Chiral Studies in Amorphous Solids: The Effect of the Polymeric Glassy State on the Racemization Kinetics of Bridged Paddled Binaphthyls

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Abstract: Optical activity, used here for the first time to gain information about the amorphous solid state, allows previously unavailable insight into the dynamic properties of polymer glasses and their effect on a chemical process. This is accomplished by dispersing in polymer glasses atropisomeric bridged binaphthyls with appended oligophenyl paddles of varying sizes and studying the racemization kinetics as a function of temperature. The racemization occurs by a simple one-dimensional twisting motion and, without effect on the intrinsic mechanism, sweeps out a variable volume of the matrix as the paddle length is increased. The racemization is limited by the polymer matrix only for probes with a minimum paddle size and only when the time scale for racemization is comparable to the time scale for segmental motion of the polymer matrix. The high barrier for this racemization is unique in probe studies of glasses and causes these overlapping time scales to occur significantly below the glass transition temperature. These measurements yield a clear quantitative view of the role of segmental dynamics on the racemization kinetics of the binaphthyls and allow the important demonstration, via the transition from first-order to stretched exponential kinetics, that heterogeneous dynamics persist deep within the glassy state.

Introduction

Constrained motion is the signature characteristic of supercooled liquids and the glassy states they form on further cooling.[1] This phenomenon, which is a subject of considerable interest,[2,3] can be seen not only in the motions of the molecules forming the glass but also in the motions of probe molecules incorporated in these materials. Investigations using probe molecules are especially common in the study of the melt and glass states formed by polymers,[4] and such efforts have proven invaluable in understanding the changes that occur as the ergodic melt is cooled into the nonequilibrium glassy state.

Many lines of evidence including these probe studies demonstrate that liquids just above the glass transition temperature T_g are dynamically heterogeneous with a characteristic length scale of nanometers.[5] The lifetimes of these heterogeneous regions increase as the temperature is lowered toward the glass transition and are at least as long as the time scale associated with motions of small portions of the polymer chain, that is, the polymer segmental relaxation.[6] Although it is reasonable that one enters the glassy state with a heterogeneity similar to that encountered in the supercooled liquid, little is known about the nature of this heterogeneity below T_g.[7] Thus, physical aging in polymer glasses is, for example, routinely interpreted with a model that does not allow heterogeneous relaxation.[8] Including this heterogeneity may well be essential to explain technologically important and commonly observed complex phenomena that occur as the glass very slowly relaxes toward equilibrium. In addition, information storage schemes based upon molecular transitions in polymer glasses[9] would be fundamentally limited by such heterogeneity.

Studies of isomerizing probes in rubbery and glassy polymers often show a crossover from exponential to nonexponential kinetics.[10] This transition to nonexponential kinetics has always been observed near T_g. But it has been argued that if nonexponential kinetics results from spatial heterogeneity, that is, if there are subensembles of molecules subject to different environments, then the transition should occur when there is

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(3) Ediger, M. D.; Angell, C. A.; Nagel, S. R. *J. Phys. Chem.* **1996**, *100*, 13200.

(4) The two broad catagories of probe studies in polymers are (i) translational and rotational motions and (ii) motions involving shape changes, that is, isomerizations of the probe. For leading references to the former large literature see: (a) Heuberger, G.; Sillescu, H. *J. Phys. Chem.* **1996**, *100*, 15255. (b) Cicerone, M. T.; Blackburn, F. R.; Ediger, M. D. *J. Chem. Phys.* **1995**, *102*, 471. For leading references to the considerable literature on probe isomerizations see: (c) Hall D. B.; Hooker, J. C.; Torkelson, J. M. *Macromolecules* **1997**, *30*, 667. (d) Bokobza, L.; Pham Van Cong, C.; Giordano, C.; Monnerie, L.; Vandendriessche, J.; De Schryver, F. C. *Polymer* **1988**, *29*, 251.

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Table 1. Molar Extinction Coefficients and Molar Ellipticities of Paddled Bridged Binaphthyls in Solutions in Cyclohexane[a]

paddled binaphthyl	molar extinction coeffient (wavelength/nm)	molar ellipticity (wavelength/nm)	paddled binaphthyl	molar extinction coeffient (wavelength/nm)	molar ellipticity (wavelength/nm)
(*R*)-BNO	103 000 (218)	1.3×10^6 (217)	(*R*)-BPBNO	64 000 (272)	1.6×10^5 (225)
	13 000 (306)	-1.3×10^6 (229)		57 000 (300)	-2.1×10^5 (238)
	9 700 (328)	7.4×10^4 (327)			1.8×10^5 (263)
(*R*)-PBNO	56 000 (215)	-7.4×10^4 (228)			-3.4×10^5 (291)
	98 000 (252)	6.0×10^5 (248)			3.0×10^4 (340)
	28 000 (294)	-7.4×10^5 (264)	(*R*)-PPBNO	150 000 (213)	-1.7×10^5 (237)
		1.0×10^5 (311)		120 000 (303)	-1.1×10^5 (271)
					-2.6×10^5 (301)
					1.8×10^4 (347)

[a] Methylene chloride for BPBNO.

an overlap between the segmental relaxation time of the polymer matrix and the time scale of the isomerization motion, which may or may not correspond to T_g.[11] Up to now the probe isomerization time scales have been so fast that they intersect the segmental motions very close to the conventionally determined T_g. Here we present a probe with a well-defined and simple invariant isomerization mechanism in which the length scale can be varied without effect on this mechanism. Because the time scale for isomerization is far longer than has been previously available, these probes can explore dynamics deep in the glassy state.

Chirality is an approach not previously considered as a means to study the properties of the glassy state although this material state is amorphous and, as for the fluid solutions classically used for chiral optical studies, is free of birefringence. However, the glassy state has served to study the nature of chirality. In fact, optical activity studies in the glassy state were first published by Biot in 1832 to counter arguments that birefringence is solely a characteristic of the crystalline state and thus to demonstrate the inherent molecular basis of optical activity[12] and, as would be understood later, chirality.

Racemization is an isomerization process in which the interconverting chiral molecules, that is, enantiomers, are of identical energy. The process is thus entirely driven by an increase in entropy. In the racemization of bridged binaphthyls in particular, molecules that owe their chirality to a nonplanar arrangement of the individually planar naphthalene rings, the racemization path is a one-dimensional twisting motion so that both the thermodynamic and kinetic aspects of the process are simple and well studied.[13] Below we show that structural adaptations to the bridged binaphthyls allow the length scale of the racemizing motion to be varied without effect on the mechanism of the process. Most important, the time scale of the racemization is quite long so the segmental motions of the polymer matrix are more rapid than the racemization rate even below T_g. Moreover, the racemization can be energized by light as well as thermally allowing a wide variation in the enantiomer lifetime at constant temperature. Observations of how the racemization characteristics of the varied binaphthyls are affected by the polymer matrix are shown in this work to yield new information concerning the time and length scales of restrictions to motion in the glassy state of a much studied model polycarbonate.

Results and Discussion

Synthesis and Characteristics of the Binaphthyls. Oligophenyl "paddles" were appended to the 6 and 6′ positions of the nearly enantiomerically pure 1,1′-bridged binaphthyls as outlined in Scheme 1. Attachment of the paddles to the binaphthyl core was carried out using conventional Suzuki coupling.[14] Either the paddle group (method A) or the binaphthyl core (method B) was functionalized with boronic acid depending on the difficulty of the synthesis of each of the paddles.

Since all the reactions involving the binaphthyl moieties were performed at temperatures below 100 °C, the loss of enantiomeric excess of the probes that originated from the starting compound (*R*)-1,1′-bi-2-naphthol (93% ee) was negligible. Table 1 shows the UV and CD characteristics of the probes while Scheme 2 exhibits information on the size of the static molecules and also the distances along the arc traversed from the ends of these paddles as each enantiomer is converted to its mirror image.

In each of the binaphthyls shown in Scheme 2 the circular dichroism (CD) spectrum was almost identical to that in a dilute solution in decalin (see below) and as well was unaffected by rotation of the sample in the beam of the CD spectrometer demonstrating the absence of birefringent effects that would arise from aggregation or crystallization of these molecules in the polymer matrix.[15] In addition, dissolution of the probes in the polymers was found to have no effect on the polymer T_g.[16] See the Experimental Section for details on the synthesis and characteristics of the probe molecules and the dissolution methods involving the glass and melt states of the polymers.

Kinetic Studies in Small-Molecule Solvents. The racemization kinetics of the four probes studied, BNO, PBNO, BPBNO, and PPBNO (Scheme 2), were characterized by excellent fits to first-order kinetics, with the rates within experimental error for any one probe in small-molecule solvents of varied structure and polarity.

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[11] (a) Richert, R. *Macromolecules* **1988**, *21*, 923. (b) Richert, R.; Heuer, A. *Macromolecules* **1997**, *30*, 4038.

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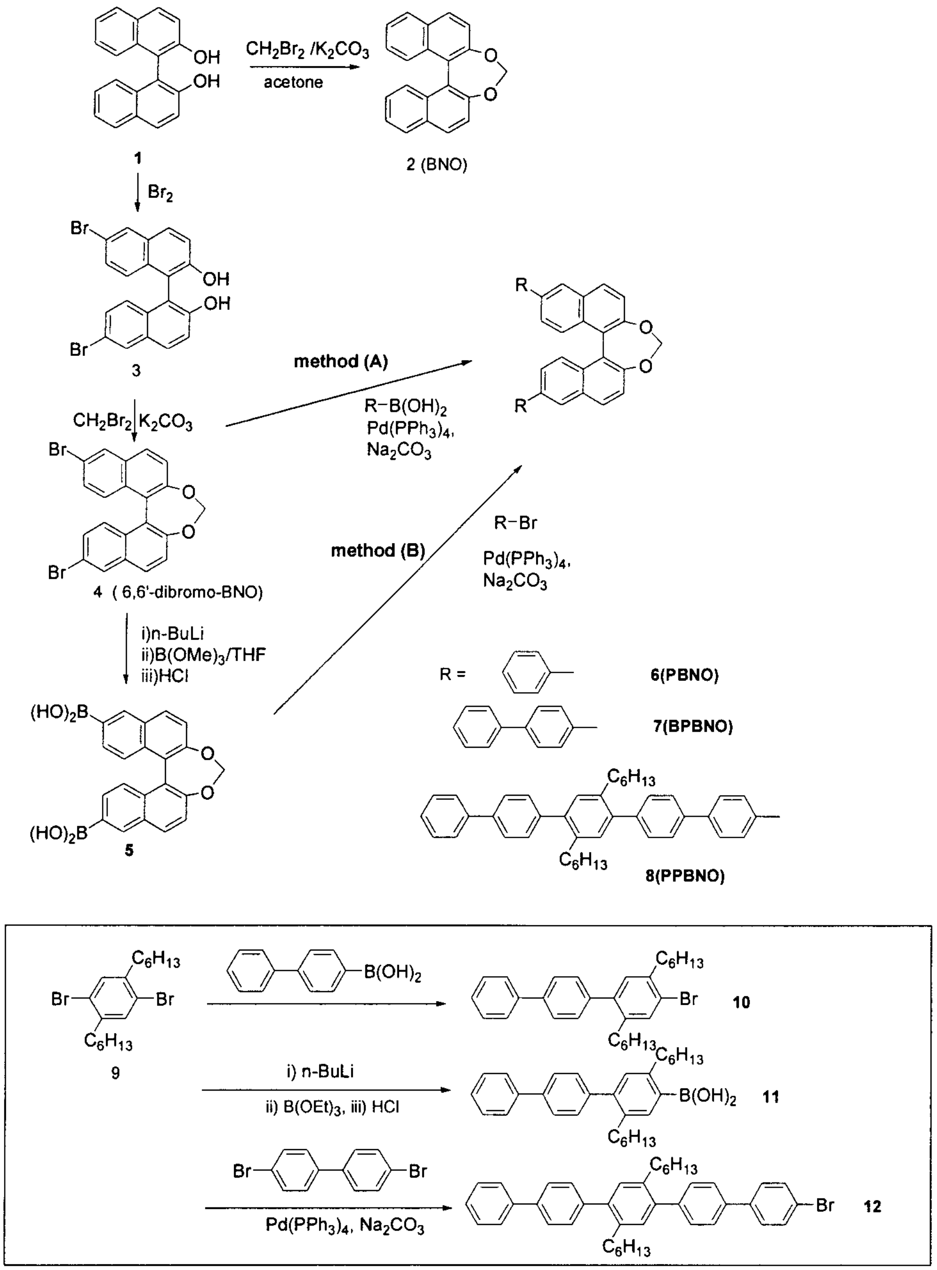
[13] (a) Carter, R. E.; Liljefors, T. *Tetrahedron* **1976**, *32*, 2915. (b) Colter, A. K.; Clemens, L. M. *J. Phys. Chem.* **1964**, *68*, 651. (c) The racemization properties of binaphthyls have been used before as a probe of a different material state, liquid crystals. Naciri, J.; Spada, G. P.; Gottarelli, G.; Weiss, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4352.

[14] (a) Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178−184. (b) Sharp, M. J.; Cheng, W.; Snieckus, V. *Tetrahedron Lett.* **1987**, *28*, 5093−5096.

[15] Kuball, H.-G.; Höfer, T. In *Circular Dichroism-Principles and Applications*, revd ed.; Berova, N., Nakanishi, K., Woody, R. W., Eds.; Wiley: New York, 2000; Chapter 5 and references therein. Observation of birefringent-derived large distortions from the isotropic solution phase CD spectrum was observed in the glassy state for a *p*-terphenyl-paddled binaphthyl (TPBNO), which was found to be the least soluble of the paddled binaphthyls, excluding it from contributing to the racemization studies in the polycarbonate matrix.

[16] The DSC for the mixture of BPBNO (1% weight to polymer) and the polycarbonate that was prepared from their solutions in chloroform gave almost the same glass transition temperature as the polymer without BPBNO: ∼145 °C.

Scheme 1. Synthesis of the 2,2′-Bridged 1,1′-Binaphthyls with Varying Paddles Attached to the 6 and 6′ Positions[a]



[a] Synthesis of the pentaphenyl paddle is shown in the box.

Analysis of the twisting about the single bond connecting the two naphthalene rings with an empirical force field program showed the force constant for this motion to be independent of the appended variable oligophenyl paddles.[17] The computer-generated plot of potential energy versus dihedral angle yielded identical force constants regardless of the probe size when the dihedral angle centered at the C(1)−C(1′) bond was varied near 55°. This can be shown from the same force field to be the most stable ground-state conformation independent of paddle size. It reasonably follows that the energy of activation for the racemization of the various probes should be identical while the preexponential factors should be reduced in proportion to the weight and therefore the number of phenyl rings in the paddle. This was experimentally confirmed as demonstrated in the Arrhenius plots in Figure 1 for racemization in dilute solution in decalin, with the energy of activation for all probes close to 33 kcal/mol and the preexponential factor varying in the range between 13.2 and 12.3 in logarithmic values, decreasing with increasing probe size.

Since the preexponential factors are obtained by extrapolating the data to infinite temperature, that is, to $1000/T \rightarrow 0$ in the Arrhenius plot in Figure 1a, even small scattering in the experimental points can cause significant errors, which may be large compared to the effect caused by the size of the paddles. Therefore, the rates of racemization for the probes at a constant temperature were compared to analyze the effect of the probe size on the preexponential factors. An inverse square relationship was found between the rate constant and the length of the paddles, which was revealed by the slope of the line of −0.5 in the plot of log(rate constant) versus log(paddle length) or log(molar mass of the paddle) (Figure 1b). Since the activation

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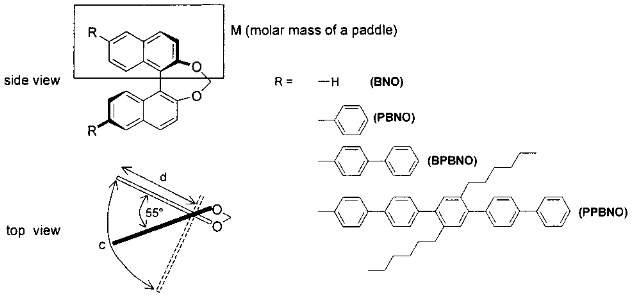
(17) The calculations were carried out on the Spartan 5.0 program with a Merck force field. We are grateful to K. Nakanishi of Columbia University for allowing use of this facility.

Scheme 2. Structures of the Bridged Binaphthyl Probes[a]



Probe	c (Å)	d(Å)	M
BNO	8.8	5.3	142
PBNO	16.0	9.6	218
BPBNO	23.1	13.9	294
PPBNO	44.6	26.8	691*

* 520 when the hexyl groups of PPBNO are not considered.

[a] Also shown are the length of the paddles, the distance along the arc traversed as one enantiomer is converted to its mirror image, and the molar mass of the paddles.

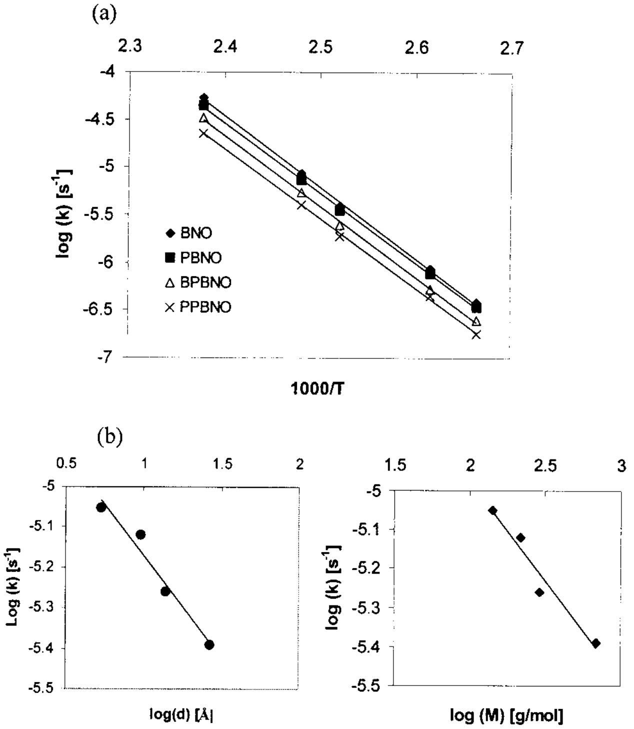
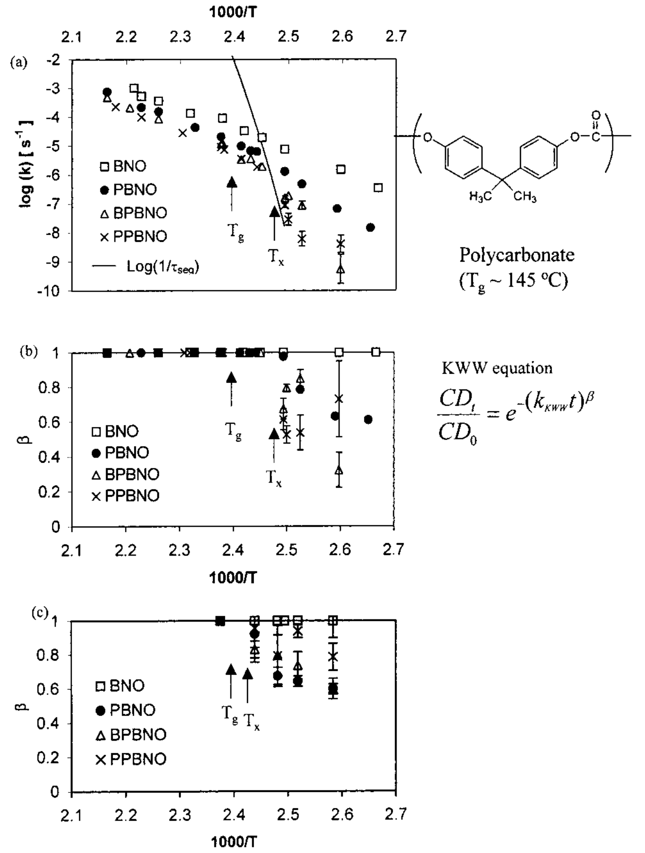


Figure 1. (a) Arrhenius plot of the rates of racemization for the four probes (Scheme 2) in dilute solution in decalin. (b) log *k* versus log(paddle length (*d*)) or log(paddle mass (*M*)). Each data point arises from a first-order kinetic plot of the racemization at 135 °C.

energies are constant for the binaphthyls of different sizes as determined experimentally (Figure 1a) as are the force constants for twisting about the 1,1′-bond independent of paddle size as determined by computation,[17] this result must arise solely from the effect of the paddle on the preexponential factor, which is consistent with the relationship between vibrational frequency and mass, $\nu \propto (\text{force constant/mass})^{1/2}$. This is an example of a "ponderal effect", which is the retardation of a chemical process caused by the weight of rotors.[18] With this basic information in hand on the properties of the binaphthyls (Scheme 2) in small-molecule solvents, we carried the studies into the glassy state.



$$\frac{CD_t}{CD_0} = e^{-(k_{KWW}t)^{\beta}}$$

Figure 2. (a) Arrhenius plot of the racemization data of the four paddled bridged binaphthyls in bisphenol A polycarbonate films. (b) KWW β parameters plotted against inverse temperature. (c) KWW β parameters for the photoracemization of the probes in bisphenol A polycarbonate films. The *x* axes in all three panels are drawn with the same scale for comparison.

Kinetic Studies in Polymer Matrixes. Figure 2a shows the thermally activated racemization rates over a wide temperature range for the probes dissolved in the bisphenol A polycarbonate. While the smallest probe, BNO, follows an Arrhenius dependence over the temperature range investigated with the same energy of activation and preexponential factor determined in decalin (Figure 1a), the larger probes exhibit different behavior at high and low temperature. At high temperature, these probes resemble BNO and exhibit nearly Arrhenius behavior with apparent activation energies similar to those observed in low-viscosity solvents. At low temperature, the larger probes show considerably slower rates than would be expected on the basis of extrapolation from the high-temperature regime.

Superimposed on the rate data for the racemization in Figure 2a is the independently determined rate of the segmental motion of the polymer matrix. The temperature dependence of the segmental relaxation, which does not obey Arrhenius dependence, is often described by the empirical Williams−Landel−Ferry (WLF) equation.[19] This motion corresponds to small segments of the overall chain rather than motion of the entire macromolecule. The latter is far slower and depends on the molecular weight of the polymer. The rate information about the segmental motions is obtained by various techniques such as transient mechanical spectroscopy, photon correlation spectroscopy, NMR, dielectric spectroscopy, or neutron scattering,

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(18) (a) de la Mare, P. B. D.; Fowden, L.; Hughes, E. D.; Ingold, C. K.; Mackie, J. D. H. *J. Chem. Soc.* **1955**, 3200. (b) Werstiuk, N. H.; Dhanoa, D.; Timmins, G. *Can. J. Chem.* **1983**, *61*, 2403. (c) O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1968**, *72*, 1866. (d) Berson, J. A.; Tompkins, D. C.; Jones, G. *J. Am. Chem. Soc.* **1970**, *92*, 5799. (e) Paquette, L. A.; Thompson, G. L. *J. Am. Chem. Soc.* **1971**, *93*, 4920.

which monitor local rather than large scale motions of the chain.[20] The steep change of the segmental rate as a function of temperature near the transformation from the melt to the glass state typifies glasses formed by polymers and is characteristic of glasses characterized as fragile.[2]

Thus, while the segmental motions of the polycarbonate are much faster than the rate of racemization at the temperatures in the melt state, the steeply slowing rate of segmental motion as the system approaches the glass boundary crosses that of the racemization somewhat below T_g. We have designated this crossover temperature as T_x in Figure 2a and observe that this approximate temperature corresponds to a relatively sudden slowing of the racemization rate for all the probes except the smallest, BNO. In contrast to the importance of this time scale overlap, the macroscopic transition from the rubbery to the glassy state of the polymer matrix, T_g, has no detectable effect on the racemization rates of any of the probes.

Figure 2b presents a plot of the Kohlrausch−Williams−Watts (KWW) β parameter vs $1/T$.[21] The deviation of β from unity expresses the deviation from first-order racemization kinetics; that is, the KWW equation reduces to a first-order relationship when $\beta = 1$. The results mirror those for the Arrhenius dependence discussed above. Only the smallest probe BNO shows $\beta = 1$ over the entire temperature range exhibited (Figure 2b). All the larger probes exhibit a deviation to $\beta < 1$ near the temperature T_x below which the Arrhenius plots in Figure 2a exhibit a steeper temperature dependence.

The results for the thermally activated racemization rates in Figure 2a,b are consistent with the following picture. At high temperatures, racemization is much slower than segmental relaxation. Any differences among different environments in the polymer matrix are averaged on the time scale of racemization, and thus simple exponential relaxation is observed. The environment surrounding the racemizing probes is effectively homogeneous in a situation perfectly analogous to a rate process in a small-molecule solvent where the dynamic motions of the solvent are far faster than the rate. However, if the racemization rate were to continue with the same temperature dependence to low temperature, probe racemization would proceed faster than segmental relaxation. While the experiments show that this is possible for the smallest probe (BNO), racemization of the larger probes requires substantial cooperation from the surrounding polymer segments, and hence segmental motions hinder the rate of racemization below T_x. In addition, in the low-temperature regime, since racemization occurs on roughly the same time scale as segmental motion, each probe experiences different environments that do not exchange significantly on the time scale of the racemization. Thus, different rates of segmental relaxation in different regions of the glass give rise to different racemization rates for the larger probes and therefore to the associated nonexponential kinetics. Previous work exploring other dynamics near T_g has also invoked the relationship between probe and segmental relaxation.[22]

There is, however, an alternative view of the nonexponential kinetics at low temperature (Figure 2b). The long half-life for the racemization below T_g may lead to physical aging[23] with a densification of the polycarbonate, and this could, in principle, contribute to the observed deviation from first-order kinetics since this would cause the environment of the probe molecules to vary during the course of the racemization. How could these alternative interpretations of the deviations from first-order kinetics be distinguished?

Speeding the racemization process would reduce the changes associated with aging of the polymer matrix over the lifetime of the racemization since the whole racemization takes place over a shorter time. If aging is contributing to the observations, accelerated racemization should be characterized by β closer to 1 at the same temperatures as in Figure 2b. Since bridged binaphthyls are subject to photochemical racemization involving excitation to the singlet state by irradiation into the binaphthyl chromophore followed by intersystem crossing to the triplet, which then has a far lower barrier for racemization than the ground state involved in the thermal racemization,[24] we studied the photochemical racemization of the various bridged binaphthyls in the same polymer matrix.

As shown in Figure 2c, the deviation from first-order kinetics now occurs at an even higher temperature than for the purely thermal racemization in Figure 2b and closer to the macroscopically observed T_g. This can only be understood if the overlap with the segmental relaxation of the polymer plays the critical role since speeding the racemization causes these time scales to overlap at a higher temperature. While the segmental motions remain identical if the racemization is thermally or photochemically activated, the faster photochemical process will intersect the segmental time scale at a higher temperature. As shown below another approach allows this to be confirmed in an entirely different way.

The time scale for segmental motion of any polymer at its T_g is on the order of 100 s.[2,19] Thus, if the binaphthyl probes are incorporated in a matrix with a higher T_g, the thermal racemization rate will be increased in the region of the glass transition. In this manner by studying the racemization in a higher temperature glass forming polymer, we gain the information yielded by the photochemical process (Figure 2c) but in a purely thermal racemization.

The results of this experiment for a copolycarbonate with a T_g near 200 °C are consistent with this picture as shown in Figure 3. Relative to T_x, determined by the intersection of the segmental and racemization time scales,[19,25] the results from this high-T_g polymer are identical to those shown in Figure 2. However, in this case, T_g and T_x are nearly the same since the racemization and segmental rates cross close to the T_g (Figure 3). Again the smallest probe is oblivious to both T_g and T_x while the larger probes exhibit a steep deviation from both the Arrhenius dependence and first-order kinetics below T_x.

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[19] The parameters for bisphenol A polycarbonate are $C_1 = 22.9$, $C_2 = 78.6$, and $T_g = 418$ K in the WLF equation: $\log[\tau(T)/\tau(T_g)] = -[C_1(T - T_g)]/[C_2 + (T - T_g)]$, where $\tau(T)$ is the segmental relaxation time at temperature T and the glass transition temperature (T_g). The $\tau(T_g)$ was assumed as 100 s for the construction of the $\log[1/\tau(T)]$ in Figure 2. For more details about the WLF equation and its parameters, see: (a) Ngai, K. L.; Plazek, D. J. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; AIP Press: Melville, NY, 1996; p 341. (b) Ferry, J. D. *Viscoelastic Properties of Polymers*; 3rd ed.; John Wiley & Sons: New York, 1980.

[20] (a) Plazek, D. J.; Ngai, K. L. *Macromolecules* **1991**, *24*, 1222. (b) Frick, B.; Richter, D. *Science* **1995**, 267, 1939. (c) Dejean de la Batie, R.; Lauprêtre, F.; Monnerie, L. *Macromolecules* **1989**, *22*, 2617.

[21] (a) Kohlrausch, R. *Ann. Phys. (Leipzig)* **1847**, *12*, 393. (b) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80. See also Analysis of Exponential and Nonexponential Kinetics Data in the Experimental Section for information on how the nonexponential kinetic data were treated.

[22] Ngai, K. L. *J. Phys. Chem. B* **1999**, *103*, 10684.

[23] (a) Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, **1978**. Probe studies have been used to study physical aging: (b) Sung, C. S. P.; Lamarre, L.; Chung, K. H. *Macromolecules* **1981**, *14*, 1839. (c) Lamarre, L.; Sung, C. S. P. *Macromolecules* **1983**, *16*, 1729. (d) Hwang, Y.; Inoue, T.; Wagner, P. A.; Ediger, M. D. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 68.

[24] (a) Irie, M.; Yoshida, K.; Hayashi, K. *J. Phys. Chem.* **1977**, *81*, 969. (b) Zhang, M.; Schuster, G. B. *J. Phys. Chem.* **1992,** *96***,** 3063. (c) Zhang, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 4852.

[25] The segmental motions of the higher temperature copolycarbonate were assigned using the WLF equation with the same parameters as for the bisphenol A polycarbonate adjusted for the higher T_g (473 K). See also ref 19 for details.

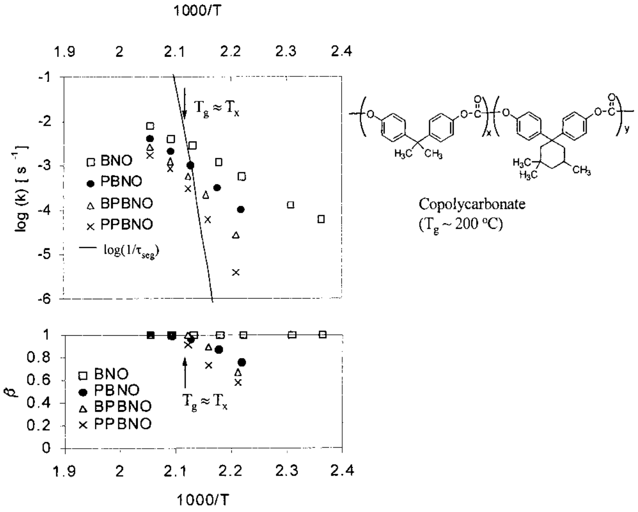

Figure 3. Arrhenius plot of the racemization data of the four paddled bridged binaphthyls in the high-T_g copolycarbonate films (top). KWW β parameters plotted against inverse temperature (bottom).

Although the above conclusions concerning time scale are based on quantitative considerations, the interpretation of the length scale information in these experiments is subject to speculation. The data show that BNO differs from all the other probes in racemizing without restriction from the surrounding matrix over the entire temperature range studied. While the length and arc length swept out by this smallest racemizing probe in the necessary twisting of the two naphthalene rings is precisely known (5.3 and 8.8 Å), it is not clear what this information means with regard to the surrounding matrix. For example, how should these distances be interpreted in comparison with recent NMR measurements[26] of the length scale of heterogeneous dynamics in a polymer just above T_g? Our results suggest that the critical racemization motion for BNO is sufficiently small that the necessary adjustments in the matrix are not motions associated with the glass transition, that is, those of the polymer segments, but rather this smallest of the probes may be in contact with polymeric moieties that relax far more quickly. Alternatively there may be sufficient free volume[27] to essentially eliminate contact between the polymer and the BNO. Experiments are in progress to attempt to discriminate between these possibilities.

Summary

The experiments discussed above demonstrate that spatially heterogeneous dynamics strongly influence molecular motion deep within the glass state of a conventional polycarbonate. This heterogeneity is not sensed until the time scales for segmental motions and probe racemization overlap and then only above a particular probe length scale. Below the temperature corresponding to this overlap, racemization is dramatically slowed by segmental relaxation of the polymer. Under these conditions, different dynamic environments give rise to different racemization rates. This picture is confirmed by the ability to vary the relationship between the two time scales by photochemical racemization in the conventional polycarbonate and by changing to a copolycarbonate with a higher T_g.

We have created, in the work reported here, a new tool based on optical activity that is applicable for exploration of time and length scales for motion in the glassy state. In the many variations of this approach, in which a wide range of chiral molecules subject to atropisomeric racemization may be considered,[28] new kinds of experiments can be designed to explore other important aspects of the glassy state such as aging[29] and as well to use the glassy properties of polymers to allow new kinds of variations of the kinetic properties of atropisomeric motion that are not possible in conventional solutions. Moreover, irradiation-induced racemization in glasses also has potential technological applications. A holographic image could be produced since an appropriate paddle allows the same wavelength of light to write an image above T_x and read the information at lower temperatures without further racemization. In addition, since the enantiomers have identical relationships to the matrix, volume change on racemization and therefore undesirable distortions in the matrix will be avoided. This is a severe problem limiting other systems that have been proposed for this mode of information storage.[30]

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 and Varian Unity 200 or 600 as noted. The shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. CD and UV−vis spectra were recorded on a JASCO J-710 spectropolarimeter. A homemade CD sample holder connected to a Cole Parmer temperature controller model 89000 was placed in the JASCO J-710 for high-temperature measurements (150−215 °C). Optical rotation was measured on a Perkin-Elmer 141 polarimeter. Glass transition temperatures were recorded on a Perkin-Elmer DSC7 series with a heating rate of 10 °C/min under nitrogen flow. Melting points were measured either on the Perkin-Elmer DSC7 or on a capillary melting point apparatus (Thomas-Hoover). Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY). MALDI data were obtained on the PerSeptive Biosystems Voyager DE-STR. A Fisher Scientific dry bath incubator connected to the Cole Parmer temperature controller was used to maintain a constant temperature for kinetic studies in the range of 100−150 °C. Gel permeation chromatographs (GPC) were recorded on a system with a Waters 510 pump in line with TSK gel HMXL and H5000 columns and dual detectors of a Waters 440 UV absorbance detector and a Waters R401 differential refractometer, in which chloroform was eluted with a flow rate of 1 mL/min at 30 °C. The molecular weights of the polymers were calculated using Waters Millennium software calibrated relative to polystyrene standards (from Polysciences). A medium-pressure mercury arc lamp (UVP, 100 W) was used for the photoracemization.

Materials. All solvents and reagents were obtained from commercial sources and used without further purification, unless otherwise noted. THF was distilled under N_2 from Na/benzophenone. Acetone was dried over $CaCl_2$. Silica (70−230 mesh ASTM) and TLC plates were purchased from Merck. Decalin (*cis*/*trans* mixture, Aldrich) was distilled under reduced pressure. All polymers were purified by precipitation into methanol from the solutions in chloroform followed by drying under high vacuum at 80 °C for 3 days. Bisphenol A polycarbonate (GE Lexan LS2) was a kind gift from Prof. G. McKenna of Texas Tech University. The copolycarbonate with a 65/35 ratio of bisphenol A and 3,3,5-trimethylhexylidenediphenol was purchased from Aldrich. 1,1′-Bi-2-naphthol was synthesized and resolved by known methods[31]

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(29) In lower T_g polymers than the polycarbonates studied here, it is possible, because of the high thermal barrier, to maintain the polymer at a temperature below T_g for long periods of time without significant racemization. Kinetic measurements of the photochemical racemization of the binaphthyl probes as a function of aging time would yield information on the aging process at the maintained temperature.

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to yield (*R*)-1,1′-bi-2-naphthol (**1**) (93% enantiomeric excess), which was used as the starting compound for all the probe molecules. (*R*)-1,1′-Binaphthyl-2,2′-diyloxymethane (BNO, **2**), (*R*)-6,6′-dibromo-1,1′-bi-2-naphthol (**3**), and (*R*)-6,6′-dibromo-1,1′-binaphthyl-2,2′-diyloxymethane (**4**) were synthesized from the (*R*)-1,1′-bi-2-naphthol (93% ee) following known methods.[32] 1,4-Dibromo-2,5-di-*n*-hexylbenzene (**9**) was synthesized as reported.[33] Phenylboronic acid and 4-biphenylboronic acid were obtained by the reaction of the corresponding Grignard reagents with trimethyl borate followed by acid hydrolysis.[34] Tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) was purchased from Aldrich.

(*R*)-1,1′-Binaphthyl-2,2′-diyloxymethane-6,6′-bisboronic Acid (5). (*R*)-6,6′-Dibromo-BNO (**4**) (3 g, 6.6 mmol) was dissolved in 50 mL of THF. To the solution was slowly added 1.6 M *n*-BuLi in *n*-hexane (16 mL) at dry ice temperature under an argon atmosphere. The temperature was maintained so as not to exceed −70 °C. The mixture was stirred for 5 h at this temperature. Trimethyl borate (4.5 mL, 39.6 mmol) was syringed into the reaction mixture. The resulting solid mass was shaken several times and stirred overnight while the temperature was increased to room temperature. The reaction was terminated by addition of 1 N HCl (50 mL). Diethyl ether (50 mL) was added, and the organic layer was separated and washed with water twice. The solution was slowly added to hexanes (200 mL) with vigorous stirring. White precipitates were collected by filtration and dried under vacuum at room temperature (1.6 g). This was used for the coupling reaction without further purification. ^{1}H NMR (300 MHz, DMSO-d_6): 5.67 (d, 2H), 7.15 (d, 2H), 7.51 (d, 2H), 7.67 (d, 2H), 8.1 (d, 2H), 8.48 (s, 2H).

(*R*)-6,6′-Diphenyl-1,1′-binaphthyl-2,2′-diyloxymethane (PBNO, 6). To a solution of (*R*)-6,6′-dibromo-BNO (500 mg, 1.1 mmol) and a catalytic amount of $Pd(PPh_3)_4$ in toluene(5 mL) were added phenylboronic acid (330 mg, 2.74 mmol) and 1 M sodium carbonate (5 mL), successively. The solution was heated overnight at 100 °C and cooled to room temperature. Water and enough chloroform were added to separate the phase. The chloroform layer was washed with water three times and dried over calcium chloride. After evaporation of the solvents, the resulting solids were dissolved in a mixture of hexanes and chloroform. The solution was filtered through silica gel and evaporated to dryness. The resulting solids were dissolved in a mixture of chloroform (minimum amount) and acetone with heating. White crystalline solids were obtained on cooling in the freezer. Yield: 260 mg (52%). $[\alpha]^{25}_{D} = -795°$ (chloroform). ^{1}H NMR (300 MHz, $CDCl_3$): 5.72 (s, 2H), 7.37 (t, 2H), 7.44−7.55 (dd, 6H), 7.57−7.68 (m, 4H), 7.73 (d, 4H), 8.05 (d, 2H), 8.15 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 103.5, 121.45, 125.83, 126.05, 126.18, 127.34,127.44, 127.50,-128.91, 130.65, 131.37, 132.15, 137.73, 140.75, 151.41. MS/EI: $m/z = 450$ (M^+), M_w(calcd) = 450.5. Anal. Calcd for $C_{33}H_{22}O_2$: C, 87.98; H, 4.92. Found: C, 86.52; H, 4.80.

(*R*)-6,6′-Bis(4-biphenylyl)-1,1′-binaphthyl-2,2′-diyloxymethane (BPBNO, 7). To a mixture of 4-biphenylboronic acid (350 mg, 1.77 mmol) and (*R*)-6,6′-dibromo-BNO (**4**) (280 mg, 0.61 mmol)0 in THF/toluene(1/2 mixture) (10 mL) were added a catalytic amount of Pd-(PPh_3)$_4$ and 5 mL of 1 M sodium carbonate, successively. The resulting solution was heated at 80 °C for 5 days. The reaction mixture was extracted with a large amount of chloroform and washed with water several times followed by drying over magnesium sulfate. After filtration, the solvent was evaporated to dryness and the solids were dissolved in a minimum amount of hot chloroform. Cooling the solution yielded the product as a white crystalline powder. Yield: 295 mg (80%). Mp: 332 °C (DSC). $[\alpha]^{25}_{D} = -728°$ (chloroform). ^{1}H NMR (300 MHz, $CDCl_3$): 5.74 (s, 2H, CH_2), 7.36 (t, $J = 7.4$ Hz, 2H), 7.46 (t, $J = 7.2$ Hz, 4H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.64−7.67 (m, 8H), 7.72 (d, $J = 8.5$ Hz, 4H), 7.82 (d, $J = 8.5$ Hz, 4H), 8.07 (d, $J = 8.9$ Hz, 2H), 8.21 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 103.5, 121.52, 125.70, 126.07, 126.87, 127.08, 127.42, 127.57, 127.66, 128.86, 130.68, 131.43, 132.20, 137.19,138.19, 139.61, 140.33, 140.69, 151.47. MS/EI: $m/z = 602$ (M^+), M_w(calcd) = 602.7. Anal. Calcd for $C_{45}H_{30}O_2$: C, 89.67; H, 5.02. Found: C, 88.69; H, 5.05.

1-Bromo-2,5-di-*n*-hexyl-*p*-terphenyl (10). To a stirred mixture of 1,4-dibromo-2,5-di-*n*-hexylbenzene (42 g, 104 mmol) and $Pd(PPh_3)_4$ (80 mg) in toluene (70 mL) were added 4-biphenylboronic acid (4.0 g, 20.8 mmol) and 1 M Na_2CO_3 (70 mL) under an argon atmosphere. The solution was stirred near 100 °C overnight. After the mixture was cooled, the organic layer was extracted with diethyl ether, dried with magnesium sulfate, and evaporated to dryness. About 20 g of excess 1,4-dibromo-2,5-di-*n*-hexylbenzene was removed by crystallization in hexanes in a freezer (−20 °C). The residual mother liquor was concentrated and purified by flash chromatography eluting with hexanes. Yield: 6.5 g (65%). ^{1}H NMR (300 MHz, $CDCl_3$): 0.82 (t, 3H), 0.89 (t, 3H), 1.08−1.69 (m, 16H), 2.54 (t, $J = 7.8$ Hz, 2H), 2.71 (t, $J = 7.7$ Hz, 2H), 7.08 (s, 1H), 7.3−7.69 (m, 10H).

2,5-Di-*n*-hexyl-*p*-terphenyl-1-boronic Acid (11). *n*-BuLi (1.6 M in *n*-hexane, 17 mL) was added to the solution of 1-bromo-2,5-di-*n*-hexyl-*p*-terphenyl (6.5 g, 13.6 mmol) in dry diethyl ether (30 mL) at dry ice temperature. The mixture was stirred overnight, being allowed to warm to room temperature. The mixture was cooled again to −78 °C. Triethyl borate (7.2 mL) was added to the mixture and stirred overnight at room temperature. HCl (1 N) (20 mL) was added to finish the reaction, and the product mixture was extracted with diethyl ether followed by washing with water. After evaporation of solvents, the solids were dissolved in a minimum amount of hexanes. HCl (1 N) was added dropwise until the formation of white solids started. The mixture was kept overnight, and the product was collected by filtration followed by vacuum-drying. Yield: 2.5 g (42%). ^{1}H NMR (300 MHz, DMSO-d_6): 0.76 (t, 3H), 0.85 (t, 3H), 1.41 (m, 2H), 1.53 (m, 2H), 1.04−1.34 (m, 12H), 2.54 (t, $J = 7.7$ Hz, 2H), 2.73 (t, 2H). Anal. Calcd for $C_{30}H_{39}BO_2$: C, 81.44; H, 8.88; B, 2.44. Found: C, 80.93; H. 8.92; B, 2.72.

1-Bromo-2‴,5‴-di-*n*-hexyl-*p*-quinquephenyl (12). To a mixture of 2,5-di-*n*-hexyl-*p*-terphenyl-1-boronic acid (**11**) (1.5 g, 3.39 mmol) and 4,4′-dibromobiphenyl (5 g, 16.0 mmol) in toluene/THF (1/1 mixture, 30 mL) were added $Pd(PPh_3)_4$ (30 mg) and 1 M Na_2CO_3 (10 mL). The mixture was refluxed for 3 days. After being cooled to room temperature, the mixture was extracted with chloroform, dried over magnesium sulfate, and evaporated to dryness. The remaining excess 4,4′-dibromobiphenyl was removed by sublimation (130 °C, 0.05 mmHg) overnight. The residual mass was chromatographed in a silica gel column eluting with hexanes. The product was recrystallized in hexane. Mp: 135−136 °C. Yield: 1.18 g (55%). ^{1}H NMR ($CDCl_3$, 600 MHz): 0.82 (t, 6H), 1.15−1.25 (m, 12H), 1.55 (m, 4H), 2.6 (t, 4H), 7.19 (s, 1H), 7.21 (s, 1H), 7.37 (t, 1H), 7.44−7.5 (m, 6H), 7.53 (d, 2H), 7.59 (d, 2H), 7.63 (d, 2H), 7.67 (d, 2H), 7.68 (d, 2H). Anal. Calcd for $C_{42}H_{45}Br$: C, 80.11; H, 7.20; Br, 12.69. Found: C, 80.24; H, 7.18; Br, 12.62.

6,6′-Bis(2‴,5‴-di-*n*-hexyl-*p*-quinquephenylyl)-1,1′-binaphthyl-2,2′-diyloxymethane (PPBNO, 8). 1-Bromo-2‴,5‴-di-*n*-hexyl-*p*-quinquephenyl (**12**) (490 mg, 0.78 mmol) and $Pd(PPh_3)_4$ (20 mg) were dissolved in toluene (10 mL). (*R*)-BNO-6,6′-bisboronic acid (**5**) (100 mg, 0.26 mmol) and 1 M Na_2CO_3 (10 mL) were successively added to the mixture. The resulting solution was heated at 90 °C for 3 days. The reaction mixture was extracted with chloroform and washed with water several times followed by drying over magnesium sulfate. The solution was evaporated to dryness. The product was obtained by chromatography through silica gel in hexane/ethyl acetate (7/3). Yield: 350 mg (97%). $[\alpha]^{25}_{D} = -590°$ (toluene). ^{1}H NMR (600 MHz, $CDCl_3$): 8.22 (s, 2H), 8.06 (d, 2H), 7.84 (d, 4H), 7.79 (d, 4H), 7.73 (d, 4H), 7.64−7.70 (m,12H), 7.53 (d, 2H), 7.48 (d, 4H), 7.45 (d, 8H), 7.36 (t, 2H), 7.2 (s, 4H), 5.55 (s, 2H), 2.61 (t, 8H), 1.5 (m, 8H), 1.1−1.3 (m, 24H), 0.82 (t, 12H). ^{13}C NMR (150 MHz, $CDCl_3$): 14.0, 22.4, 29.3, 31.55, 31.6, 32.7, 103.37, 121.2, 125.38, 125.70, 126.22,126.4, 126.61, 126.8, 127.1, 127.25, 127.4, 128.4, 129.4, 129.5, 130.32, 130.6, 131.05, 131.8, 136.37,136.9,137.30, 138.0, 138.65, 139.21, 139.62, 140.03, 140.61, 140.80, 141.5, 151.5. MS/MALDI: $m/z = 1395$ (MH^+), M_w(calcd) = 1395.9. Anal. Calcd for $C_{105}H_{102}O_2$: C, 90.34; H, 7.36. Found: C, 90.27; H, 7.52.

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Kinetics of Thermal Racemization in Decalin. The probes were dissolved in decalin at dilute concentrations suitable for CD measurements. The solutions of each probe were split into five glass ampules and sealed under a slightly negative vacuum. All ampules were placed in a temperature-controlled heating stage at the same time. The CD spectrum of the solution was recorded one by one after every desired interval.

Kinetics of Thermal Racemization in Polymer Films. The binaphthyl probes of an amount of less than 1% of the polymers by weight were dissolved in the solutions of the polymers in chloroform, where the polymer concentration was about 2.5% w/v. The resulting probe/polymer solutions were dropped on quartz disks. After the films stood at room temperature overnight, they were dried under high vacuum for 3 days at 40 °C or baked at 100 °C for 2−3 h.

Prior to kinetic measurements, the films were heated to above the glass transition temperatures of the polymers. The probe/bisphenol A polycarbonate films were heated at 160 °C for 15−20 min and cooled to room temperature. The probe/copolycarbonate films were heated at 205 °C for 5 min and then cooled to room temperature.

For kinetic runs above temperatures of about 150 °C, the film was placed in a homemade sample holder with a temperature controller (stability ±0.2 °C) attached. CD spectra were recorded at appropriate intervals. For kinetic measurements at temperatures below about 150 °C, the initial circular dichroism of the film was recorded before the films were heated. Then the films were heated in a temperature-controlled heating stage (stability ±0.5 °C) that is placed outside of the CD instruments. After the desired interval, the CD measurements were made at ambient temperatures. The samples were returned to the heater for further measurements as soon as the measurements were completed.

The extrema in the CD spectra of the probes were normally read for the kinetic analysis. The intensity of the circular dichroism signal of the films was directly utilized. PBNO, BPBNO, and PPBNO have strong positive and negative signals in the wavelength range longer than 240 nm, at which the polymer films prepared as above usually exhibited a UV cutoff. The difference of the two extrema was used for the analysis. The relatively weak CD signal of BNO in the range longer than 240 nm could be overcome by using thicker films. The CD maximum value near 325 nm was subtracted from that at 370 nm (baseline).

Kinetics of Photoracemization in Bisphenol A Polycarbonate. The probe/polymer films were prepared in the same way as for the samples for thermal racemization. The films were placed in a black anodized aluminum-based heating block with deep cylindrical holes with a slightly larger diameter than that of the quartz disk on which the film was coated. The films were irradiated vertically from right above at a constant distance for all samples to be compared. The films were blocked from the light until the sample was heated to the desired temperature and the lamp was fully warmed. After a desired time, the lamp was shut off and the CD spectrum of the film was measured.

Analysis of Exponential and Nonexponential Kinetic Data. For first-order kinetics, the rate constant of the racemization was calculated by a linear regression using the usual expression for a reversible first-order racemization reaction: $k_1 + k_{-1} = (1/t)\ \ln(\mathrm{CD}_0/\mathrm{CD}_t)$, where t is the elapsed time and CD_t and CD_0 are the circular dichroism signals at times t and zero, respectively. Since the equilibrium constant $K = 1$, $k_1 = k_{-1}$ and therefore $k = k_1 = k_{-1} = (1/2t)\ \ln(\mathrm{CD}_0/\mathrm{CD}_t)$. The decay rate of the CD signal is twice the rate constant (k).

For nonexponential kinetics, the normalized circular dichroism signal, $\mathrm{CD}_0/\mathrm{CD}_t$, was fitted to the KWW equation, $\exp[-(k_{\mathrm{KWW}}\ t)^{\beta}]$, where k_{KWW}, the KWW fitted rate constant of racemization, was used instead of the usual $1/\tau$ (relaxation time) for this equation. The average rate constant, k, was calculated using the equation $(1/2)k_{\mathrm{KWW}}\beta/\Gamma(1/\beta)$, where Γ is a gamma function. For the exponential kinetics, the rate constant (k) of the racemization is equal to $(1/2)k_{\mathrm{KWW}}$ with $\beta = 1$.

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