1212 *Macromolecules* **1990,** *23,* 1212–1214

# Notes

## Effect of Temperature on Intermolecular Orientational Correlations between Chain Segments in Strained Polyisoprene: A Fourier Transform Infrared Dichroism Investigation

B. AMRAM, L. BOKOBZA,* P. SERGOT, AND
L. MONNERIE

*Laboratoire de Physico-Chimie Structurale et Macromoléculaire, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France*

J. P. QUESLEL

*Manufacture Française des Pneumatiques Michelin, Centre d'Essais et de Recherches de Ladoux, 63040 Clermont-Ferrand, Cedex, France.* *Received June 9, 1989*

### Introduction

Measurements of molecular orientation in stretched polymeric networks are of particular importance for the understanding of rubber elasticity. Various spectroscopic techniques such as fluorescence polarization, $^2$H NMR, and infrared dichroism have proved to be suitable for a quantitative measurement of this orientation. Some of the studies developed in this field have suggested that local intermolecular orientational correlations of segments with their neighbors contribute to orientation.

An experimental work on fluorescence polarization[1] of deformed networks of polyisoprene labeled with a fluorescent group (dimethylanthracene) has shown that deviations of segmental orientation from the predictions of the affine model are significant. An extra orientation of dry networks, which increases near the glass transition and is strongly reduced upon swelling, was observed at low and moderate elongations. This extra orientation was interpreted by assuming the existence of weak nematic-like interactions between segments.

$^2$H NMR experiments performed on poly(dimethylsiloxane) networks[2-5] demonstrate that short-range orientational correlations take place in the deformed network. On the other hand, fluorescence polarization measurements carried out on rigid rods, flexible probes, or dangling chains in deformed *cis*-1,4-polyisoprene networks[6-8] lead to similar conclusions.

These studies have provided evidence that probes introduced into the network (solvent molecules or polymer chains) acquire an orientational order that reflects that exhibited by the network chain segments.

The actual nature of this intermolecular orientational correlation—as a nematiclike interaction with temperature dependence or a purely entropic one—still remains a basic question. Indeed, the temperature dependence observed by fluorescence polarization could arise from a chain-labeling effect. To clarify this point, we have performed infrared dichroism experiments that do not require any additional label.

### Experimental Section

The polymer investigated, kindly supplied by Manufacture Française des Pneumatiques Michelin, was a synthetic polyisoprene of high cis-1,4 configuration (Shell, IR 307: 92% cis and 5% trans, $T_g$ (DSC) = −60 °C), cross-linked with dicumyl peroxide with 1.0 wt % in bulk. The cross-linking density was characterized by the mean molecular weight, $M_c$, of network chains between adjacent network junctions. An $M_c$ value of $5.55 \times 10^3$ was determined from the phantom modulus according to Queslel and Mark's topological treatment.[9]

The sample preparation and stretching conditions, as well as the methodology used to access to the orientation function from the infrared dichroic ratio measurements, have been described previously.[10]

Low-temperature measurements were performed with an original experimental device realized in our laboratory. The stretching machine with the film located at the convergent point of the infrared beam is placed in a thermostated box in the sample compartment of the spectrometer. The temperature of the sample can be monitored from −60 to +50 °C by a flow of gaseous nitrogen precooled to the desired temperature and obtained from liquid nitrogen. This equipment allows a temperature higher than +10 °C near the polarizer, which prevents it from water condensation, and, for the same reason, a heating of the KBr optical windows was assured by electrical resistances. A flexible mechanical link allows one to perform asymmetrical stretching at constant temperature from the outside of the box.

### Results and Discussion

In a previous paper,[10] infrared dichroism has been successfully applied in the case of *cis*-1,4-polyisoprene to access of the second moment of the orientation function $\langle P_2(\cos\theta)\rangle$ given by the expression

$$\langle P_2(\cos\theta)\rangle = (3\langle\cos^2\theta\rangle - 1)/2$$

where $\theta$ is the angle between the local chain axis and the stretching direction.

Figure 1 represents a plot of the coefficient $\langle P_2\rangle$ of the orientation distribution function at 298 K as a function of the extension ratio. For the sake of comparison, Figure 1 also displays results obtained from fluorescence polarization experiments performed in our laboratory on similar networks.[11] A higher orientation is obtained from the fluorescence experiments. We have to point out that the two methods observe two different specific vectors. In the case of infrared dichroism, we follow the transition moment vector associated with a vibrational mode and then determine the orientation of the local chain segment with regard to the stretching direction. An angle of 20° has been found between the local chain axis and the transition moment related to the double bond of the *cis*-1,4-polyisoprene monomer unit.[10] The fluorescence polarization technique measures the orientation of a fluorescent label whose emission transition moment lies as shown in Figure 2.

Such a difference between the $\langle P_2\rangle$ values determined by infrared spectroscopy and fluorescence polarization can be ascribed to the presence of the fluorescent label, which can perturb the state of strain in the surrounding domain. Effectively in a recent paper devoted to an analysis of the effects of chain structure and network constitution on segmental orientation in deformed amorphous networks,[12] Erman and Bahar have shown that an enhancement of the orientation can occur by the incorporation of bulky groups such as dimethylanthracene into the chain, which is required for fluorescence experiments. This fact

0024-9297/90/2223-1212$02.50/0

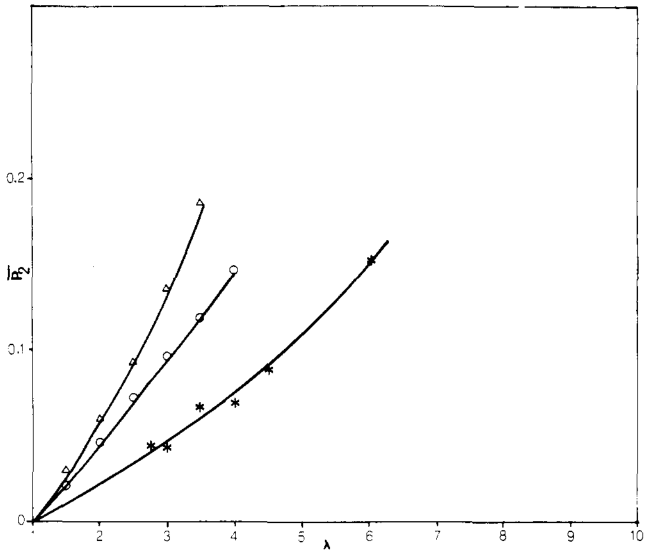

**Figure 1.** Second moment of the orientation distribution versus draw ratio for polyisoprene networks at 25 °C. Fluorescence polarization data from ref 11: $M_c = 6.1 \times 10^3$ (△); $M_c = 8.5 \times 10^3$ (○). [The $M_c$ values, different from those reported in ref 11, have been recalculated according to Queslel and Mark's treatment[9]]. Infrared dichroic data: $M_c = 5.55 \times 10^3$ (*).

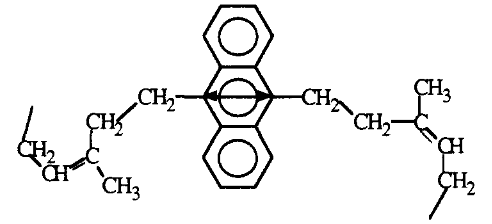

**Figure 2.** Labeled chain containing a dimethylanthracene fluorescent group. The arrow represents the transition moment.

is attributed to local configuration perturbations, thus causing a "stiffening" effect on the orientational behavior of the chain.

Let us now consider the temperature dependence of segmental orientation quite important to infer whether the intermolecular correlations are purely entropic or if an enthalpic component sensitive to temperature exists.

We have performed two sets of experiments. In the first one, the samples were cooled in the undeformed state, with a cooling rate of about 15°/h, and then stretched at constant temperature. In Figure 3 are displayed, at two different temperatures, the $\langle P_2 \rangle$ values determined from the infrared dichroic measurements as well as the second moment of orientation of the fluorescent label reported from ref 1 as a function of extension ratio. The results show that, within experimental error, the orientation does not depend on temperature for the infrared data while a strong temperature dependence was observed for the fluorescence polarization measurements.

In the second set of experiments, the samples were stretched at room temperature and then cooled (cooling rate ≈15°/h) at constant length ater a 30-min relaxation. The data reported in Figure 4 show that the orientation function measured by infrared dichroism is no more influenced by cooling the sample from room temperature to the vicinity of the glass transition temperature while the fluorescence polarization experiment exhibits a considerable increase of orientation when cooling the polyisoprene network.[13]

So the infrared dichroic measurements lead us to believe that the intermolecular correlation presents an entropic nature and rule out its nematic character suggested on the basis of the temperature dependence of the orientation by fluorescence polarization. Once more, the only reason that can explain the difference between infrared dichroism and fluorescence measurements is the presence of the label in the latter case. Changes in temperature may affect the conformational properties of bonds around the label. The effect of the size and type of fluorescent probes dissolved in deformed networks has been analyzed by fluorescence polarization.[6,7] These studies reveal that the degree of coupling between flexible probes like 9,10-di-*n*-alkylanthracene molecules increases linearly with the length of the probe chain while it is inversely proportional to rod length in the case of rigid rods dissolved in similar networks.

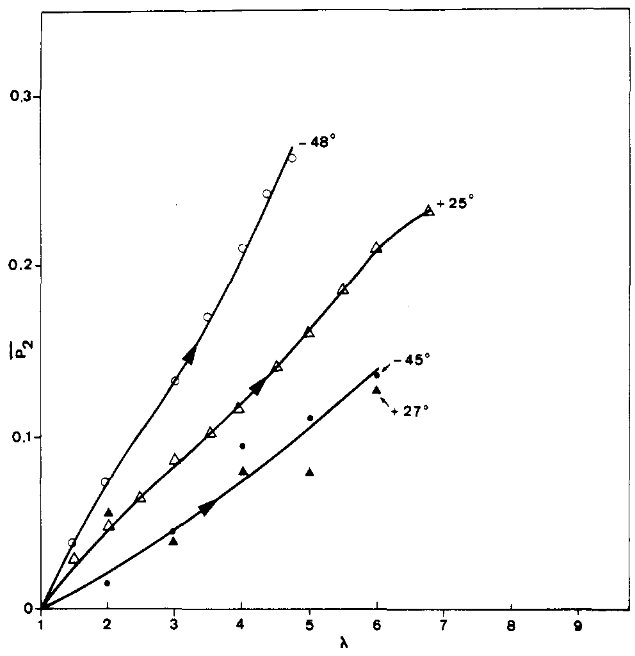

**Figure 3.** Orientation function versus draw ratio for polyisoprene networks. Results from infrared dichroic measurements at 27 °C (▲) and -45 °C (●), $M_c = 5.55 \times 10^3$. Results from fluorescence polarization experiments[1] at 25 °C (△) and -48 °C (○), $M_c = 5 \times 10^3$.

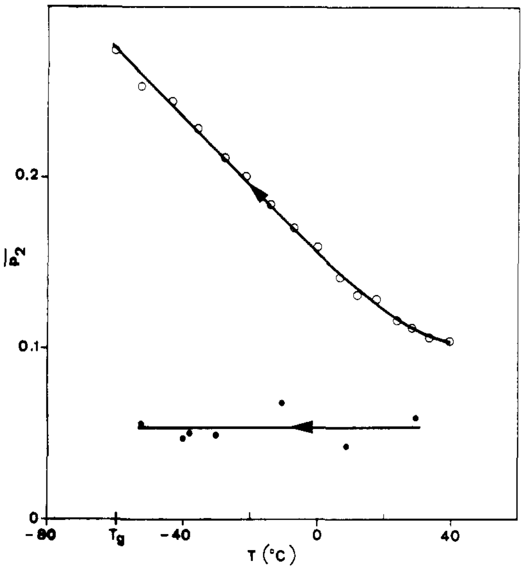

**Figure 4.** Temperature dependence of the orientation function: (●) experiment performed by infrared dichroism at constant length (λ = 4 before cooling; $M_c = 5.55 \times 10^3$); (○) experiment performed by fluorescence polarization[13] at constant length (λ = 2.5 before cooling; $M_c = 5 \times 10^3$).

## Conclusion

The fact that no appreciable temperature effect was observed in the infrared experiments leads us to conclude that the local orientational correlations between neighboring chain segments in *cis*-1,4-polyisoprene exhibit an entropic character.

## References and Notes

(1) Jarry, J. P.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1879.
(2) Deloche, B.; Dubault, A.; Herz, J.; Lapp, A. *Europhys. Lett.* **1986**, *1*(12), 629.
(3) Dubault, A.; Deloche, B.; Herz, J. *Macromolecules* **1987**, *20*, 2096.
(4) Sotta, P.; Deloche, B.; Herz, J.; Lapp, A.; Durand, D.; Rabadeux, J. C. *Macromolecules* **1987**, *20*, 2769.
(5) Sotta, P.; Deloche, B.; Herz, J. *Polymer* **1988**, *29*, 1171.
(6) Erman, B.; Jarry, J. P.; Monnerie, L. *Polymer* **1987**, *28*, 727.
(7) Queslel, J. P.; Erman, B.; Monnerie, L. *Polymer* **1988**, *29*, 1818.
(8) Erman, B.; Queslel, J. P.; Monnerie, L. *Polymer* **1988**, *29*, 1823.
(9) Queslel, J. P.; Mark, J. E. *J. Chem. Phys.* **1985**, *82*, 3449.
(10) Amram, B.; Bokobza, L.; Queslel, J. P.; Monnerie, L. *Polymer* **1986**, *27*, 877.
(11) Queslel, J. P.; Erman, B.; Monnerie, L. *Macromolecules* **1985**, *18*, 1991.
(12) Erman, B.; Bahar, I. *Macromolecules* **1988**, *21*, 452.
(13) Queslel, J. P., unpublished results.

---

# An AM1 Computational Study of the Cationic Polymerization Mechanism of Cyclic Acetals

PAUL M. LAHTI* AND C. PETER LILLYA

*Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003*

JAMES C. W. CHIEN

*Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003.*

*Received April 28, 1989;*
*Revised Manuscript Received July 3, 1989*

## Introduction

A long standing problem in cationic polymerization of cyclic acetals is identification of the propagation mechanism and active species.[1] The complexity of polymerization systems has prevented direct study of active species by spectroscopic techniques. However, Penczek and co-workers have used model compounds and "nonpolymerization" conditions to make a detailed study of 1,3-dioxolane polymerization.[2] They propose nucleophilic ring opening of cyclic oxonium ions (**1**, eq 1) as the main propagation pathway. Two of us have recently suggested that the alternative pathway involving an $\alpha$-oxycarbenium ion (**3**) is important in polymerization of the 2-substituted acetals 2-butyl-1,3-dioxepane (**4**, eq 2),[3] and 2-butyl-1,3,6-trioxocane.[4]

For complex chemical processes where the choice between mechanistic pathways cannot be made unambiguously based on experimental results, computational chemistry may be useful to help clarify matters. Although the inherent approximations in computational modeling render such models imprecise for obtaining *absolute* answers for real reactions, the level of experimental concordance with recent computational algorithms makes computation a practically useful tool for comparison of relative trends in a variety of cases. As a complement to Penzcek's model experimental data, we have applied the AM1 semiempirical molecular orbital method of Dewar and co-workers[5] toward examining whether cyclic acetal polymerization under cationic conditions occurs *via* simple $\mathrm{S_N}2$-type attack or by ring opening of the complexed acetal followed by addition. We report below the results of this study.

## Computational Methods

In all computations herein, the QCPE program AMPAC[6] was used, as adapted for the University of Massachusetts chemistry department Celerity 1260-D UNIX computer. For all molecules, the AM1 parameterization[5] was used for optimization of both energy minimum and transition-state structures, using restricted Hartree–Fock (RHF) closed-shell wave functions. The transition states were obtained by using the SADDLE routine in AMPAC[6] and were verified in each case by finding a single imaginary vibrational mode at the AM1-RHF level. Geometry punch files in typical AM1-RHF Z-matrix format are listed in supplementary material for energy minimum and transition-state structures discussed in this paper. Readers are referred to this material for complete computational structural information.

Before considering our results, it is worth recalling the assumptions of the computational model used. All energies computed are theoretical gas-phase enthalpies of formation based upon semiempirical parameterization and so do not explicitly include effects of entropy or substrate solvation. Such effects would certainly affect absolute numbers obtained in our study. However, comparison of relative trends ought not to be so greatly affected as to obviate their usefulness, hence we approach the interpretation of our results in a manner to emphasize such trends between similar processes. The success of such comparisons in past semiempirical reaction studies is,[7] in our opinion, sufficient justification for use of this approach.

## Results

We initially studied the energetics of cyclic oxonium cations versus their ring-opened counterparts (the quasi-cyclic carbenium forms), using different ring sizes and different substitution patterns at the 2-carbon (vide infra). The transition state for unsubstituted and 2-methyl-substituted 1,3-dioxolane ring opening was also found, from which the indicated activation barriers $E_a$ were computed[8] by using heats of formation and structures obtained directly from the AMPAC program. Figure 1 sumarizes these results.

Since the effect of ring size on the thermodynamics of ring opening is small at the AM1-RHF level of theory, we carried out our study on reactions modeling eq 1 versus eq 2 for the simplest, dioxolane case only, compound

0024-9297/90/2223-1214$02.50/0