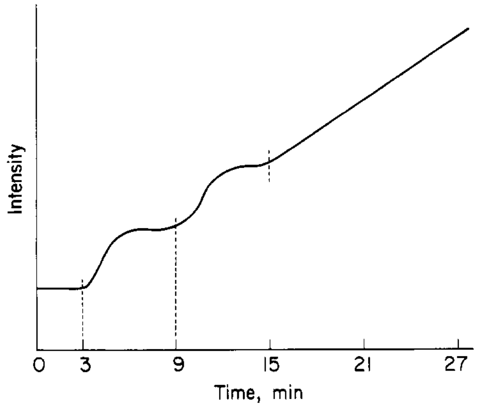

Figure 3. Intensity vs. time response for an immiscible blend.

of the acrylics in polystyrene.

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Appendix

In the melt titration technique the photocell unit records the intensity as a function of time. To obtain an intensity vs. concentration (or weight fraction) curve from the intensity vs. time data, the following procedure was adopted.

A typical intensity vs. time response for an immiscible blend is shown in Figure 3. The residence time in the extruder is 3 min, so the polymer film at the die is clear and intensity is constant. At the end of 3 min the second component, in the form of a second phase, is seen at the die and there is an increase in the scattered light or intensity. The concentration of the second component is approximately equal to the ratio of the flow rates of the two components. This concentration remains the same until the second component is recycled into the hopper of the extruder. At this time, the concentration at the inlet of the extruder is twice the ratio of the flow rates of the two components. The total residence time in the system for the polymer is 6 min, so there is an increase in the intensity after 9 min. It is observed that the intensity vs. time response becomes linear after about two residence times in the system. After this time the concentration of the second component is taken as an average. For quite miscible blends the curve is shifted to the right, and the miscibility limit is calculated from the shift in time.

The following equations are used to calculate the weight fraction of the second component (weight fraction (W) $\simeq$ concentration):

$$W = 0 \qquad 0 \leq t \leq 3 \tag{13}$$

$$W = M_2/M_1 \qquad 3 < t \leq 9 \tag{14}$$

$$W = 2M_2/M_1 \qquad 9 < t \leq 15 \tag{15}$$

$$W = (t - 3)M_2/Z \qquad t > 15 \tag{16}$$

where t is the time corresponding to the location of the cloud point, M_2 and M_1 are the mass flow rates of components 2 and 1, respectively, and Z is the total quantity of component 1 in the system.

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Model Estimate for the Relaxation Time of the Counterion Distribution in the Radial Direction around a Rodlike, Charged Macromolecule

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ABSTRACT: A deviation of the equilibrium counterion distribution around a charged macromolecule, disappearing in a direction perpendicular to the chain, is investigated. To estimate the relaxation time τ of such a process, an approach, based on the Katchalsky cell model of polyelectrolyte solutions without salt, is developed and a steady-state counterion flow in the radial direction with respect to the macromolecular rod is considered. The results of a numerical analysis show for τ a remarkable independence of electrostatic interactions and values which lie close to those for free diffusion.

Introduction

Many properties of polyelectrolyte solutions reflect the strong interaction of the counterions with the macroions. The counterions concentrate in the vicinity of the polymer chain and stay there during a certain time, trapped in the strong electrostatic potential existing around the charged macromolecule. Lifson and Jackson[1] have studied the average time of association in relation to the problem of

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the low self-diffusion constant of ions in polyelectrolyte solutions. They estimated the average time of escape, i.e., the time it takes a counterion to move from the region close to the macromolecular chain to a specified boundary, under the combined effect of thermal agitation and a stationary field of force. The latter was derived from the solution of the Poisson–Boltzmann equation assuming cylindrical symmetry, which yields the equilibrium distribution of the counterions in the radial direction.[2]

A problem closely related to the preceding one seems to be relevant for understanding the dielectric properties of polyelectrolyte solutions. Both the static value and the frequency dependence of the electric permittivity are thought to be related to the properties of the counterion cloud around the polyion which in the absence of additional salt and for relatively high charge densities on the macromolecular chain may be assumed to be rodlike. In that case the relaxation times of a fluctuation in the counterion density disappearing by charge transport in the axial and in the radial direction may be important quantities.[3] In this paper we consider the latter process for a charged macromolecule in the absence of additional salt and estimate the characteristic time for the disappearance in the radial direction of a perturbation in the equilibrium distribution of the counterions. This perturbation will be expressed in terms of an "excess ion concentration" with respect to the equilibrium distribution and the charge transport will occur in the electrostatic field of the screened polyion charge. The influence of the excess ion concentration on this field and the way it affects the relaxation process will be taken into account.

Model and Estimate for the Relaxation Time

The Katchalsky cell model[2] was chosen to describe the polyelectrolyte solution. The polyion is represented as a uniformily charged rod of radius a in the axis of a coaxial cell. The radius R of this cell is inversely proportional to the square root of the volume fraction of the polyelectrolyte and end effects are neglected. For a full description of the model the original papers should be consulted.

Under equilbrium conditions all nonuniform quantities inside a cell only depend on the distance r from its axis. The following equations, compatible with the ones used by Katchalsky, hold in the absence of salt and for a negatively charged polyion:

$$\tilde{\mu}(r) = \psi^\circ + kT \ln n(r) + zq\psi(r) \tag{1}$$

$$m(r) = \nu - z\int_a^r n(r) 2\pi r \, \mathrm{d}r \tag{2}$$

$$\psi(r) = \psi(R) + \frac{q}{2\pi\epsilon_0\epsilon}\int_R^r m(r) \, \mathrm{d} \ln r \tag{3}$$

Here $\tilde{\mu}(r)$ is the the local electrochemical potential of the positive counterions, μ° their standard chemical potential, and z their valency. The local counterion number density and average electrostatic potential at position r are given by $n(r)$ and $\psi(r)$, respectively. The linear charge density ν of the rod is expressed as the number of elementary charges q per unit length. Then $m(r)$ represents the net number of charges per unit length of a coaxial cylinder with radius r containing the polyion and counterions and eq 3 follows from Gauss's law. Note that SI units are used throughout and that ϵ_0 and ϵ stand for the absolute permittivity of free space and the relative permittivity of the solvent (considered here to be a continuum). At equilibrium the cell, which is electroneutral, can be subdivided into sections of height dh which are normal to the axis and for which the electroneutrality condition also holds. This can be expressed by

$$m_0(R) = 0 \tag{4}$$

(the subscript zero indicating a value referring to equilibrium). The electrochemical potential must be uniform throughout, which yields the Boltzmann distribution of counterions:

$$\ln \frac{n_0(r)}{n_0(R)} = -\frac{zq}{kT}[\psi_0(r) - \psi_0(R)] = -\frac{zq}{kT}\Delta\psi_0(r) \tag{5}$$

We now assume that the axial distribution of counterions has been perturbed and is no longer uniform in that direction. Consequently, the total number of counterions in each section is changed and, although electroneutrality over the complete cell is maintained, this is no longer true for each section. Such a perturbation will give rise to a current of counterions determined by the gradient of the electrochemical potential. In a first-order approximation we assume that within a given section the perturbation is cylindrically symmetrical and that eq 1–3 are still obeyed. We therefore consider within a section only the current in the radial direction. Under these conditions the total current per unit length which crosses the cylindrical surface at r will be given by $B(r)$

$$B(r,t) = -2\pi r n(r,t) u \, \partial\tilde{\mu}/\partial r \tag{6}$$

where u is the counterion mobility, assumed to be position independent. As a consequence of this current, the local counterion density will, in general, change with time

$$\frac{\partial n(r,t)}{\partial t} = -\frac{1}{2\pi r}\frac{\partial}{\partial r}B(r,t) = +\frac{u}{r}\frac{\partial}{\partial r}\left[r n(r,t) \frac{\partial \tilde{\mu}}{\partial r} \right] \tag{7}$$

subject to conditions 1–3. We consider only small perturbations $n'(r,t)$ of the local counterion density with respect to its equilibrium value

$$n(r,t) = n_0(r) + n'(r,t) \tag{8}$$

and neglect in all expressions contributions in n'^2 or higher powers of n'. The time and position-dependent electrochemical potential $\tilde{\mu}(r,t)$ according to (1) may be written in the following way, using also (5):

$$\begin{aligned} \tilde{\mu}(r,t) = {} & \\ & \mu^\circ + RT \ln n_0(r) + RT\frac{n'(r,t)}{n_0(r)} + zq\psi(r,t) + \mathcal{O}(n'^2) = \\ & \mu^\circ + RT \ln n_0(R) + zq\psi_0(R) + RT\frac{n'(r,t)}{n_0(r)} + \\ & zq\psi'(r,t) + \mathcal{O}(n'^2) \end{aligned} \tag{9}$$

Here the definition of $\psi'(r,t)$ has been used

$$\psi'(r,t) \equiv \psi(r,t) - \psi_0(r) \tag{10}$$

The potentials ψ_0 and ψ' may be obtained from (2)–(4) in the following form:

$$\begin{aligned} \Delta\psi_0(r) \equiv \psi_0(r) - \psi_0(R) = {} & \frac{q\nu}{2\pi\epsilon\epsilon_0}\ln\frac{r}{R} - \\ & \frac{zq}{2\pi\epsilon\epsilon_0}\int_R^r\left[\int_a^r n_0(r')2\pi r' \, \mathrm{d}r'\right]\frac{\mathrm{d}r}{r} = \\ & \frac{-zq}{2\pi\epsilon\epsilon_0}\int_R^r\left[\int_R^r n_0(r')2\pi r' \, \mathrm{d}r'\right]\frac{\mathrm{d}r}{r} \end{aligned} \tag{11}$$

$$\Delta\psi'(r,t) \equiv \psi'(r,t) - \psi'(R,t) = \frac{-zq}{2\pi\epsilon\epsilon_0}\int_R^r\left[\int_a^r n'(r',t)2\pi r'\,\mathrm{d}r'\right]\frac{\mathrm{d}r}{r} \quad (12)$$

Substituting (9)–(12) into (6), the counterion current may be written up to linear terms in n' as follows:

$$-B(r,t) = 2\pi rukT\,\frac{\partial n'}{\partial r} - \frac{(zq)^2u}{\epsilon\epsilon_0}\left(n'\int_R^r n_0 2\pi r'\,\mathrm{d}r' + n_0\int_a^r n' 2\pi r'\,\mathrm{d}r'\right) + \mathcal{O}(n'^2) \quad (13)$$

This expression shows that within the linear approximation in n' the counterion current contains three contributions: the first one corresponds to the free diffusion of the excess counterions (with respect to the equilibrium situation) without any electric effect, the second would correspond to the current of the excess counterions moving under the influence of the local field strength $\partial\psi_0/\partial r$ as existing at equilibrium, and, finally, the last contribution would arise from the current of the counterions as distributed at equilibrium moving under the influence of the perturbation of the local field strength $\partial\psi'/\partial r$.

If we would consider a localized, instantaneous fluctuation at $t = 0$ appearing on the surface of the polyion and of amplitude A, i.e., $n'(r, t = 0) = A\delta(r - a)$, substitution of (13) into (7) and solving the differential equation subject to the condition $\lim_{t\to\infty} n'(r,t) = 0$ would yield an expression for $n'(r,t)$ describing the decay of this fluctuation. Such a procedure is, however, difficult to perform. Therefore we describe a somewhat different situation which will enable us nevertheless to estimate the relaxation time of a perturbed counterion distribution. Consider the case where we impose a steady state with a time-independent distribution $\bar{n}(r) = n_0(r) + \bar{n}'(r)$ deviating from the equilibrium one by injecting continuously counterions near $r = a$ and removing counterions near $r = R$, subject to the condition $\bar{n}'(R) = 0$. The condition of stationarity

$$\partial\bar{n}(r)/\partial t = 0 \quad (14)$$

imposes that in such a state the counterion current $\bar{B}$ should be position independent, as follows from (7). In this stationary state the counterion density at any position r does not change as the constant current $\bar{B}$ takes care of maintaining the distribution $\bar{n}(r)$ constant in time. If at a sudden moment this current $\bar{B}$ could be "switched" off, the excess counterions would disappear with an *initial* velocity equal to the current $\bar{B}$. Therefore we may define a time τ by

$$\tau = \frac{1}{\bar{B}}\int_a^R \bar{n}'(r)2\pi r\,\mathrm{d}r \quad (15)$$

which may be considered a measure for the relaxation time of the decay of an additional input of ions superimposed on the equilibrium counterion density, provided such a process is purely exponential.

To evaluate τ from (15) solutions for $\bar{n}'(r)$ and $\bar{B}$ compatible with (7), (8), (13), and (14) are required. No analytical solution has been found but fortunately a numerical approach is possible. If we consider a small variation Δr, we have

$$\bar{n}'(r + \Delta r) \simeq \bar{n}'(r) + \left(\frac{\partial\bar{n}'}{\partial r}\right)_r\Delta r \quad (16)$$

But $(\partial\bar{n}'/\partial r)_r$ may be obtained from (13) in a form suitable for further numerical evaluation. Thus

$$\bar{n}'(r + \Delta r) \simeq \bar{n}'(r) + \frac{\Delta r}{2\pi rukT}\left[\frac{(zq)^2u}{\epsilon\epsilon_0}\left(\bar{n}'(r)\int_R^r n_0(r'')2\pi r''\,\mathrm{d}r'' + n_0(r)\int_a^r \bar{n}'(r'')2\pi r''\,\mathrm{d}r''\right) - \bar{B}\right] \quad (17)$$

The equilibrium counterion density $n_0(r)$ is known from the analytical solution of the Poisson–Boltzmann equation;[2] therefore $\bar{n}'(r + \Delta r)$ can be calculated from (17) if $\bar{n}'(r'')$ for $a \le r'' \le r$ and $\bar{B}$ are known.

The following procedure has been followed. First a value for $\bar{n}'(a)$ is chosen together with a first estimate for $\bar{B}$. (Note that, as both $\bar{B}$ and $\bar{n}'$ are linearly dependent on $\bar{n}'(a)$, an arbitrary choice of $\bar{n}'(a)$ does not affect the value of τ.) Repeated use of (17) yields a value for $\bar{n}'(R)$, which is then compared to the value imposed by the boundary condition; i.e., $\bar{n}'(R) = 0$. As long as $\bar{n}'(R) > \delta$, where δ is a specified small value, the procedure is repeated after modification of $\bar{B}$. The value of δ is chosen in such a way that any value of $\bar{B}$ and the corresponding distribution $\bar{n}'(r)$ satisfying the condition $\bar{n}'(R) < \delta$ yield the same value of τ within 0.01% according to (15).

Numerical Results and Discussion

Only monovalent counterions ($z = 1$) have been considered. The following values were assigned to the parameters involved: $T = 293$ K, $u = 3.1 \times 10^{11}$ m s^{-1} N^{-1}, $\epsilon = 80$, and $a = 0.15$ nm. The length of the macromolecular rod carrying one monovalent charged group was generally chosen to be $h = 0.25$ nm, corresponding to a completely charged, monofunctional vinylic-type polyelectrolyte. In a few cases, $h = 0.075$ nm was also considered. Calculations have been performed for different values of the cell radius R corresponding to different polymer concentrations according to the formula $C = 10^{-3}(\pi N_{\mathrm{Av}}hR^2)^{-1}$, where C is expressed in equivalents (or monomol) per liter.

Special attention has been paid to the choice of the magnitude of the step length Δr in (17) in order to obtain with sufficient detail the equilibrium distribution $n_0(r)$ by numerical solution of the Poisson–Boltzmann equation proposed by Katchalsky[2] and to perform the numerical integration adequately. A variable Δr was used, changing from $\Delta r = 2 \times 10^{-5}R$ in the vicinity of the rod surface ($r = a$) to $\Delta r = 5 \times 10^{-4}R$ close to the boundary of the cell ($r = R$), with a total of 5000 steps.

The relaxation time τ has been calculated considering four different situations. The first one corresponds to free diffusion and in (13) only the contribution of the first term on the right-hand side of the equation is taken into account; this relaxation time is simply given by $\tau^{(1)} = R^2/4\pi kT$. In the second situation the third term on the right-hand side of (13) has been neglected, implying that the counterions move in the field of the equilibrium potential; values of $\tau^{(2)}$ thus obtained are related to those of the average time of escape τ_{LJ} as calculated by Lifson and Jackson.[1] In the third situation the second term on the right-hand side of (13) has been omitted, for reasons of comparison only ($\tau^{(3)}$). Finally the relaxation time has been calculated by using the complete expression (13). The results obtained in these different calculations are compared in Figure 1 and in Table I. In Figure 2 the excess concentration of counterions as a function of r are represented for different cases.

The results compiled in Table I and Figure 1 reveal that the relaxation time, under all circumstances, is a decreasing

Table I
Estimates for the Relaxation Times τ in Radial Directions[a]

R, nm	h, nm	C, equiv L^{-1}	relaxation time, s			
			τ	$\tau^{(1)}$	$\tau^{(2)}$	$\tau^{(3)}$
26	0.25	3×10^{-3}	1.2×10^{-7}	1.4×10^{-7}		
46	0.25	10^{-3}	4.0×10^{-7}	4.3×10^{-7}	3.9×10^{-6}	2.7×10^{-7}
46	0.075	3.3×10^{-3}	3.9×10^{-7}	4.3×10^{-7}	3.9×10^{-6}	2.7×10^{-7}
82	0.25	3×10^{-4}	1.3×10^{-6}	1.4×10^{-6}	1.3×10^{-5}	8.7×10^{-7}
82	0.075	10^{-3}	1.3×10^{-6}	1.4×10^{-6}	1.3×10^{-5}	8.7×10^{-7}
260	0.25	3×10^{-5}	1.3×10^{-5}	1.4×10^{-5}	1.4×10^{-4}	8.9×10^{-6}
600	0.25	3×10^{-7}	1.3×10^{-3}	1.4×10^{-3}	1.6×10^{-2}	9.0×10^{-4}

[a] See text for symbols.

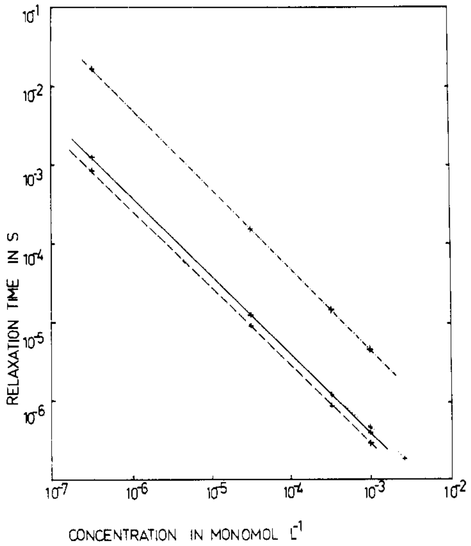

Figure 1. Calculated concentration dependence of the relaxation time as a function of concentration (h = 0.25 nm): (···) $\tau^{(1)}$; (·–·) $\tau^{(2)}$; (– – –) $\tau^{(3)}$; (—) τ from complete expression (13).

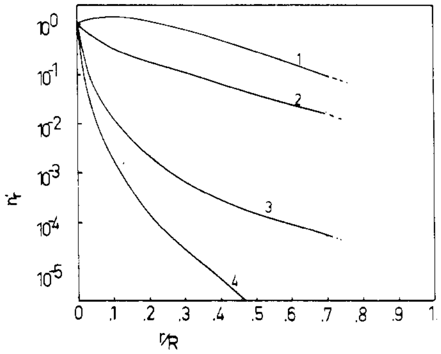

Figure 2. Steady-state distribution of n' (in arbitrary units) as a function of r ($R = 0.46 \times 10^{-7}$ m, $C = 10^{-3}$ equiv l^{-1}) for different situations according to (17): (1) third term in (17) not taken into account (as for $\tau^{(2)}$); (2) case of free diffusion (as for $\tau^{(1)}$); (3) all terms taken into account (as for τ); (4) second term in (17) not taken into account (as for $\tau^{(3)}$).

function of concentration at constant h (constant charge density). Remarkably enough, it is the value of R, independently of the concentration and h, which determines the value of τ. Different concentrations but corresponding to different values of h such that R is constant yield practically the same value for the relaxation time according to the present calculation. Although a change in the linear charge density on the rod at constant R has an important effect on the equilibrium distribution of the counterions, the relaxation time of a perturbation in this distribution seems to be unaffected.

It is evident also that the different contributions appearing in the current $\bar{B}$ have separately an important effect on the value of τ but that some mutual compensation seems to arise when taken into account all together. A simple explanation for this compensation, which leads to the surprising conclusion that the relaxation time for "free" diffusion does not differ significantly from the relaxation time calculated with the complete expression (13), is at present not available. It is the more remarkable as the distribution of the excess counterions does significantly depend on the various contributions taken into account for the calculation of $\bar{B}$, as shown in Figure 2.

The discrepancy between the values for τ as calculated here and the results of Lifson and Jackson should be emphasized. The time necessary for an ion to escape the equilibrium potential τ_{LJ} is remarkably longer than the relaxation time for the disappearance of an excess counterion density as calculated here. The ratio $\tau_{LJ}/\tau^{(1)}$ is proportional to $\exp(-q|\Delta\psi|/2kT)$, where $|\Delta\psi|$ represents the absolute value of the potential difference between the position where the ion is trapped and the position where it is assumed free. Although the exact value of $|\Delta\psi|$ may be open to discussion, it is reasonable to assume that $q|\Delta\psi|2kT$ is at least 2 or larger, which makes τ_{LJ} smaller than either $\tau^{(1)}$ or τ by a factor 10 or larger. Possibly this may be due to the fact that the excess ion density determines an additional electrostatic field which accelerates the ions.

In the present treatment it has been assumed that the perturbation of the equilibrium distribution is axially symmetric. Justification of this assumption depends on the time scales involved. In general, counterions will also exhibit motions around the axis of the macromolecular chain on coaxial equipotential surfaces. Provided these motions are much faster in comparison to the motion in perpendicular direction with respect to the macromolecule's axis, the assumption may be reasonable.

The relaxation time considered here may, among other things, be of importance in relation to the understanding of dielectric properties of polyelectrolyte solutions. It is generally assumed that the charged macromolecules are characterized by a large polarizability which is attributed to the associated counterions, the distribution of which along the more or less stretched macromolecular chain can be perturbed by an applied electric field. The electric dipole moment thus induced and its buildup may be affected by a counterion current perpendicular to the polyion axis, the latter being initiated by the field-induced local perturbation of the equilibrium between associated and free counterions. Such a mechanism has been considered in a separate paper[3] and its influence on polarizability and relaxation discussed. The relaxation time as estimated here may be used as an estimate for the characteristic time of the exchange process, as has been done previously,[3] but it should be realized that the models used in both papers are different and therefore may lead to some inconsistencies. In particular, it is not clear which value of R should be used in the evaluation of τ according to the present treatment in order to match the conditions of the two-phase model used in the other paper. Therefore conclusions concerning the dipole moment and its relaxation behavior of polyelectrolytes based on the mechanism discussed previously[3] and on the numerical values of τ derived here should be considered with proper care.

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Excimer Fluorescence as a Molecular Probe of Blend Miscibility. 4. Effect of Temperature in Solvent Casting

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ABSTRACT: Excimer fluorescence from poly(2-vinylnaphthalene) (P2VN) is utilized in conjunction with observations of optical clarity to assess the thermodynamic state of blends of P2VN with poly(*n*-butyl methacrylate) (PnBMA), poly(ethyl methacrylate) (PEMA), or poly(methyl methacrylate) (PMMA). When blends are prepared by solvent casting at temperatures greater than the glass transition temperature of the binary polymer 1/polymer 2 system, followed by quenching to an examination temperature below T_g, the fluorescence and optical properties are characteristic of the morphology in thermodynamic equilibrium at the casting temperature. The phase relationships for such equilibrium P2VN/PnBMA blends are described quite well by a Flory–Huggins treatment with a temperature-dependent binary interaction parameter. All P2VN/PMMA and P2VN/PEMA blends prepared by solvent casting below T_g are in nonequilibrium states; apparent miscibilities for the P2VN/PMMA blend are much higher than predicted by the Flory–Huggins treatment.

Introduction

Due to the relative ease with which material properties may be modified by physical blending, considerable attention has been focused recently on the thermodynamics of amorphous polymer blends.[1-5] Although a number of sophisticated experimental techniques, including neutron, light, and X-ray scattering, pulsed nuclear magnetic resonance, differential scanning calorimetry, and electron microscopy, have been used to observe phase separation, none provides detailed information on the segmental level. Moreover, the existing methods lack the sensitivity for detection of blend components at concentrations less than about 10%.

This is part of a series of papers in which a relatively new spectroscopic method, excimer fluorescence, is used as a molecular probe of polymer blend morphology. A critical requirement for application of the excimer probe technique is the existence of "excimer-forming sites", which result when two identical aromatic rings in their electronic ground states are physically apposed in a coplanar sandwich arrangement at the equilibrium van der Waals separation distance.[6] Excitation of one member of this paired structure by direct absorption of light or by energy transfer from a nearby excited ring may lead to the formation of an electronically excited complex, the excimer. Since the ground state of the excimer is repulsive, there is no absorption spectrum characteristic of the complex; the excimer may be examined only by fluorescence methods.

Excimer fluorescence has been observed in a wide variety of aromatic vinyl polymers in which the excimer-forming site may result from intramolecular association between aromatic rings on adjacent or nonadjacent repeat units or from intermolecular association between rings on different polymer chains. Excimer-forming sites are of great photophysical importance in aromatic vinyl polymers, even at low concentration, because the electronic excitation energy can migrate from chromophore to chromophore. This migration takes place nonradiatively by resonance transfer between an electronically excited chromophore and a ground-state chromophore. Radiationless energy transfer has been reviewed for aromatic molecules in general by Förster[7] and Berlman[8] and for aromatic vinyl polymers in particular by Klöpffer.[9]

In this work, as in previous studies, excimer fluorescence from an aromatic vinyl polymer introduced as a guest in a matrix of a nonfluorescent host polymer is used to study low-concentration miscibility and small-scale phase separation. Previous papers focused on three variables important to polymer–polymer miscibility: enthalpic segmental interaction between guest and host polymer,[10] concentration of the guest polymer in the host matrix,[11] and molecular weights of the guest and host polymers.[12] The objective of this study is to determine the effect of casting temperature. Major emphasis is placed on two series of blends in which the guest aromatic vinyl polymer is poly(2-vinylnaphthalene) (P2VN) and the nonfluorescent host polymer is either poly(*n*-butyl methacrylate) (PnBMA) or poly(methyl methacrylate) (PMMA). A smaller amount of work is performed on blends of P2VN with poly(ethyl methacrylate) (PEMA). These particular hosts were selected because the enthalpic interactions with P2VN are sufficiently dissimilar to yield distinctly different phase relationships, and the glass transition temperatures differ widely, providing an opportunity to study nonequilibrium aspects of solvent casting.

Experimental Section

P2VN was prepared by bulk thermal polymerization and purified by precipitating three times from toluene by addition of methanol.[10] PnBMA and PMMA were obtained from Polysciences (PnBMA, catalog no. 2061, lot no. 21-38-7; PMMA, catalog no. 4553) and purified by precipitating three times from acetone by addition of deionized water. The sample of PEMA was an Elvacite acrylic resin type 2043 obtained from du Pont and purified in the same manner as PnBMA and PMMA. It was not a pure homopolymer, as indicated by the manufacturer's notation that it was

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