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Chiral Studies across the Spectrum of Polymer Science[†]

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ABSTRACT
This Account describes how stereochemical ideas focused on chirality have been directed widely across polymer science allowing experiments that could not be conducted on small molecules and leading to new insights and new kinds of materials. In one approach, a helical polymer was studied, and it was discovered how the chiral information necessary to choose helical sense is greatly amplified. In another approach, the racemization kinetics of atropisomers were used to characterize the restrictions to motion associated with a polyelectrolyte that forms clusters around hydrophobic groups in water and in an entirely different system, the glassy state formed by polymers.

Introduction

Optical activity has played a valuable historical role in studies of biological macromolecules and their synthetic analogues.[1] The kinetics of protein denaturation were first studied by following the change in optical activity.[2] This was later suggested to arise from loss of helical conformations in the native protein,[3] a hypothesis that was substantiated by studies of helix−coil transitions in synthetic polypeptides.[4] The role of triple helix formation in the gelation of gelatin has been studied using optical activity.[5] Optical activity enables following the conformational changes in polypeptides that are composed of D- and L-amino acids,[6] a study which acts as a precedent for observations to be reported in this Account. Optical activity has also been used to study the exceptional solvent-dependent helical properties of poly(L-proline).[7]

In the formation of stereoregular polymers leading to the Nobel Prize for Ziegler and Natta, chirality is involved as the key element, although optical activity cannot be measured because of the symmetry consequences of very long chains.[8,9] However, such chains adopt helical conformations, which can be induced to take an excess helical sense by incorporation of chiral side chains.[8] Recently, optical activity has been increasingly used for the study of conformational properties in synthetic polymers and their supramolecular states.[8,10,11]

In this Account we show that optical activity can be used as a highly effective tool to study three widely divergent problems in polymer science. First, we studied how a helical polymer responds to chiral information in choosing helical sense. We discovered a large amplification of chirality, which can be described by the tools of statistical physics and leads to materials with a new kind of relationship between optical activity and temperature. Second, we used the racemization kinetics of an atropisomeric molecule to investigate the hydrophobic-driven capsule formation properties of a polyelectrolyte in water and discovered unexpected features that had been missed in decades of photophysical work. This led to a new kind of free-radical cage effect, opening up pH-dependent methods to form water-soluble graft copolymers. Finally, we used the racemization of bridged binaphthyls with oligophenyl "paddles" to yield otherwise unavailable information on restrictions to motion and heterogeneity within polymeric glasses. This work may lead to chiral-based approaches to information storage technology.

A Model for How Helices Tell Left from Right

Polyisocyanates[12] adopt a helical conformation without a preference for helical sense.[12−14] Figure 1 shows that stereospecific replacement of deuterium for one of the diastereotopic hydrogens of either the methylene group α or β to the isocyanate function in poly(n-hexyl isocyanate) leads to a large circular dichroism spectrum, which is caused by a large excess of one helical sense.[15,16]

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[†] Dedicated to the memory of our beloved colleague and teacher, Professor Shneior Lifson, of the Weizmann Institute.
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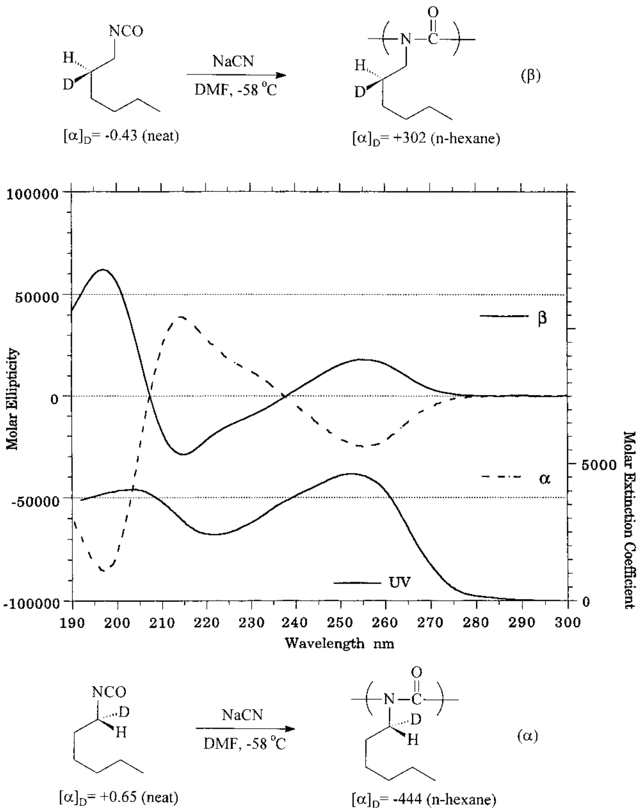
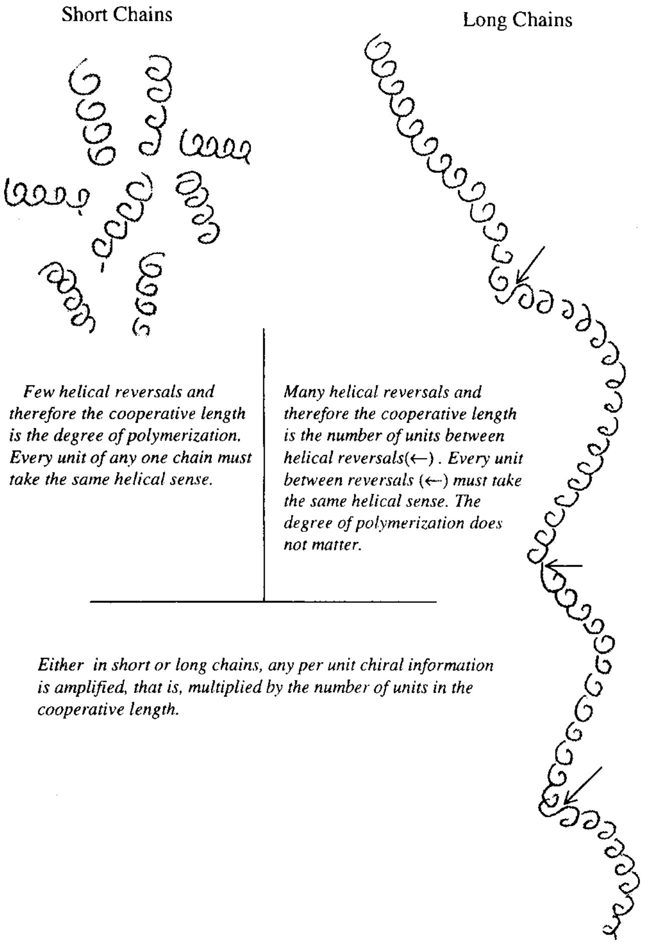


FIGURE 1. Circular dichroism and ultraviolet spectra of deuterated polyisocyanates. Reprinted with permission from ref 14.



Few helical reversals and therefore the cooperative length is the degree of polymerization. Every unit of any one chain must take the same helical sense.

Many helical reversals and therefore the cooperative length is the number of units between helical reversals(←). Every unit between reversals (←) must take the same helical sense. The degree of polymerization does not matter.

Either in short or long chains, any per unit chiral information is amplified, that is, multiplied by the number of units in the cooperative length.

FIGURE 2. Explanatory diagram of the cooperativity of a stiff helical polymer. Reprinted with permission from ref 13.

An overall qualitative picture to attempt to understand this surprisingly large influence of a small chiral effect is expressed in Figure 2, which shows that two energies would be involved. One is the free energy favoring one or the other helical sense per monomer residue, ΔG_h, while the second is the excess energy of converting a helical conformation to a helical reversal, ΔG_r.

The larger is ΔG_r, and the lower the temperature, the fewer the helical reversals and therefore the larger will be the number of units that must take the same helical sense. This is the cooperative length, L. A partition function was written[17] to describe this conformational picture, which gives rise to eq 1 for very long chains and eq 2 for short chains (Figure 2). These show how the ratio of the observed optical activity to the optical activity corresponding to a single helical sense, the chiral order parameter, $M = [\alpha]/[\alpha]_m$, moves toward unity with increasing the cooperative length. Thus in eq 2, for short chains, the term L does not appear, but rather the degree of polymerization, N, is the cooperative length and becomes the limit to the amplification. In eq 1, on the contrary, for long chains the population of helical reversals, determined by the Boltzmann relationship, $e^{\Delta G_r/RT}$, determines L.

$$[\alpha]/[\alpha]_m = M = (L\Delta G_h/RT)/((L\Delta G_h/RT)^2 + 1)^{1/2} \quad (1)$$

$$[\alpha]/[\alpha]_m = M = \tanh(\Delta G_h N/RT) \quad (2)$$

The predictions of this statistical physical analysis were quantitatively matched by experimental studies of the change of optical activity with temperature and degree of polymerization for both of the deuterated poly(n-hexyl isocyanates) shown in Figure 1. In this way, both controlling energies, ΔG_h and ΔG_r, were obtained.[18] The latter energy was in the range of about 4 kcal/mol, corresponding to about 800 units between helical reversals in poly(n-hexyl isocyanate) at ambient temperature.

The experimental studies[18] yielded a chiral bias energy, arising from the deuterium substitution (Figure 1), of near to a single small calorie per mole, an energy that would have virtually no effect in the absence of the amplification encountered here. This leads to an interesting situation, since such a minute energy cannot be interpreted by any available structural theory.[19]

This barrier to interpretation was taken to a further extreme by dissolving poly(n-hexyl isocyanate) in a series of nonracemic chiral solvents.[20] Here the chiral influence arises from outside the chain. Circular dichroism allowed observation of the excess helical sense produced, and application of the statistical physical approach in this case, while yielding approximately the same value of ΔG_r as above, gave ΔG_h values an *order of magnitude lower* than those energies arising from the deuterated polymers in Figure 1. The interesting relationships between the chiral solvent structures and their effect on the helical excess and sense also cannot be interpreted.[20,21]

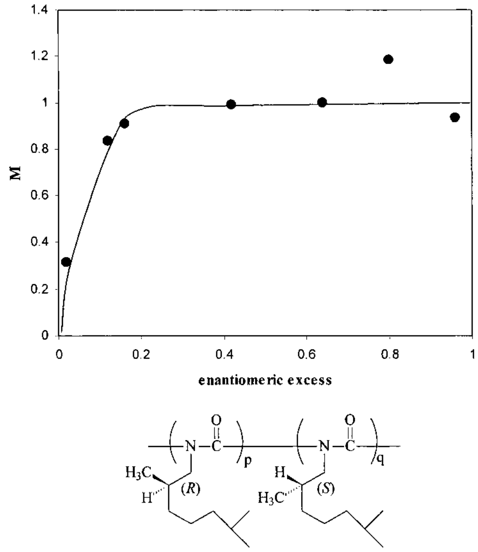


FIGURE 3. Fit of theory to experiment for the quenched random field Ising model and the optical activities of a majority rule copolyisocyanate. Adapted from ref 23.

Figure 3 shows how the chiral order parameter M changes with enantiomeric excess in a random copolymer synthesized from a mixture of enantiomers.[22] Why should the excess helical sense rise so steeply as one deviates slightly from the racemic state but then level off as the enantiomeric excess grows larger (Figure 3)? In a random system there are many different chains, so there is not a single applicable partition function and therefore not a specific description of the system as there was in eqs 1 and 2, where every chain is identically substituted.

This problem attracted the attention of statistical physicists who developed an approximate algebraic solution for the necessary Ising model. Consider conditions where the degree of polymerization is high and the number of helical reversals, arising from the magnitude of ΔG_r and the temperature, is low. Equations 3 and 4 then predict the relationship between the helical sense excess, expressed by the chiral order parameter M and the controlling parameters.

$$M = \mathrm{erf}[(2L_{\mathrm{rf}})^{1/2}(p - 1/2)] \tag{3}$$

$$L_{\mathrm{rf}} = (\Delta G_r/2\Delta G_h)^2 \tag{4}$$

In eq 3, as the proportion of the excess enantiomer, p, grows from 0.5, M will increase steeply and then level off as $p - 1/2$ grows larger following the mathematical nature of the error function, erf. This prediction is seen in the solid line passing through the experimental points in Figure 3.[23]

The key parameter in eq 3 is L_{rf}, the random field domain, the magnitude of which is defined by eq 4. In this random copolymer, in conflict to the deuterated system (Figure 1), the number of units between helical reversals, that is, the cooperativity, becomes a subject of the conflict in this system as defined by eq 4. This leads to a surprising, counterintuitive, prediction.

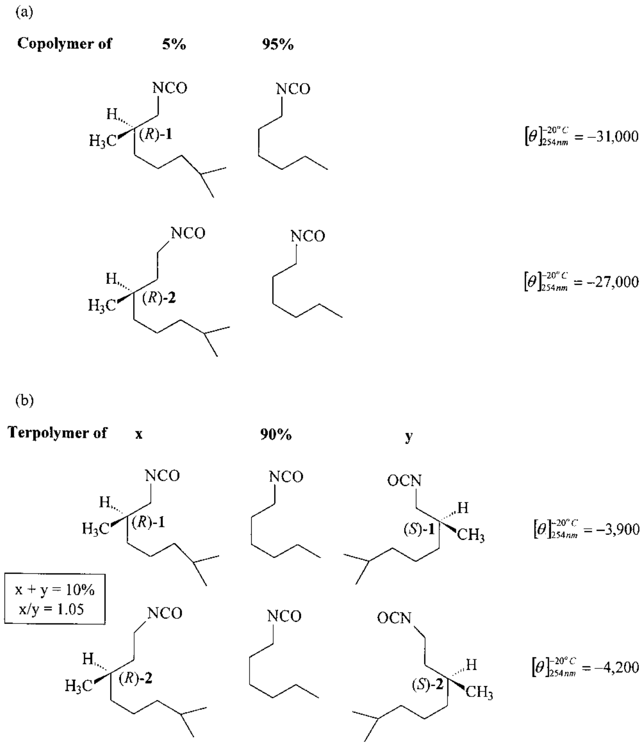


FIGURE 4. Effect of the extent of chiral bias on the helical sense properties of a copolyisocyanate and a terpolyisocyanate with different enantiomeric excesses.

Inspection of eqs 3 and 4 demonstrates that the larger the chiral bias, ΔG_h, the smaller will be the value of L_{rf}, and therefore the smaller will be the value of M. In other words, it is predicted that the *larger* the chiral force favoring one helical sense, the *smaller* will be the excess of that sense and therefore the optical activity.

Support for this surprising prediction can be seen experimentally by comparison of the top and bottom of Figure 4.[24] The top part of this figure, which corresponds to normal expectation, compares the molar ellipticity, which measures the excess helical sense in the two polyisocyanates. The chiral entities in the compared copolymers are both near to enantiomerically pure and differ in their relationship to the backbone by a single methylene group. Reasonably, the stereocenter that is farther away has less influence on the helical sense and the optical activity is lower, as observed (Figure 4, top).

In Figure 4 (bottom), the chiral units in each of the compared terpolymers are in a near to racemic state. In this majority rule system,[22] in contrast to the observation in the top part of Figure 4, the stereocenter *closer* to the helical backbone now yields the *smaller* optical activity.

In a cooperative situation one gets more by using less force.

What if the chiral units competing to control the helical sense were structurally different instead of enantiomers?[25] Since their structures are different, a balance will be achieved at some ratio other than 50:50. Moreover, in contrast to enantiomers, these structurally different chiral moieties would be affected differently by temperature. Each composition of the competing chiral units would

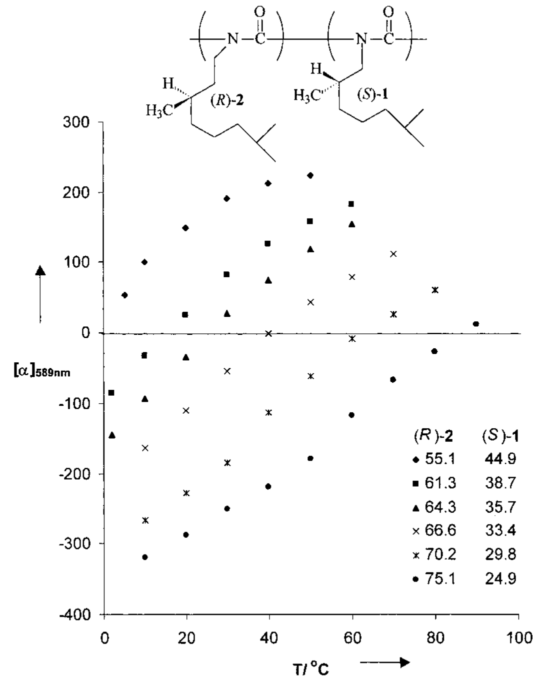


FIGURE 5. Temperature dependence as a function of composition for copolymers of structurally different enantiomers. Adapted from ref 25.

have a different balance temperature, and deviation below and above that temperature would favor one or the other of the chiral units competing for helical sense control. This is seen in the experimental data in Figure 5, which offer an unprecedented relationship between optical activity and temperature.[25−27]

Clearly, helical polymers offer many opportunities for new kinds of stereochemical experiments but, as shown below, polyelectrolytes, which focus on a completely different set of polymeric properties, yield equally interesting opportunities in a different manner, demonstrating how the fundamental nature of chiral studies offers wide applicability.

Chiral Insights into a Polyelectrolyte: Complexation of Hydrophobic Molecules

Whereas the increasing repulsion between anionic charges during the neutralization of poly(acrylic acid) (PAA) leads to a smooth expansion of the chain, poly(methacrylic acid) (PMA), which differs only in the presence of a methyl group at the tertiary carbon, resists expansion before a critical charge density is attained.[28]

In addition, whereas the p*K* of the polyelectrolyte rises smoothly with increasing ionization due to the increasing free energy required to ionize the remaining carboxylic acid groups in PAA, during the titration of PMA the p*K* first rises and then exhibits a plateau region before rising again.[29] This plateau region was interpreted as being due to a transition to a more expanded local conformation in PMA, so that a more highly ionized expanded conformation and a less highly ionized contracted conformation in equilibrium with each other have the same linear charge density and therefore the same p*K*.[30]

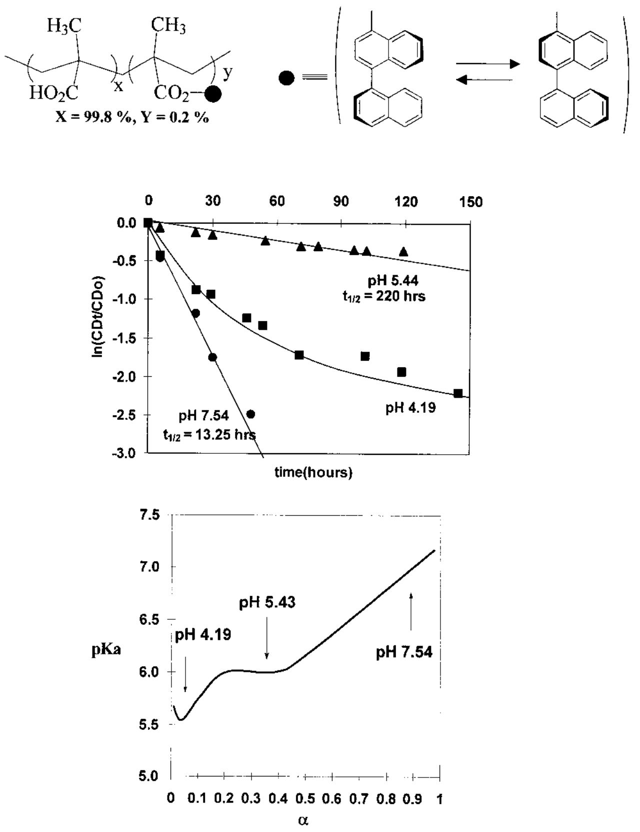


FIGURE 6. Racemization rate data as a function of pH and titration curve for a poly(methacrylic acid) with appended binaphthyl groups. Adapted from ref 36.

Aromatic species exhibit greatly enhanced fluorescence in aqueous PMA solutions below the pH characterized by the end of the p*K* plateau.[31] Fluorescence enhancement can be associated with hydrophobic environments or with restrictions to molecular motion, and both effects might result from the encapsulation of the chromophore by a portion of the PMA chain.[32,33] Despite intense effort using photophysical methods, little insight could be gained into these effects.[31−33]

We explored the racemization kinetics of a 1,1′-binaphthyl moiety attached to PMA as a measure of the extent to which the encapsulation interferes with molecular motion.[34−36] The results of the kinetic measurements of the racemization at three different pH are presented in Figure 6.[36] The racemization of the binaphthyl probe at the highest pH, 7.54, in the region[37] where the chain is no longer shielding the probe from its aqueous environment, yields racemization kinetics that are unaffected by the nearby macromolecule.

At the opposite extreme, near pH 4, the rate of racemization is slower and the intrinsic first-order kinetics are lost (Figure 6). This characteristic can be shown to arise from the atactic nature of the chain since in the stereoregular labeled syndiotactic PMA the rate, although still greatly slowed, follows strict first-order kinetics.[36] Apparently, the differing local stereochemical arrangements along the chain backbone in the neighborhood of the appended probe in the atactic polymer offer different encapsulated environments at pH 4.

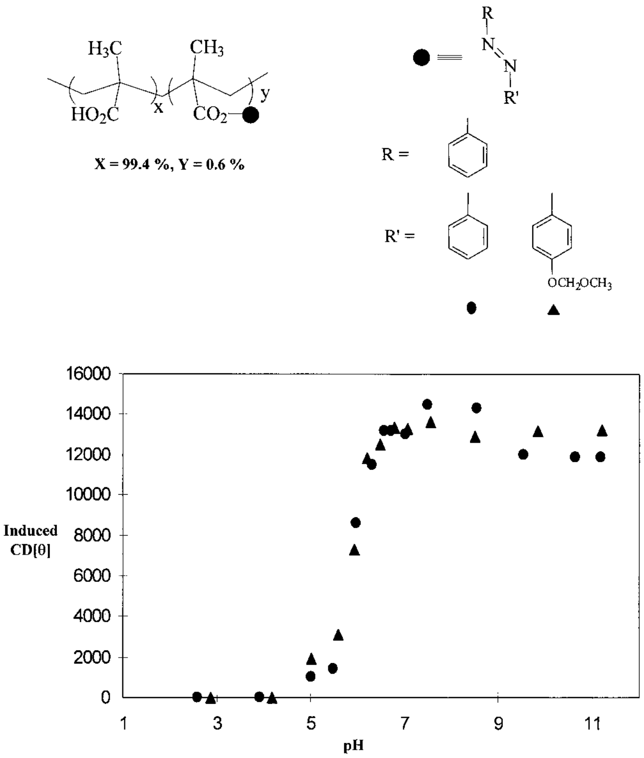


FIGURE 7. Induced circular dichroism intensity vs pH for poly(methacrylic acid) with appended azo dye molecule probes in the presence of α-cyclodextrin.

Against expectation (Figure 6), atactic PMA in the plateau region at pH 5.4, where the two local conformations are in equilibrium with each other,[30] exhibits slower racemization than that encountered at both higher and lower pH and exhibits excellent first-order kinetics.

Apparently, there is some readjustment of the capsule about its hydrophobic captive in the plateau region. This occurs just before increasing charge density forces the system to the most expandable conformation, which causes a loss of the racemization dependence on tacticity and allows the capsule to increase its restrictions on the racemization process.

The system readjusts its grip and holds tightest just before being forced to let go.

Could the hydrophobic capacity of a cyclodextrin be competitive with that of the PMA so that changing the pH could reversibly move the probe from one site to another with an interesting optical consequence? Aromatic chromophores in cyclodextrin cavities give rise to induced circular dichroism (CD) signals[34] so that reversible transfer of the aromatic moiety from the polyelectrolyte to the cyclodextrin could be detected by a chiral optical signal: "on" at high pH and "off" at low pH. Figure 7 confirms this expectation,[34−36] using various azo dyes and α-cyclodextrin, with a sharp pH dependence for the induced circular dichroism creating a pH-dependent chiral optical switch.

There is a reactive consequence of this polyelectrolyte encapsulation phenomenon. By appending small proportions of hydrophobic photoinitiators of polymerization to PMA chains, we created a cage effect for free radicals, which shows the same pH dependence found for the racemization properties of the binaphthyl probe. This leads to pH-dependent control for formation of graft copolymers in water, which form new kinds of physical hydrogels.[38]

Constraints to motion, as surprisingly seen in this polyelectrolyte in dilute solution in water, are often associated with the polymeric glassy state. Can stereochemistry play a role in the polymeric glassy state as well?

Atropisomeric Motion under Constraint in Polymeric Glasses

Polymer glasses offer a field of study of fascinating theoretical complexity in concert with great practical utility.[39]

Isomerizing probes have played an important role in gaining insight into the polymeric glassy state.[39,40] But the probe isomerization time scales have been so fast that they intersect the time scale of movements of small segments of the polymer chain very close to or above the conventionally measured temperature, T_g. This temperature defines the boundary between the rubbery and glassy states. It is the nature of these segmental motions, rather than motions of the entire polymer chain, that determines the temperature parameters defining the boundary to the glassy state. [41]

A valuable addition would be an isomerization with a far longer, and ideally variable time scale, especially one in which length scale could be varied without effect on the mechanism of the process. Such a probe might allow insights into the region below T_g that is difficult to study, that is, within the glassy state rather than at its boundary. Length scale is also important in studies of the glassy state since it may allow definition of the space available for motion in the highly entangled matrix.

Figure 8 shows a series of nonracemic atropisomeric-bridged binaphthyls with appended oligophenyl paddles at the 6 and 6′ positions and the kinetic data for their racemization in dilute solution in decalin.[42] As a side benefit to the use of these molecules for study of glasses, the data in Figure 8 provide a beautifully perfect example of a ponderal effect on rate, which is the retardation of a chemical process caused by the weight of rotors.[43] The slope in Figure 8b is precisely 0.5, which fits the relationship between vibrational frequency and mass, $\nu \propto (\text{force constant/mass})^{1/2}$. Since the force constant for twisting about the 1,1′ bond is independent of paddle mass,[42] increased mass of the paddle simply reduces the frequency for twisting about the 1,1′ bond, causing fewer passages over the barrier and therefore a reduced rate, which is reflected only in the preexponential factor.

With an energy of activation corresponding to a very slow rate of racemization, even at the T_g's of common polymer glasses, for example near 150 °C for conventional polycarbonate, these optically active atropisomers are unique candidates for studies within the polymeric glassy state.[44]

Figure 9a presents the dependence of the rate of

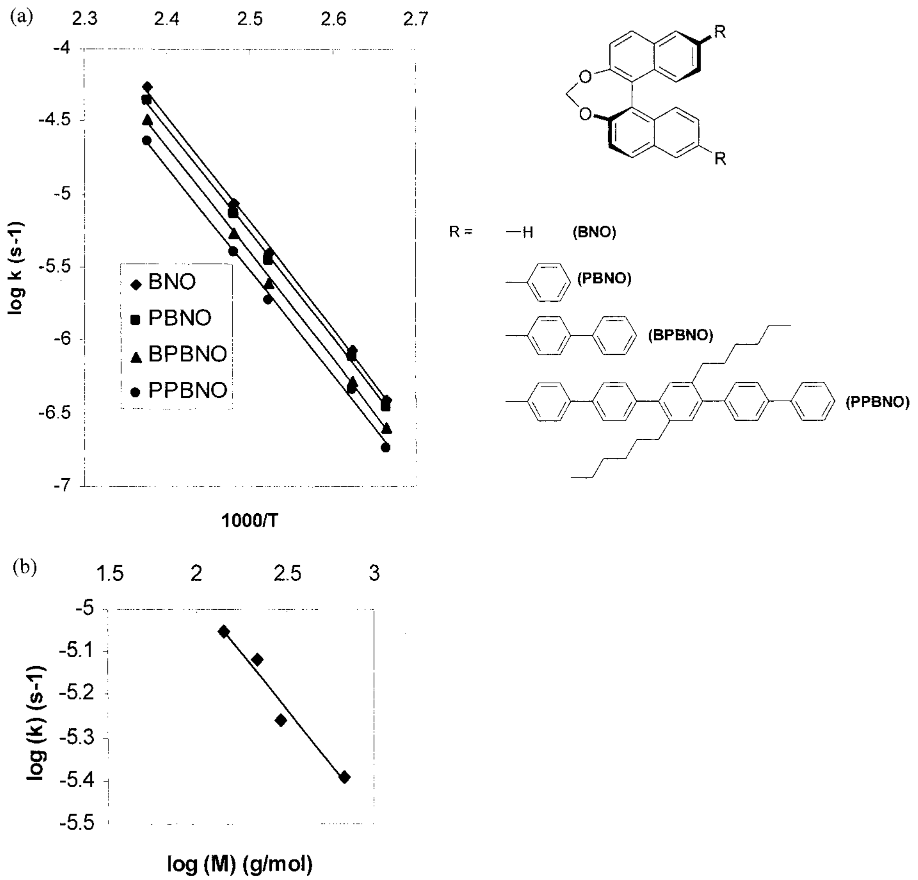


FIGURE 8. Racemization rate data in decalin as a function of paddle size for 6,6′-oligophenyl-substituted bridged 1,1′-binaphthyl-2,2′-diol. Adapted from ref 42.

racemization on inverse absolute temperature for the various binaphthyls shown in Figure 8 dissolved in a standard polycarbonate. The solid line crossing the racemization rate data is the independently determined rate of segmental motion of the polycarbonate with the two arrows pointing, respectively, to the glass transition temperature T_g and a temperature T_x at which the racemization rate approximately crosses that of the polymer segmental motions.

Three general points can be made. First, crossing T_g has no effect on the racemization rate for any of the probes studied. Second, there is a strong deviation from Arrhenius dependence only when the racemization rate crosses that of the segmental motion at T_x. Third, the smallest probe, BNO, is not affected by the motions of the matrix that affect the larger probes.

The data in Figure 9b point to loss of first-order kinetics for the racemization process when β deviates from unity. This is seen for all the probes at temperatures below T_x with the exception of the smallest probe, BNO, which in behavior parallel to what is seen in the Arrhenius dependence, is impervious in its rate expression not only to T_g, but to T_x as well.

This deviation from first-order kinetics may be interpreted in two ways. First, it may arise from the glass changing slowly with time over the time scale of the racemization, that is, from aging or structural relaxation. This is a well-known phenomenon in glasses, arising from their out-of-equilibrium nature.[45] Alternatively, the deviation from first-order kinetics may be associated with a heterogeneity of the glass[42] with a lifetime that is long compared to the racemization rate. In either situation there would be populations of probe molecules undergoing racemization in different environments.

If aging were the source of the deviation from first-order kinetics, speeding the rate of racemization should reclaim first-order kinetics since the racemization would be sampling its environment over a shorter time. But the opposite result would be expected if the source of the deviation from first-order kinetics were a long-lived heterogeneity.

This distinction was accomplished in two ways. Photochemical activation of the racemization in the polycarbonate, which speeds the rate, led to deviation from first-order kinetics occurring at higher temperature, that is, nearer to T_g. This is exactly opposite to the result that would be expected if aging plays a role in the kinetic results.

All polymer glasses have similar rates of segmental motions at their glass transition temperatures. This means that incorporating the probes in a structurally different polycarbonate, with a T_g higher than that studied in Figure 9, would lead the thermal rate of racemization to increase with respect to the segmental motions near to T_g. The racemization would be occurring at a higher temperature and therefore faster, but the segmental motions of the

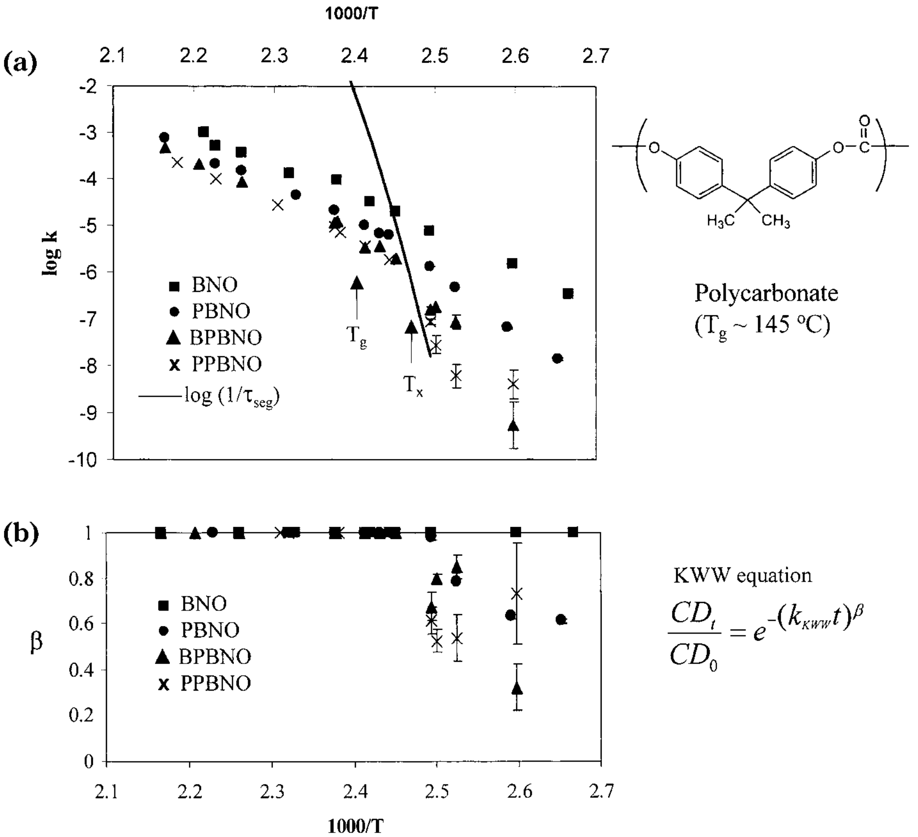


FIGURE 9. Arrehenius plots and kinetic order as a function of temperature for racemization of bridged paddled binaphthyls dissolved in polycarbonate. Adapted from ref 42.

glass forming matrix would remain about the same. Again the deviation from first-order kinetics was encountered closer to T_g,[42] the opposite of the result expected if aging were contributing to the kinetic observations.

These detailed kinetic experiments offer a quantitative picture of how the glass affects the probe motion. When the racemization rate crosses the time scale of the segmental motions (Figure 9a), the probes (with the exception of BNO) cannot undergo racemization faster than the polymer segments with which they are entangled. This is seen in the strong change in slope of the Arrhenius plot at T_x. In a parallel way, the glass heterogeneity is fixed on the time scale of the racemization only below T_x, so that there is an ensemble of microscopic environments leading to deviation from first-order kinetics. Only above T_x are the segmental motions of the polymer matrix fast compared to the rate of racemization allowing interconversions of these microscopic environments. The glass is then no longer heterogeneous on the time scale of the racemization. Finally, we discover from this work the minimum length scale for the entanglement with the polymer segments since BNO is unaffected. This yields the first quantitative measure below T_g of the length and time scale of the restriction to motion and heterogeneity of the glassy state.

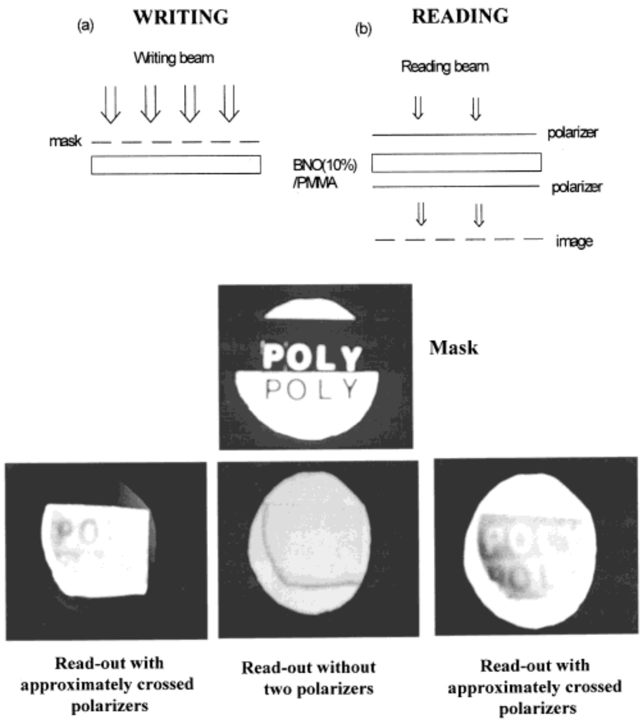


FIGURE 10. Chiral optical image in poly(methyl methacrylate) matrix. The two images are read with approximately crossed polarizers that are twisted in opposite directions.

Biot, early in the 19th century, used the glassy state to counter arguments that optical activity in the solid state arose from crystalline order. In that manner, the glass state added to the evidence that chirality had a molecular basis.[46] In this new tool based on atropisomerism,[47] molecular chirality, in a manner of speaking, returns the favor and is used to explore the nature of the glassy state itself.[48]

This effort might be of practical interest. The necessary index of refraction changes associated with ongoing attempts to develop a digital information storage material in a glassy polymer matrix are based on light-induced processes leading to shrinkage and light scattering.[49] An achiral polymer matrix would be oblivious to the changes associated with photochemically writing an image using racemization. Figure 10 shows such an image produced recently here at Brooklyn Poly.[50] It was made by photoracemization of a masked plastic disk of poly(methyl methacrylate) incorporating BNO (Figure 8). The image is then read between approximately crossed polarizers. Although this is not a digital image, it is the first demonstration we are aware of that chirality may be used to develop an image.

Summary

In our effort to use stereochemical ideas focused on chirality in the explorations of macromolecules, we gain new ideas and materials in diverse areas of polymer science. In helical polymers the work demonstrates how helical sense is chosen. The experimental observations are in quantitative agreement with statistical physical analysis. In addition, the effort pointed to a way to invent a material offering a new kind of relationship between optical activity and temperature.

The breadth of chirality allows us to move to an area of polymer science entirely unrelated to the helical studies. Atropisomeric binaphthyl groups appended as probes to poly(methacrylic acid) in dilute aqueous solution show surprising restrictions on the racemization rate, resembling what might be encountered in a polymer glass. This yields new information on the nature of the hydrophobic capsules formed by this polyelectrolyte and also leads to new kinds of materials in which aromatic chromophores can be passed between the polyelectrolyte capsules and cyclodextrins giving rise to pH-dependent changes in optical activity. These studies allow creation of poly(methacrylic acid) capsules acting as pH-dependent free radical cages when hydrophobic photolabile groups are appended to the chain, providing new ways to synthesize water-soluble graft copolymers.[38]

These restrictions to motion in polyelectrolytes suggest stereochemical studies directly on polymer glasses. In studies of atropisomeric racemizations, we are able to study restrictions to motion in polymer glasses below the glass transition in a manner allowing precise definition of both the length scale and the time scale of the entanglements. One gains previously unavailable insight into the glassy state and defines the nature of its heterogeneity. In addition, this work opens the door to the possibility for development of new approaches to information storage technology based on chirality.

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