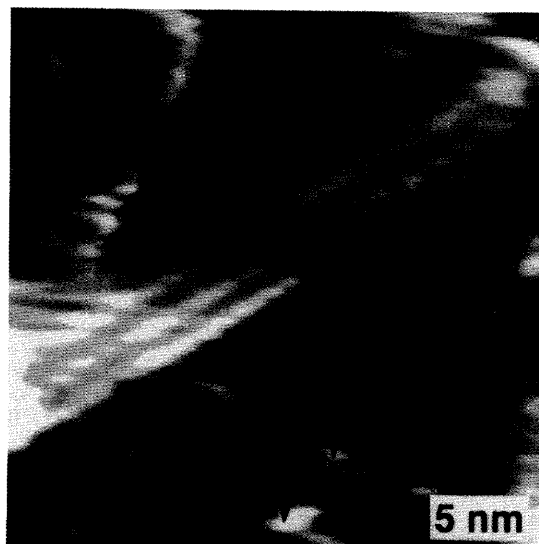
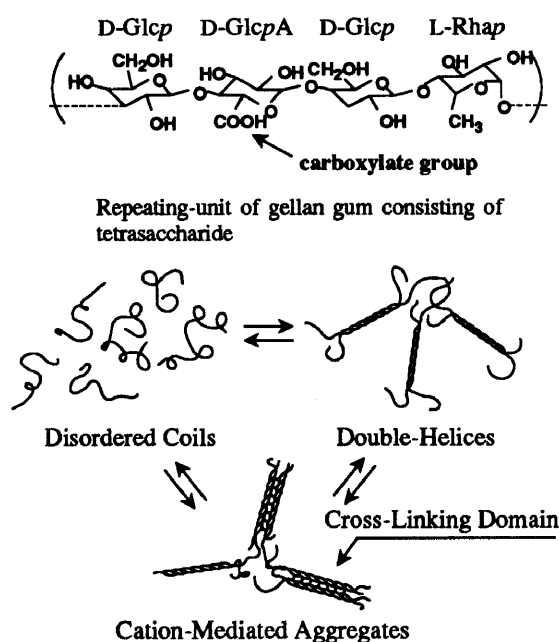


Figure 5. STM top view image of a film of K^+ -gellan on an HOPG substrate⁵⁾. Scan size is $60.1 \times 60.1 \text{ nm}^2$.

Figure 4. Repeating-unit of gellan gum and schematic representation of a model for the conformation and functional interaction between gellan molecules.

to form cross-linking domains. In this study, we observed thin films of gellan gum with several kinds of salts (including gellan gum without salts) deposited on HOPG. Typical sample preparation is as follows. An aqueous solution (0.46 wt%) of gellan was stirred above 80°C and held there for 20 min to solubilize the gum. An appropriate amount of KCl was added to the agitated solution and kept at 90°C for 10 min. The K^+ concentration of the solution (for example 113 mM) was sufficient for strong gelation after cooling below the gel point T_m . Then, STM samples were prepared (1) deposition of the hot aqueous solution onto a freshly cleared HOPG substrate followed by immediate spin-coating at 2500–4000 rpm for 60 seconds, (2) left as it is for an hour for drying.

Figure 5 shows typical example of STM top view image of a film of K^+ -gellan on a HOPG substrate [5]. The scan size is $60.1 \times 60.1 \text{ nm}^2$. The biased voltage and the tunneling current was -1.0 V and 0.50 nA , respectively. The scan rate was 78.1 Hz and the constant current mode was adopted. In the figure, three distinct rows with bright spots run parallel to each other in the middle. Fast Fourier Transform (FFT) taken along the center row reveals the periodicity along the rows is 2.59 nm . After taking several dozens of STM images with other tips and scanners, the average periodicity along rows turned out to be 2.6 nm . An X-ray diffraction study by Chandrasekaran *et al.* [12] for bulk crystals of gellan revealed that half a pitch was 2.8 nm .

Figure 6 shows a cross-sectional profile perpendicular to the strand axis for Fig. 5 and Table 1 shows a comparison between the STM observation and the X-ray results [5]. There is a large discrepancy for the separation

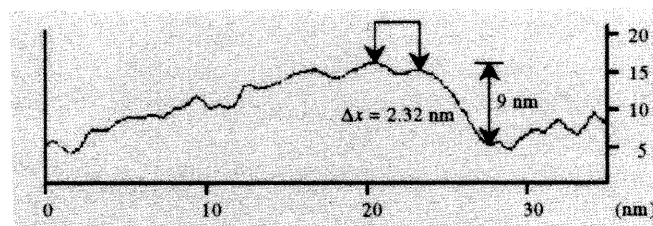


Figure 6. A cross-sectional profile perpendicular to the strand axis for Fig. 5.

between strands. The discrepancy may be due to the strong interaction between the cross-linking domain and the substrate. The difference of co-existing cations was investigated by STM observation and the results were summarized in Table 2 [5]. The average length of the strands is influenced by the co-existing cations and the strength of the gel becomes stronger with longer strands. This behavior can be explained qualitatively based on a zipper model.

3.3 Observation of topochemically photopolymerizable conjugated aromatic compound [7, 8]

It will be very interesting if we can manipulate a single polymer chain in nanoscopic scale for the development of molecular devices. To do this it is important to manipulate polymerizable monomers. Figure 7 shows an example of topochemically photopolymerizable conjugated aromatic compound (1,4-bis [β -pyridyl-(2)-vinyl] benzene (P2VB)) and a model of polymerization. P2VB has three aromatic rings and two olefinic double bonds. P2VB molecules will undergo a solid-state polymeriza-

Table 1
Comparison between the STM observation⁵⁾ and the X-ray results¹²⁾.

	STM (gel state)	X-ray ¹²⁾ (solid state)
half a pitch of double helix (nm)	2.6	2.815
separation between strands (nm)	2.3	1.575

Table 2
Average strand length of four types of gellan observed by STM⁵⁾.

	strand length (nm)*	strength
p-gellan	17	weak
Na ⁺ -gellan	30	thixotropic
K ⁺ -gellan	40	strong
Ca ²⁺ -gellan	70 <	very strong

* The averaging procedure of strand length was conducted measuring several dozens of strands for each type of gellan.

tion caused by ultraviolet (UV) irradiation to form a linear polymer having a recurring cyclobutane structure with a 1,3-trans configuration and 1,4-arylene units alternately in the chain [13].

As a first step, ultra-high-vacuum (UHV) STM was applied to observe the initial stage of absorption of P2VB individual molecules on a Si(100) surface. This

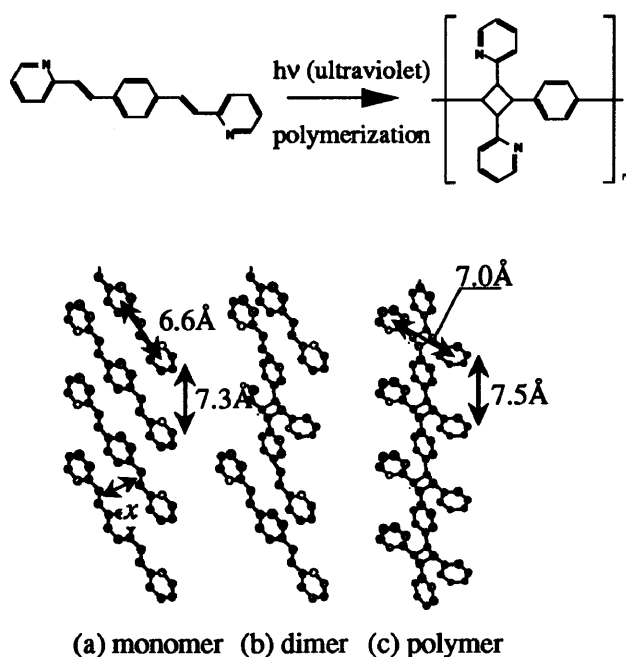


Figure 7. Topochemically photopolymerizable conjugated aromatic compound (1,4-bis [β -pyridyl-(2)-vinyl] benzene (P2VB)) and a model of polymerization.

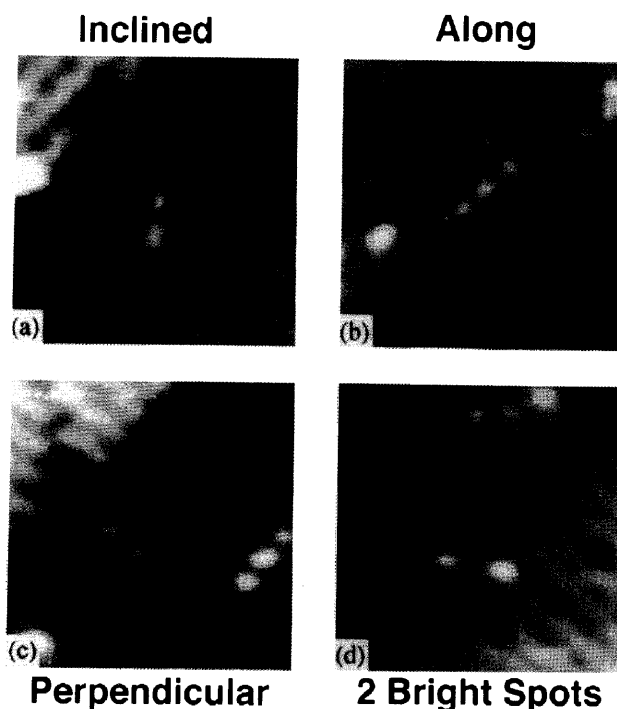


Figure 8. Four different directions of P2VB molecular adsorption on Si(100)- 2×1 surface⁷⁾.

surface was selected as a substrate because (1) a clean Si(100) surface can be easily obtained by merely a series of heatings, (2) several reports on the adsorption of organic molecules on Si(100) surface have been published [14-16], and (3) the future development of molecular devices may be based on Si(100) or Si(111) surfaces.

A clean Si(100)- 2×1 surface was prepared under UHV (below 2×10^{-10} Torr) and it was introduced into the STM chamber. Then, we deposited P2VB molecules using a homemade doser made of tantalum. The base pressure of the STM chamber was kept below 5×10^{-11} Torr. In this condition, a few dozen P2VB molecules were adsorbed on the area of $40 \times 40 \text{ nm}^2$ for 20 min deposition, which corresponded to about 10^{-5} ML. Scanning tips electrochemically etched from (111) oriented single crystal W wires were used. The STM images were taken at a bias voltage ranging -2.5 to $+2.5$ V and a constant tunneling current of 20 pA. Figure 8 shows individual P2VB molecules on Si(100)- 2×1 surface with scan size of $7 \times 7 \text{ nm}^2$ at -2.0 V bias voltage [7]. It is found that there are only four different directions of P2VB regarding to the Si(100) dimer row. Namely, in (a) and (d) P2VB is inclined to the dimer rows, in (b) it is along a dimer row, in (c) it is perpendicular to the dimer rows. We should note that a molecule is imaged as three bright spot, except in the case of (d). Because of the adsorbed structure appearing in (d), a simple explanation that these bright spots correspond to three aromatic rings included in a P2VB molecule is not valid. After several considerations, we can conclude that STM reveals the electronic states of Si(100) dimers modulated by the adsorbed molecules, rather than the molecules themselves.

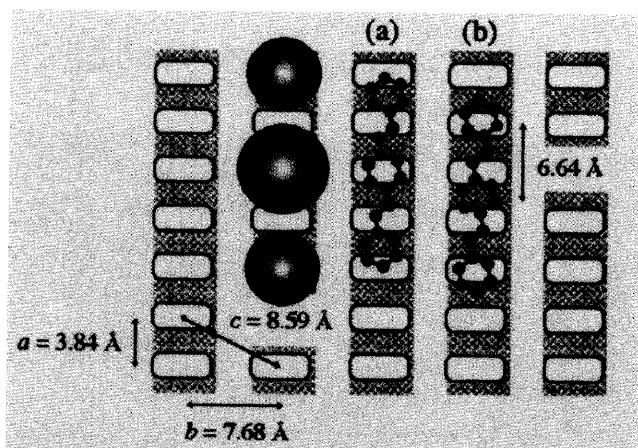


Figure 9. Comparison between the structure obtained by STM and (a), (b) possible interpretations in the case of molecular adsorption along a dimer row⁷⁾.

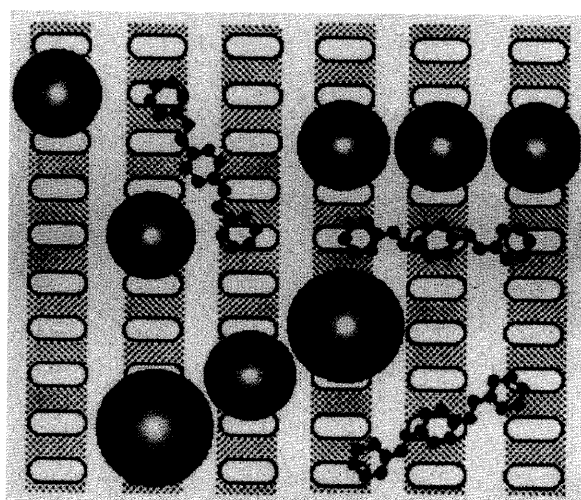


Figure 10. Schematic illustration of the adsorption site for the other three cases⁷⁾.

Figures 9 and 10 show the schematic illustration [7].

During STM observation of P2VB molecules we could calculate the probabilities of four different adsorption directions and we could make a simple model of very initial stage of adsorption of a P2VB molecule. It is shown in Fig. 11. If we assume that a molecule adsorbs on a Si dimer at its end first and it falls toward the Si(100) surface in random direction at almost equal probability as shown in Fig. 12, then Table 3 [7] can be obtained. The comparison between the measured distribution and the calculated distribution for the initial stage of P2VB adsorption is quite satisfactory.

The next step is to locate P2VB molecules to a specified position and apply UV to do polymerization. Some preliminary studies are now going on and the results will be reported in the near future. These works are underway as a joint project with Advanced Research Laboratory of Hitachi, Ltd.

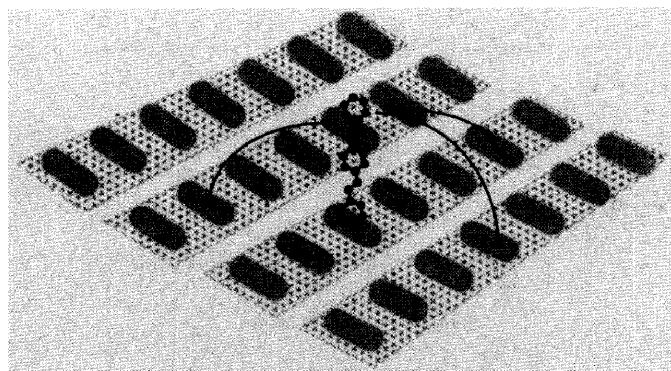


Figure 11. A simple model of very initial stage of adsorption of a P2VB molecule.

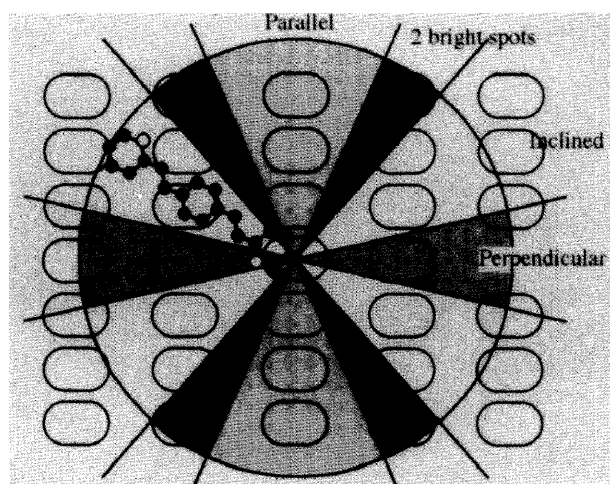


Figure 12. Simple calculation for obtaining the distribution of initial stage of adsorption.

3.4 Nanorheological properties of polymer blends [9]

Polymer materials are often used as soft materials where rheological properties are very important. It is an interesting problem to study rheological properties in nanoscopic scale where dynamics of polymer chains may play a key role. To study nanorheological properties of polymers we have constructed AFM where we can change scanning speed and/or measure dynamic force curves in a wide range.

Table 3

Comparison between the measured distribution and the calculated distribution for the initial stage of P2VB adsorption⁷⁾.

	measured (%)	calculated (%)
Inclined	50 ± 10	40
Parallel	25 ± 8	25
Perpendicular	15 ± 7	15
2 bright spots	10 ± 6	20

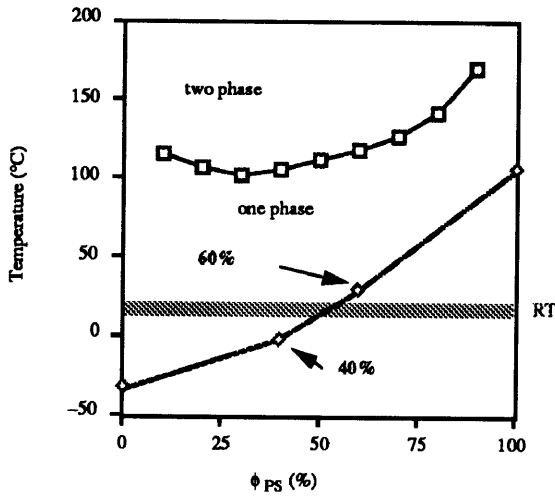


Figure 13. Phase diagram for polystyrene (PS)/poly(vinyl methyl ether) (PVME) polymer blends⁹⁾.

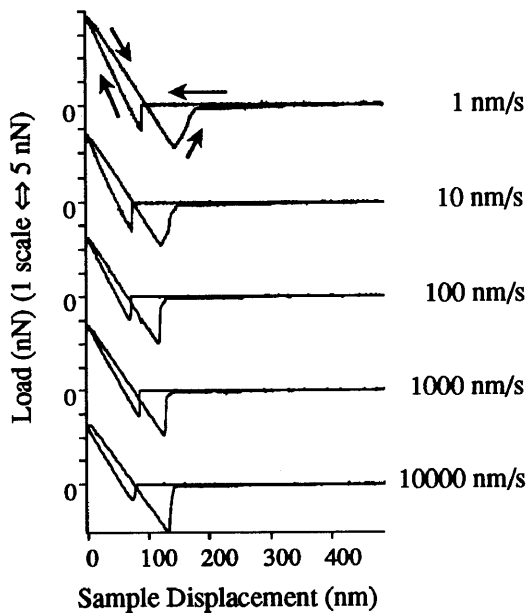


Figure 14. Dynamic force curves for PS at room temperature⁹⁾.

As a first step we chose miscible polymer blends and Fig. 13 shows the phase diagram. The system is the mixture of polystyrene (PS) and poly(vinyl methyl ether) (PVME) with lower critical solution temperature (LCST) type phase diagram [17]. The weight average molecular weight (M_w) for PS and PVME was 10,400 and 140,000, respectively. The glass transition temperature (T_g) for PS and PVME was 110 and -35°C , respectively. The system is molecularly miscible below the phase diagram and the T_g for the blend can be changed by adjusting the PS volume % between -35 to 110°C .

Figure 14 shows dynamic force curves for PS at room temperature [9]. There is not much change in the force curve at 1 nm/s to 10000 nm/s which is the speed of

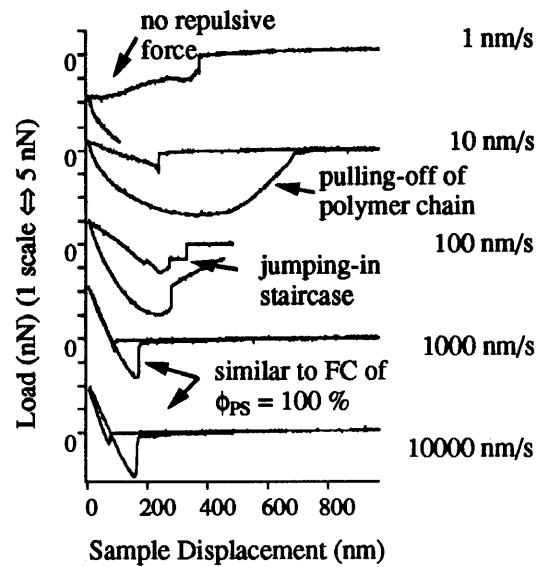


Figure 15. Dynamic force curves for PS/PVME = 40/60 at room temperature⁹⁾.

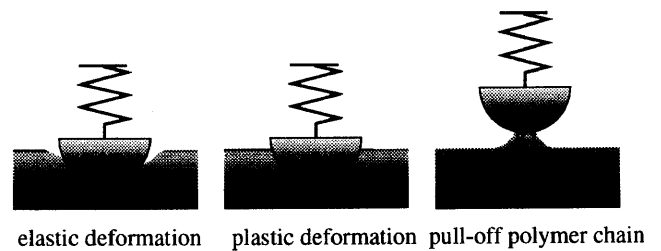


Figure 16. A model of nanoscopic study of viscoelastic property (nanorheology) of polymers.

the tip approaching to the sample or separating from the sample. This is quite reasonable since PS is a glassy solid at room temperature. However, for PS/PVME = 40/60 blend the situation is very different as shown in Fig. 15 [9]. At low speed the force curve is for viscous liquid and at high speed the force curve is for glassy solid. In the intermediate speed there is a very long tail in the force curve corresponding to a pulling-off of polymer chains. Figure 16 shows a model of nanoscopic study of viscoelastic property of polymers.

4. Conclusion

In this short article we have shown some examples of application of STM and AFM to nanoscopic studies on polymer molecules. They are direct observation of poly (macromonomer)s, structure of a cross-linking domain of gel, and topochemically photopolymerizable conjugated aromatic compound. Possibility of the study of nanorheological properties of polymer by AFM is also presented. There can be many other applications of STM and AFM

to polymers or soft materials. At present, there are many problems for the preparation of samples. However, we believe these studies will open a new field for polymer science and engineering in nanoscopic scale.

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