Methods for Characterizing Polymer Surfaces and Interfaces

Thomas P. Russell*

Abstract. The behavior of polymer molecules at surfaces and interfaces has been receiving a considerable amount of attention over the past few years. Numerous developments have been made theoretically using simulations and analytic approaches. Experimentally, advances have been made in the development of new techniques and the use of old techniques not commonly used in the investigation of polymers to probe the interfacial and near surface behavior of polymers. In this article, some of the experimental developments that have been made recently will be discussed. The approach will be to focus on the behavior of thin films of diblock copolymers and diblock copolymers at the interface between immiscible polymers, describing the different techniques used to study these problems.

Introduction

The behavior of diblock copolymers in the bulk is a relatively well understood field [1]. For example, knowing the composition of the block copolymer, the molecular weight and the *Flory-Huggins* interaction parameter, χ, the morphology of copolymer in the microphase separated state and the temperature at which the order-disorder transition occurs can be predicted with reasonable accuracy. However, an equally important question to ask concerning diblock copolymers is their behavior at surfaces and interfaces. The more important applications of block copolymers come from their ability to modify the surface characteristics of a material, to act as a surfactant or compatibilizing agent, or to promote adhesion between two immiscible polymers. Due to these characteristics, block copolymers have found many uses in areas ranging from biomedical applications to microelectronics. However, it is precisely the behavior of copolymer at interfaces where the least is known. This lack of knowledge stems from the unavailability of techniques capable of probing polymers with sufficient spatial resolution. It must be kept in mind that questions on the interface between polymers requires a spatial resolution that approaches or is less than the size of an individual molecule and have sufficient penetration depth to probe an interface that is buried within a polymer film.

* *Correspondence*: Dr. T. P. Russell
IBM Research Division
Almaden Research Center
650 Harry Road
San Jose, California 95120–6099, USA

There are several techniques that have been used to obtain the concentration variation in polymers. X-Ray photoelectron spectroscopy (XPS) provides information on the composition profile in a specimen with a resolution that approaches 1 Å. However, the penetration depth of XPS is only 75 Å limiting the techniques to the air/polymer interface. Forward recoil spectrometry (FRES) has a much greater penetration depth (several microns) but only has a spatial resolution of 800 Å. While one obtains absolute information on the concentration of components, it is most difficult to examine behavior on the molecular level. Dynamic secondary-ion mass spectrometry (DSIMS) on the other hand, has a penetration depth of several thousand Å with a spatial resolution of ~ 125 Å. While the resolution is much improved over that obtained by FRES, the information that one receives is only relative. Background signals contribute significantly to the observed depth profiles hampering an absolute determination of the concentration profile. Transmission electron microscopy (TEM) has an unlimited penetration depth owing to the manner in which the specimen is microtomed and has a spatial resolution of 10Å. However, the microtoming process and the staining that is necessary to examine the different components is always a source of concern and, in fact, limits the utility of the technique to those systems with a natural electron density contrast or to those that can be readily stained. It is, also, difficult to place the concentration on an absolute level due to the uncertainties mentioned above. Neutron and X-ray reflectivity techniques, on the other hand, provide a penetration depth that is on the order of several thousand Å and yield the concentration profiles with a resolution of ~ 10 Å. The actual penetration depth is limited by the resolution of the spectrometer. Unfortunately, the information that one obtains by reflectivity techniques is the optical transform of the density variation in the specimen. This means that one is faced with the inverse problem, and modeling of the concentration profile is necessary to calculate the observed reflectivity. This leads to the question of uniqueness in that more than one concentration profile may yield the same reflectivity profile. Thus, it is clear that each technique has its own strengths and weaknesses, and that several techniques need to be combined to define the concentration profile in a specimen. In fact, the more techniques that one uses, the more confident one can be in defining the composition profile.

In this article, the ordering of diblock copolymers at surfaces and the behavior of diblock copolymers at the interface between immiscible homopolymers will be treated. The two subjects will be used to illustrate the manner in which these different techniques can be used to compliment each other. We shall focus on symmetric diblock copolymers of poly(styrene) (PS) and poly(methylmethacrylate), (PMMA) denoted P(S-b-MMA), as a model system.

Surface Ordering of Diblock Copolymers

In the bulk, the product of the number of segments in a symmetric diblock copolymer, N, and the *Flory-Huggins* segmental interaction parameter, χ, determine the morphology [2]. In the absence of concentration fluctuations, if $\chi N < 10.5$, the copolymers are phase mixed, whereas if $\chi N \geqslant 10.5$, the copolymer microphase separates into a lamellar morphology with a characteristic period L. At or near an interface, which could be the copolymer/air or copolymer/substrate interfaces, the specific interactions of the segments of the block copolymer at the interface can markedly alter the behavior of the copolymer. Recently, *Fredrickson* [3] developed a mean field theory to describe the surface ordering of diblock copolymers near the microphase separation transition temperature (MST). At temperatures above the MST an exponentially damped, oscillatory segment density profile is predicted normal to the film surface. The extent to which this surface effect propagates into the bulk will depend upon the relative proximity of the system to the MST. The closer one is to the MST, the further is the effect of the surface felt. Consequently, while the bulk of the specimen is phase mixed, the copolymers begin to exhibit microphase separation near the surface.

To illustrate this point consider the symmetric, diblock copolymer of P(d-S-b-MMA), *i.e.* a copolymer of PS and PMMA where the PS block is labeled with

D. The molecular weight of the copolymer is 29,780 with a total of 263 monomer segments. Recent small angle neutron scattering studies [4] on this copolymer in the bulk have shown that χ is given by

$$\chi = 0.0284 + 3.902/T \qquad (1)$$

where T is the absolute temperature. From χ and N an MST of 65° is calculated. Thus, for all temperatures above the glass transition temperature, the copolymer is phase mixed.

Angle-resolved XPS studies on films of P(d-S-b-MMA), on the other hand, show that there an excess of PS, the lower surface energy component, at the air surface [5]. Making use of the differences in the binding energies of the carbon and oxygen electrons, XPS can be used to obtain the relative concentration of S and MMA segments over a depth which depends upon the electron take-off angle. The average bulk fraction of S segments is 0.5. However, the XPS results revealed that the fraction of S segments at the surface was 0.65. Consequently, nearly a 30% excess of the S segments was found at the surface. Subsequent XPS studies on P(S-b-MMA) copolymers as a function of temperature [6] and copolymer molecular weight [5] yielded quantitative agreement with the arguments of *Fredrickson* [3].

Due to the limited penetration depth of XPS, neutron reflectivity was used to extend the XPS studies over greater depths [7]. While the densities of PS and PMMA are quite similar, labeling the S block with D provided sufficient contrast to determine the concentration profile. Specimens for neutron reflectivity are typically prepared on thick (5 mm) Si or glass substrates by solvent-casting techniques. The specimens are then annealed at a specific temperature and quenched rapidly below the glass transition temperature. After annealing the P(d-S-b-MMA) at 170° for 24 h the reflectivity profile shown in *Fig. 1* was obtained as a function of the neutron momentum in vacuum k_0. This is

$$k_0 = (2\pi/\lambda)\sin\theta \qquad (2)$$

where λ is the wavelength and θ is the grazing angle of incidence. The reflectivity profile is characterized by total external reflection below the critical value of $k_0 \approx 5 \times 10^{-3}$ Å. At higher k_0, the overall reflectivity decreases rapidly. The most noteworthy feature of the profile is the high frequency oscillation characteristic of the total sample thickness (~ 1400 Å). The absence of any sharp reflections clearly demonstrates that there is no long range ordering in the specimen. Calculations of the reflectivity profile assuming that the film was homogeneous do not describe the measured reflectivity profile as shown by uppermost curve in *Fig. 1*. Since the XPS results showed that there was an excess of S

segments at the air surface and due to the interconnected nature of the blocks in the copolymer, it is reasonable to assume that concentration profile could be described by

$$\phi(z) = \phi_e e^{-z/\xi}\cos(2\pi z/L) + \bar{\phi} \qquad (3)$$

where ξ is the correlation length, L is the copolymer period, $\bar{\phi}$ is the average concentration in the bulk, ϕ_e is the excess surface concentration, and z is the distance from the surface. Assuming such a profile from the air surface only yielded the results in *Curve 2* of *Fig. 1*. While this describes the results at the high values of k_0, marked disagreement is seen at the lower values of k_0. *Curve 3* shows the reflectivity profile calculated assuming that the oscillatory variation in the concentration occurs only at the Si substrate. Here, good agreement is found at low k_0 only. Thus, it was mandatory to assume a damped oscillatory profile from both the air and Si surfaces to describe the reflectivity results. In both cases, $L = 150 \pm 10$ Å and $\xi = 95 \pm 7$ Å with the only difference being ϕ_e at the two interfaces. At the air surface, the concentration of S segments was 0.65, in agreement with the XPS measurements, whereas at the Si interface at the concentration of MMA segments was 1. From the arguments of *Fredrickson*, $\xi = 104$ Å and $L = 150$ Å which is in precise agreement with the experimental observation.

Now consider the case of P(S-b-MMA) where the molecular weight of each block is $\sim 5 \times 10^4$. By increasing the molecular weight $\chi N > 10.5$ and, hence, the diblock copolymer will microphase separate. DSIMS revealed a most interesting response of the copolymer to the presence of the air and substrate interfaces [8] [9]. In DSIMS, an ion beam is rastered across a surface ejecting charged particles from the surface with a masses that are characteristic of the components at the surface. These particles are then fed into a mass spectrometer where the number of particles of a given mass can be recorded as a function of time. Since the ion beam removes the material at the surface, then time or cycles corresponds to depth from the surface. Labeling one of the components with D affords an easy means of differentiating between the components, since one needs only monitor the particle of mass 1 and 2 corresponding to H and D, respectively.

Shown in *Fig. 2* is a series of DSIMS profiles for a P(d-S-b-MMA) diblock copolymer after annealing the copolymer at 170° for 0(1), 5(2), 15(3), 240(4), and 480(5) min. These results show that the as cast film is essentially homogeneous. Upon annealing, oscillations in the concentration of d-S and MMA segments develop from both the air and substrate interfaces. These two waves propagate into the bulk of the specimen as a function of time, they meet one another and merge together. Increasing the annealing time further results in the formation of a multilayered morphology
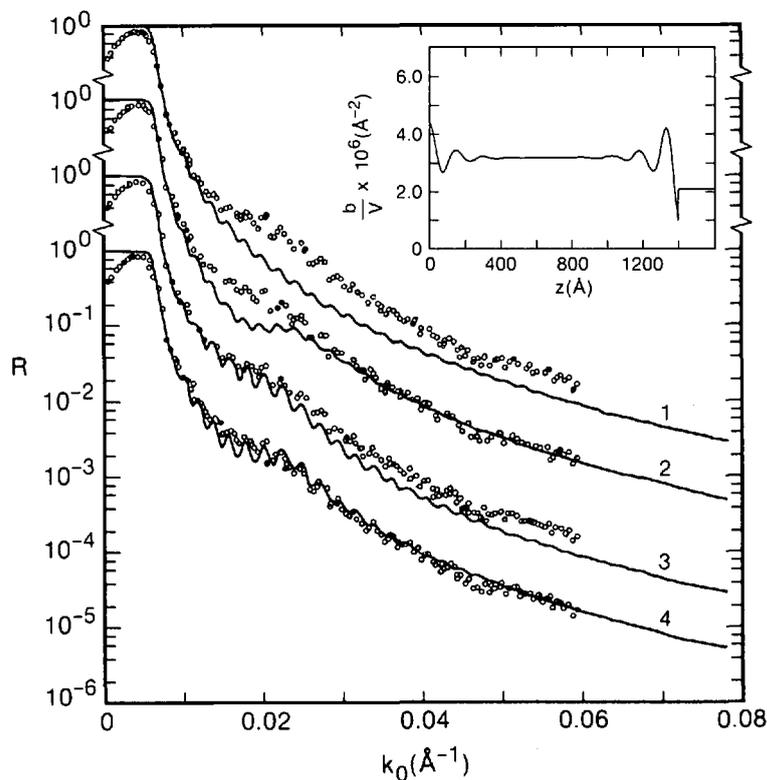

Fig. 1. *Neutron reflectivity profile for a P(d-S-b-MMA) diblock copolymer annealed at 170° for 24 h.* The open circles are the experimental points and the solid lines are calculated reflectivity profiles assuming (*1*) a homogeneous film (*2*) an exponentially damped cosine function from the air interface, (*3*) an exponentially damped cosine function from the Si interface, and (*4*) exponentially damped cosine functions from both interfaces. The scattering length density profile shown in the inset was found to best describe the reflectivity profile [7].

with MMA adjacent to the Si substrate and PS at the air surface. Substitution of the Si substrate with Au produces a similar multilayered structure, but, in this case, S segments are located at both interfaces. The period of the multilayered morphology is found to be identical to the period of the diblock copolymer in the bulk.

In the case of a Si substrate, the multilayering forces the thickness of the specimen at any one point to be given by $(n + 1/2)L$ where n is an integer. A specimen with an initial thickness different from $(n + 1/2)L$ (which is usually the case) forms terraces or depressions on the surface where the step change in the thickness of the specimen corresponds to precisely L. This is easily seen using white light as a source in a reflection microscope and observing the interference colors [8] [10]. Coupling the multilayer formation with the high spatial resolution of neutron reflectivity has permitted a quantitative examination of the morphology of diblock copolymers and a critical comparison to current theoretical treatments [11].

Diblock Copolymers at Homopolymer Interfaces

The interface formed between two immiscible polymers is, normally, narrow with very little interpenetration of the two polymers. However, in many applications of polymers where multiple layers of similar and dissimilar polymers are placed on top of one another, lack of interpenetration between the layers results in poor adhesion between the layers. This poor adhesion between the layers will give rise to a delamination during subsequent processing or while in use. Such behavior is frequently met in the microelectronics industry where multiple layers of electronic circuitry are placed on top of one another with a thin film polymer dielectric separating the circuitry. In bulk applications of multicomponent polymer, it is often necessary to obtain a fine dispersion of one polymer in another. Due to the inherent immiscibility of polymers, coarse phase separation results. In both these applications, the linking of two incompatible polymers *via* a chemical bond to form a block copolymer plays an important role. In the first case, the diblock copolymer can be used to promote adhesion between successive layers, and in the second, it can be used to limit the extent of phase separation and serve a means by which stresses can be transferred from one domain to another. As a result of these and other examples, the investigation of the behavior of diblock copolymers at homopolymer interfaces has received substantial theoretical attention. However, only recently have the experimental techniques become available to probe this question.

As a model, consider the case of PS and PMMA. In the bulk, these two homopolymers are immiscible and will coarsely phase separate. The interface formed be-

Fig. 2. *DSIMS profiles showing the $^2H^+$ counts as a function of the sputtering time for a P(d-S-b-MMA) diblock copolymer after annealing for* (1) *0*, (2) *5*, (3) *15*, (4) *240, and* (5) *480 min* [8]

tween layers or domains of PS and PMMA is 50 Å [11] [12]. While this is broader than the interfacial width seen for most immiscible polymer (typically 10–20 Å), the adhesion between PS and PMMA is poor [13]. Placing P(S-b-MMA) diblock copolymer at the interface between the homopolymers produces a dramatic increase in the adhesion between PS and PMMA as a result of the bridging of the copolymer across the interface and the entanglement of the copolymer blocks with the homopolymers [13]. The effect of the copolymer on the interfacial toughness is very clear, but in order to develop an understanding of the behavior of the copolymers at the interface, it is necessary to know, whether the copolymer orders at the interface, the concentration of copolymer retained at the interface and the segment density distributions of the homopolymers and copolymers at the interface. This information would allow a quantitative comparison with existing theories, give insight into the mechanism of adhesion, and guide the way to developing a general description of the interfacial behavior of block copolymers.

The segregation of block copolymers to the interface between immiscible was initially investigated by *Jerome* and coworkers [14] using transmission electron microscopy. Using a block copolymer with a

unsaturated link between the two blocks, they were able to stain the junction point with OsO_4 and to show that the interface between the homopolymer domains was preferentially stained. These experiments, while providing limited information, were critical, since they showed unequivocally that the copolymer segregated to the interfacial region and the junction points were restricted in their position spatially. More quantitative measurements have been made since that time using FRES [15] [16], DSIMS [17] and neutron reflectivity [18].

FRES relies on the recoiling of nuclei during interactions with a stream of incident alpha particles. The number of particles detected as a function of energy will depend upon the mass of the particle, the energy of the incident alpha particles, the stopping power of the specimen, and the depth location of the nuclei. From the energy spectrum, the depth profile of the nuclei can be determined. With FRES, one typically uses the mass difference between H and D to label the component of interest. With a spatial resolution of 800 Å, FRES can not provide a detailed description of the segment density profiles of the components at the interface, since this occurs on a much shorter distance scale, but does provide a means of determining the total excess of the copolymer localized to
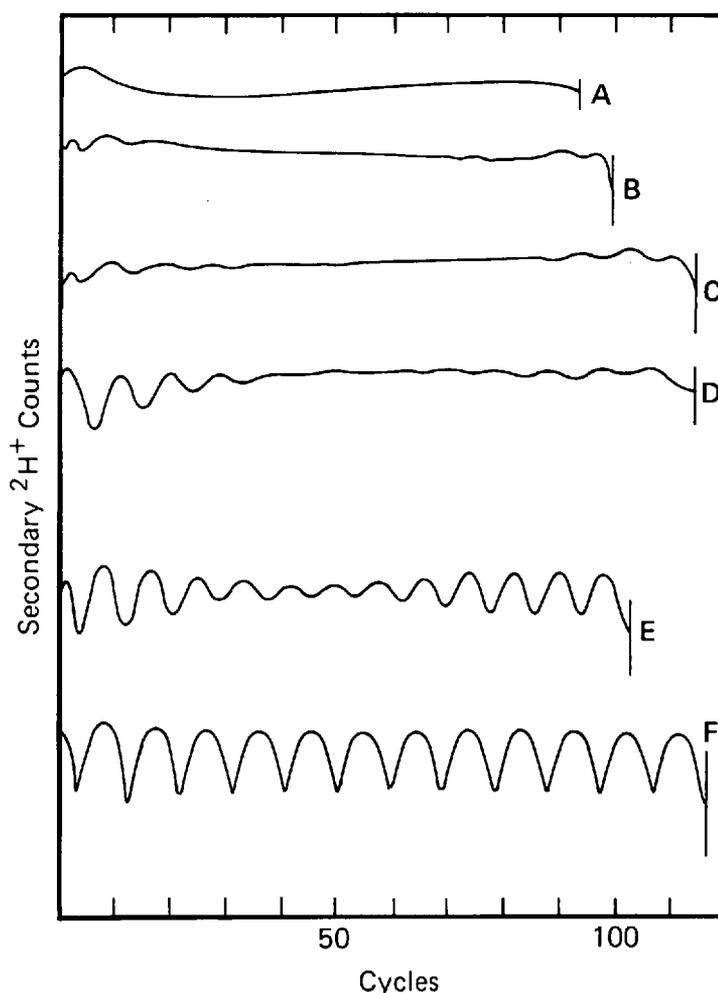
the interfacial region. This is of critical importance, since it provides a direct measure of a calculable quantity and provides a basis on which other measurements can be based. Indeed, it has been found that the concentration of the copolymer at the interface increases up to the critical micelle concentration, at which point the incremental increase in the copolymer excess at the interface decreases.

DSIMS, on the other hand, yields a depth profile of the normal and D-labeled components directly. One must be cautioned, however, since the sputtering rate of the ion beam in the different components may vary which could hamper interpretation. Nonetheless, one obtains the concentration profiles smeared with the spatial resolution of 130 Å. In the case of P(S-b-MMA) at the interface between PS and PMMA, DSIMS has been used to show that the copolymers segregate preferentially to the interface and that there is not a significant extension of the molecules at the interface [17]. In addition, DSIMS on thin layers of PS and PMMA homopolymers in the presence of P(S-b-MMA) showed that, not only is there a segregation of the copolymers to the homopolymer interface, but there can, also, be a segregation of the copolymer to the air surface and to the substrate interface [19]. This depends upon the specific interactions of the individual blocks of the copolymer with the air and substrate surface in comparison to those of the homopolymers. These studies clearly pointed to the complexity of such systems and an unexpected behavior of the copolymers.

Neutron reflectivity studies on the segregation of P(S-b-MMA) to the interface between PS and PMMA have been able to quantify the segment density distributions of the homopolymers and copolymers at the interface [18]. Using a series of experiments where the different components are labeled with D, it has been possible, by the solution of a set of simultaneous equations to describe the system fully. There are several interesting results which have stemmed from these studies. First, it has been shown that in the presence of a copolymer the interface between the S and MMA segments is substantially broadened. In fact, an interfacial width of 75 Å is found, whereas for the pure homopolymer

interface and for the interface between the lamellar microdomains of the bulk diblock copolymer a interface of only 50 Å is observed. Coupled to this is the observation that the homopolymers penetrate deeply into the interfacial region and overlap with one another, even though theory would predict that the extent of homopolymer penetration should be small. Secondly, it is directly evident that the copolymer orders at the interface with the junction points between the S and MMA blocks being confined to a narrow region at the interface. Thirdly, it was quantitatively shown that the copolymers are not substantially stretched at the interface and are comparable in dimension to that which is found in the bulk lamellar morphology. Finally, the area per copolymer molecule at the interface is increased by nearly 30% due to the penetration of the homopolymer into the interfacial region.

Thus, by a combination of a variety of techniques, an in depth picture of the state of the copolymer molecules at the interface is beginning to emerge. This problem is, however, far from solved, since there are numerous parameters that must be taken into account. These include the molecular weights of the copolymer and homopolymers, the χ parameter between the blocks of the copolymers and the homopolymers, the symmetry of the copolymer molecules, and the correlation of these findings with the mechanical properties and adhesion between the homopolymers.

Conclusion

In this article, it has been shown that there have been several important developments in the methods that can be used to address the surface and interfacial behavior of polymers. In particular, the subject of diblock copolymers was used as an example where significant progress has been made over the past few years utilizing the different techniques that have become available. It was intended that this article give the reader a flavor of the type of studies that are now possible by a combination of techniques, and it has been stressed that no one technique provides all the answers. Each technique has its own strengths and weaknesses. Only by using these tech-

niques in a complementary manner can a quantitative description of the behavior of molecules be made.

The two areas selected are by no means the only areas where advances have been made. These happen to be areas in which the author is directly involved. There are many areas (far too many to enumerate here) where similar type of advances have been made. It is very clear that, experimentally, the interfacial behavior of molecules can now be addressed to obtain an absolute measure of the concentration profiles and critical comparisons can be made with existing theories. As more experimental results emerge in the next few years, it is inevitable that modifications and advances will be made theoretically.

[1] See, *e.g.* 'Developments in Block Copolymers-1', Ed. I. Goodman, Applied Science Pub., Essex, England, 1982.
[2] L. Leibler, *Macromolecules* **1980**, *13*, 1602.
[3] G. Fredrickson, *Macromolecules* **1987**, *20*, 2535.
[4] T. P. Russel, R. P. Hjelm, Jr., P. A. Seeger, *Macromolecules* **1990**, *23*, 890.
[5] P. F. Green, T. M. Christensen, T. P. Russel, *J. Chem. Phys.* **1990**, *92*, 1478.
[6] P. F. Green, T. M. Christensen, T. P. Russell, *Macromolecules,* in press.
[7] S. H. Anastasiadis, T. P. Russell, S. K. Satija, C. F. Majkrzak, *Phys. Rev. Lett.* **1989**, *62*, 1852.
[8] G. Coulon, T. P. Russell, V. R. Deline, P. F. Green, *Macromolecules* **1989**, *22*, 2581.
[9] T. P. Russel, G. Coulon, V. R. Deline, D. C. Miller, *Macromolecules* **1989**, *22*, 4600.
[10] G. Coulon, D. Aussere, T. P. Russell *J. Phys. Fr.* **1990**, *51*, 777.
[11] S. H. Anastasiadis, T. P. Russell, S. K. Satija, C. F. Majkrzak, *J. Chem. Phys.* **1990**, *92*, 5677.
[12] P. F. Green, T. P. Russell, R. Jerome, M. Granville, *Macromolecules* **1989**, *22*, 908.
[13] H. R. Brown, *Macromolecules* **1989**, *22*, 2859.
[14] R. Fayt, R. Jerome, Ph. Teyyssié, T. Ouhadi, *Polym. Commun.* **1986**, *27*, 212.
[15] K. Shull, E. J. Kramer, G. Hadziioannou, W. Tang, *Macromolecules,* in press.
[16] P. F. Green, T. P. Russell, submitted to *Macromolecules.*
[17] V. S. Wakharkar, T. P. Russell, V. R. Deline, submitted to *Macromolecules.*
[18] T. P. Russell, S. H. Anastasiadis, A. Menelle, G. P. Felcher, S. K. Satija, submitted to *Macromolecules.*
[19] V. S. Wakharkar, T. P. Russell, V. R. Deline, *Proc. Mat. Res. Soc.,* in press.