Racemization Kinetics of Bridged Binaphthyls Do Not Reflect Microviscosities of Rubbery Polymer Matrices

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ABSTRACT: The racemization kinetics of a series of atropisomeric 1,1′-2,2′-bridged binaphthyls with and without appended oligophenyl "paddles" were studied in decalin and in a number of rubbery polymers as a function of temperature. The racemization has an energy barrier of about 33 kcal/mol and a half-life of the order of hours. For the unsubstituted bridged binaphthyl, BNO, the rate was very similar in decalin and the polymeric matrices. In decalin, the attachment of the paddles elicited a ponderal effect, reducing the racemization rate by a factor inversely proportional to the square root of the mass of the group moving in the conformational transition. In the polymers, the temperature dependence of all rates followed the Arrhenius relation rather than the WLF equation, showing that the process was not coupled to the local polymer dynamics. The paddles reduced the rate by a factor that depended on the nature of the paddle and on the polymer but not on temperature and did not, therefore, reflect the "microviscosity" of the polymeric matrix.

Introduction

More than half a century ago, Grün[1] was surprised to find that gases diffuse through lightly cross-linked rubber as fast as through water. Later it was found that the dependence of this diffusion on temperature follows, for small gas molecules, the Arrhenius relation with no break at the glass transition temperature, T_g.[2] This was interpreted as showing that the diffusion involves a "hopping" of the diffusant particles between cavities in the polymer. However, the temperature dependence of motions of larger molecules in rubbery polymers is expected to be governed by a "microscopic viscosity", η_m, proportional to the relaxation time of segmental motions, τ_R, of the polymer, whose dependence on the temperature T is expressed, according to the WLF equation, by the shift factor a_T

$$\log a_T = \log \tau_R(T) + \text{const} = -C_1(T - T_g)/[C_2 + (T - T_g)] \quad (1)$$

where C_1 and C_2 are constants characteristic of a given polymer.[3]

In the past, three types of experiments have been used in which the motions of such molecular probes are governed by the segmental mobility of rubbery polymers:

(a) Linear diffusion of ^{14}C-labeled dodecane and hexadecane in a number of rubbery polymers was studied by Chen and Ferry.[4] The linear diffusion of photochromic dyes in a variety of polymeric matrices was measured by Ehlich and Sillescu by forced Raleigh scattering from the diffusion decay of holographic gratings,[5] and the diffusion of tetracene and rubrene in two rubbery polymers was studied by Ediger and his collaborators using holographic fluorescence recovery after photobleaching.[6] In the latter two studies it was found that the diffusion coefficients increase with rising temperature somewhat less rapidly than predicted from theWLF relation, and this was interpreted either as due to only partial coupling of the motion of the probe and that of polymer segments[5] or as due to a microheterogeneity of the polymer matrix.[6]

(b) Rotational diffusion in polymeric matrices was first studied by ESR using nitroxide spin probes.[7,8] Later, Jarry and Monnerie employed for this purpose the depolarization of fluorescence of rodlike molecular probes,[9] and Ediger with his collaborators used the same method for measuring the rotational diffusion coefficient D_r of tetracene and rubrene.[6] In all these studies the temperature dependence of D_r was found to be represented by the WLF relation.

(c) A third technique utilized a bichromophoric probe which forms an intramolecular excimer.[10] Under certain conditions, the ratio of the emission intensity of the excimer and the isolated chromophore indicates the probability that the conformational transition required for excimer formation occurs within the excited lifetime of the chromophore. The rate of this transition is then taken as characterizing the local mobility of the polymeric matrix, and it was found, in fact, that it scaled as the WLF relation.

Here we report, in various rubbery polymers, the rate of racemization of atropisomeric bridged binaphthyls carrying varying lengths of oligophenyl "paddles", which had been previously studied in polymeric glasses.[11] While the racemization involves a conformational transition of the probe, analogous to the transition involving intramolecular excimer formation, there is a crucial difference between the two processes: The relaxation time of the intramolecular excimer formation is of the order of nanoseconds, whereas the half-life of the racemization of the probes used in this study is of the order of hours even at temperatures above 150 °C. The results of this study were most unexpected. With the bridged binaphthyl carrying no "paddles", the racemization rates were very similar in decalin and the rubbery polymers. With the bridged binaphthyls carrying oligophenyl "paddles", the racemization rates in the rubbery polymers were reduced, in comparison with that observed in decalin, by a small factor, which depended on the nature of the oligophenyl and the polymer *but*

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Scheme 1. Structure of Bridged Binaphthyls with Substituents of Variable Size Attached to the 6,6′ Position

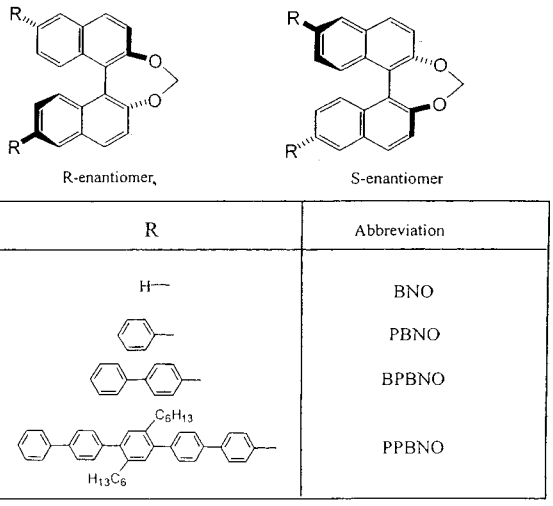

Table 1. Dependence of Racemization Kinetics in Decalin Solution at 150 °C on the Mass of the Unsubstituted and Substituted Naphthyl Group

	BNO	PBNO	BPBNO	PPBNO
10^5k (s^{-1})	6.44	5.22	3.83	2.83
m	126	202	278	665
k_p/k_{BNO}	1.00	0.79	0.69	0.44
$(m_p/m_{BNO})^{-1/2}$	1.00	0.79	0.67	0.43

was independent of temperature and thus of the microviscosity of the polymeric matrix.

Results

Scheme 1 shows the structures of the bridged binaphthyl probes. Their syntheses and other experimental procedures describing the kinetic measurements have been previously reported.[11] In the case of PPBNO, attachment of the alkyl substituents was necessary to render the probe miscible with the polymers. Racemizations in decalin and in the rubbery state of a low molecular weight polystyrene (PS, T_g = 75 °C), bisphenol A polycarbonate (PC, T_g = 145 °C), poly(methyl methacrylate) (PMMA, T_g = 109 °C), poly(ethyl methacrylate) (PEMA, T_g = 63 °C), and poly(*n*-butyl methacrylate) (PnBMA, T_g = 20 °C) all followed first-order kinetics. The ratio of the rate constant in decalin of a probe with a "paddle", k_p, and that of BNO, k_p/k_{BNO}, was found to be proportional to the inverse square root of the ratio of the corresponding masses of the substituted and unsubstituted naphthyl groups $(m_p/m_{BNO})^{-1/2}$ (Table 1). This "ponderal effect" was as expected from the dependence of the vibrational frequency on mass, since the force constant for the twisting about the single bond connecting the two naphthalene rings is independent of the appended oligophenyls.[11]

The racemization rate constants of the probes in polymeric matrices reflects an effect of the polymeric medium superimposed on the ponderal effect observed (Table l) in decalin solution. Table 2 lists the rate constants in decalin (k_{dec}) and in the polymeric matrices (k_{pol}) at 150 °C, and Table 3 lists the corresponding k_{pol}/k_{dec} ratios reflecting the effect of the polymer matrices on the racemization rate.

The temperature dependence of the racemization rate constants, both in decalin and in the polymeric matrices, followed the Arrhenius equation. In decalin the activation energy was 33 kcal/mol; a similar value was observed for BNO and the paddled probes in the rubbery polymers. Attachment of paddles to BNO reduced the racemization rate in the polymeric media by a factor that was independent of temperature, as illustrated for the racemizations in PC in Figure 1.

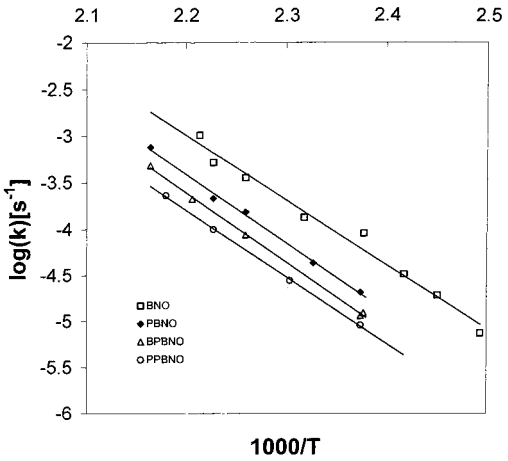

Figure 1. Arrhenius plots of the racemization data obtained in bisphenol A polycarbonate matrices for temperatures above the glass transition. Lines are drawn to show the apparent Arrhenius dependence of the data points.

Table 2. Racemization Rate Constants (10^5 s^{-1}) in Polymers above T_g and in Decalin at 150 °C

	BNO	PBNO	BPBNO	PPBNO
decalin	6.44	5.22	3.83	2.83
PS	7.50	3.18	1.70	1.21
PC	7.16	2.41	1.47	1.07
PMMA	6.52	1.59	0.58	0.48
PEMA	8.52	1.91	1.04	0.72
PnBMA	9.16	2.65	2.17	1.20

Table 3. Ratio of the Racemization Rate Constants at 150 °C in a Polymeric Matrix and in Decalin, k_{pol}/k_{dec}

	BNO	PBNO	BPBNO	PPBNO
PS	1.17	0.6.1	0.46	0.43
PC	1.11	0.46	0.38	0.38
PMMA	1.01	0.30	0.15	0.17
PEMA	1.32	0.37	0.27	0.25
PnBMA	1.42	0.51	0.57	0.42

Discussion

Since the temperature dependence of the racemization rate constants of our probes in the various rubbery polymers follows the Arrhenius rather than the WLF relation, we have to conclude that the racemization is not coupled with the segmental motions of the polymer. This conclusion is also supported by the observation that the racemization is unaffected by the distance of the temperature from T_g. Table 2 shows that the racemization at 150 °C is significantly slower, for all binaphyl probes, in PMMA (41 °C above T_g) than in PC (only 5 °C above T_g).

It is striking that BNO racemizes at very similar rates in decalin and in the polymeric matrices PS, PC, and PMMA. This similarity of the racemization rate in the polymers and in decalin is in sharp contrast with the translational and rotational diffusion of probes of similar size, which are strongly reduced in polymeric matrices.

It is particularly instructive to compare the behavior of the racemization rate of BNO with the rate of intramolecular excimer formation in the bichromophoric probe used by Jarry and Monnerie.[9] The BNO racemization took place at the same rate in a low molecular weight solvent and in polymeric matrices and exhibited the same temperature dependence in both media. By contrast, the intramolecular excimer formed much faster in methylcyclohexane than in polybutadiene or polyisoprene, and the apparent activation energy between 40 and 80 °C, which was 3.5 kcal/mol in methylcyclohexane, was 9 kcal/mol in PB and 14 kcal/mol in PI.

The dramatically different behavior of the excimer and the racemization probe must be a consequence of the large difference in the barrier height and relaxation time in the two conformational transitions. The low barrier for the intramolecular excimer formation causes its relaxation time to be comparable to that of the motions of the polymer segments while for the racemizations studied in this report they were higher by some 14 orders of magnitude.

In fact, a similar behavior has been previously observed in the *cis*−*trans* isomerization of azobenzene residues appended to poly(ethyl methacrylate).[12] This process, which has a somewhat lower activation energy of 23 kcal/mol,[13] compared to the racemization studied here, was found to take place at the same rate (with a half-life of 30 min at 60 °C) in a bulk polymer above T_g as in dilute solution. We have also observed that the racemization of a binaphthyl derivative with a half-life of about 25 h at room temperature exhibits almost the same rate in water and in the 1200 times more viscous glycerol.[14]

On attachment of the "paddles", the polymeric matrix slows down the racemization rate of the bridged binaphthyl, as compared to the rate in decalin solution, but the effect is surprisingly small, with k_{pol}/k_{dec} never less than 0.15. Since the Arrhenius plots of the racemization rates of BNO and the paddled binaphthyls in Figure 1 are parallel, *the factor by which the paddles reduce the racemization rate is independent of temperature.* This is a most striking observation. Using $C_1 = 22.9$ and $C_2 = 78.6$ for polycarbonate,[3b] the WLF equation predicts that the "microscopic viscosity" of this polymer should decrease by a factor of 5,000,000 between 150 and 180 °C. We must then conclude that the effect of the paddles on the racemization rate is not due to an increased viscous resistance but to some undefined geometric factor, which depends on both the nature of the paddle and the nature of the polymer. The data in Table 3 show that the paddles are more effective in reducing the racemization rate in PMMA than in PC or PS. In the various polymethacrylates, the attachment of biphenyl groups to BNO reduces k_{pol}/k_{dec} by factors of 7, 5, and 2.6 in PMMA, PEMA, and PnBM, respectively; i.e., the effect appears to decrease with an increasing spacing between the backbones of the polymer chains. Finally, it is striking that k_{pol}/k_{dec} values are similar for BPBNO and PPBNO; the effect of the extension of the paddle from biphenyl to pentaphenyl seems to be counteracted by the pentyl groups appended to the third phenyl group.

Since the microscopic viscosity seems to have no effect on the racemization rate of our probes, we should review the procedures that can be used to estimate its magnitude.

In the first approach it is assumed that η_m at T_g is 10^{13} P as first suggested by Ferry and Parks.[15] The WLF equation predicts then

$$\log \eta_m = 13 - C_1(T - T_g)/(C_2 + T - T_g) \qquad (2)$$

The second approach uses experimental data of the motion of a probe and defines the microscopic viscosity as the viscosity in a structureless continuum which would lead to the same motion of a particle whose dimensions approximate those of the probe. For translation, the Stokes−Einstein relation gives

$$D_t = kT/f_t$$

where the frictional coefficient for translation is

$$f_t = 6\pi\eta r$$

for spherical particles of radius r and

$$f_t = 6\pi\eta R/x(p)$$

for prolate ellipsoids of revolution with a volume of a sphere with a radius R and an axial ratio p with $x(p)$ given by Perrin.[16] The rotational diffusion coefficient D_r is given by

$$D_r = kT/f_r$$

where for spherical particles Stokes obtained[17]

$$f_r = 8\pi\eta r^3$$

and for ellipsoids of revolution with a semiaxis of revolution a_1 and equatorial radius a_2

$$f_r = 8\pi\eta a_1 a_2^2/y(p)$$

with $y(p)$ derived by Perrin.[18] Thus, the microscopic viscosity can be estimated from D_t or D_r by approximating the dimensions of the probe to those of a sphere or an ellipsoid.

The two approaches do not lead to the same result. This is undoubtedly due to the assumed microviscosity at T_g, since Ehlich and Sillescu[5] found that the diffusion rate of a given probe may vary by several orders of magnitude in different polymers at the glass transition temperature. Thus, the estimate based on the experimentally observed motion of a probe is to be preferred. The discrepancy between the results obtained in estimating η_m by the two above methods may be illustrated on the experiment of Jarry and Monnerie,[9] who studied the rotational diffusion of three rodlike probes in polyisoprene. When they approximated their probes by ellipsoids of revolution, they obtained a microscopic viscosity of 0.15 P at 40 °C. The use of eq 2 with $T_g = -60$ °C and the WLF constants[3b] $C_1 = 17.3$ and $C_2 = 51.6$ leads to $\eta_m = 31$ P.

Unfortunately, an estimate of the viscosity of a medium from the rate of a conformational transition is intrinsically much more uncertain. Kramers predicted that above a characteristic viscosity the rate should be inversely proportional to the viscosity.[19] Over a narrow range of viscosities, this prediction seemed to agree with the viscosity dependence of rates of the intramolecular excimer formation in a homologous series of alcohols and alkanes.[20] When the intramolecular excimer formation

was studied in mixtures of ethanol and ethylene glycol,[21] the viscosity dependence of the process was found to be sharply dependent on the bulk of the groups that have to move during the conformational transition. Doering et al.[22] tried in a similar manner to demonstrate the importance of friction by a comparison of the rates of anti−syn rearrangements involving alkene groups of differing extension, but they could not arrive at an unambiguous conclusion.

Theoretical reinvestigations of the effect of friction on the rate of conformational transitions[23] led to a weaker dependence on viscosity than predicted by Kramers. These conclusions were substantiated by studies of the rate of the conformational transition of cyclohexane,[24] the cis−trans isomerization of stilbene,[25] and other reactions.[26] All these studies dealt with processes with subsecond relaxation times, and we are unaware of any studies of viscosity effects on conformational transitions with very long half-lives other than those referred to above.

At this time we have no satisfying explanation for the surprising observation that the rates of conformational transitions with very long relaxation times are insensitive to the viscosity of the medium. It would be desirable to carry out a series of studies of such processes with gradually increasing relaxation times, so as to determine the manner in which this behavior is approached. Also, the "paddle effect" on the entropy of activation of conformational transitions should be documented in a greater variety of rubbery polymers and for other processes, such as the thermal cis−trans isomerization of azobenzene derivatives.

Finally, we would like to mention a curious observation. The fluorescence behavior of aromatic moieties attached to poly(methacrylic acid) (PMA) has long been interpreted as being due to a clustering of a section of the polymeric chain around the fluorophore. We have now found that when a binaphthyl residue is appended to PMA dissolved in water at low pH, the racemization rate is reduced by an order of magnitude.[27] Thus, the intimate association of the atropisomer with a polymer chain impedes a process that is unaffected by the microscopic viscosity of a polymeric matrix or a simple solvent.

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