them, their data fall on our line. There is also plotted in this figure the directly observed melting temperatures of solution crystals that were reported by Wunderlich, *et al.*[16] The melting temperatures were determined by light microscopy and rapid heating rates, greater than 10°/min, were utilized in order to avoid structural reorganization. Their data are seen to be coincident with the same straight line. The somewhat larger variation in the crystallite thickness than is usually observed has been attributed by the investigators to the deliberate nonisothermal crystallization procedures that were adopted at the high temperatures.[16] It is clear that within the uncertainty of the crystallite size determination these directly observed melting temperatures are virtually identical with the critical temperatures determined from annealing experiments. They yield the same value for T_m^0 and σ_{ee} and confirm the conclusions that have been made above.

Bair, Huseby, and Salovey[15,31] have attempted to determine the melting temperature of solution formed crystals by utilizing differential calorimetry at heating rates of 10°/min. However, prior to fusion, the samples were subject to very high irradiation doses. The underlying reason for this procedure is the assumption that was made[15] that lamella thickening, and other structural reorganizations, would be retarded without altering any of the thermodynamic quantities governing fusion. Their melting temperature determinations are also given in Figure 4. The solid straight line, designated *B*, representing these data, has been transposed from their original paper. As is indicated in the plot, the melting points determined by this procedure are from 4 to 6 deg higher for comparable values of ζ than is obtained by the other methods indicated. However, the extrapolated value obtained for T_m^0 is 145.8°.[31] The basis for the difference in the melting points appears to reside in either the method of measurement or in the introduction of the crosslinks into the highly crystalline system. It still remains to be established that at the heating rates employed structural reorganization is prevented by this procedure and furthermore that no other changes occur by virtue of the cross-linking. It is known, for example, that the enthalpy of fusion is changed by this process.[32] It is also theoretically expected that the cross-linking of a highly crystalline system should result in an elevated melting temperature.[33] In view of these possibilities we note that the data can be given another representation. This is indicated by the dashed line of Figure 4. This new straight line is approximately parallel to the one from Figure 3 and would indicate that about the same interfacial free energy is involved. However, this line extrapolates to a much higher value of T_m^0. This latter representation would thus be in accord with theoretical expectations.[33] Hence for this particular set of data it could also be argued that the cross-linking process has altered the thermodynamic properties.

The new data that have been presented here, together with the data in the literature that have been cited, substantiate the premise that the annealing phenomenon and the attendant change in properties are a consequence of fusion. There is, therefore, a very natural explanation for the changes in properties observed upon annealing. It is thus not necessary that chain units within the interior of the crystals be endowed with any extraordinary mobility. The mobility and motion of the chain units that are involved are merely a consequence of the fusion process. The concept[2,7,9,10] that a regularly structured interface is maintained during annealing is clearly not acceptable.

(31) H. E. Bair, T. W. Huseby, and R. Salovey in "Analytical Calorimetry," R. S. Porter and J. F. Johnson, Ed., Plenum Publishing Corp., New York, N. Y. 1968, p 31.

(32) A. M. Rijke and L. Mandelkern, *J. Polym. Sci., Part B*, in press (1969).

(33) P. J. Flory, *J. Amer. Chem. Soc.*, **78**, 5222 (1956).

Dielectric Dispersion in Branched Polypropylene Oxides

W. H. Stockmayer[1] and J. J. Burke

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 and Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755. *Received July 21, 1969*

ABSTRACT: Liquid trifunctional star polymers of propylene oxide resemble the parent linear polymers in showing two distinct regions of dielectric dispersion. The principal peak occurs at the same frequency as in the linear polymer. The small secondary dispersion peak again corresponds to a parallel dipole moment component of 0.18 D per repeat unit, and its relaxation time can be predicted from the molecular weight and viscosity by means of the theoretical formulas of Ham or Zimm and Kilb.

Linear polymers of propylene oxide show two distinct regions of dielectric dispersion.[2] The principal relaxation peak is found in the same frequency region (at a given temperature and pressure) for all molecular weights;[2,3] it has been correlated[3] with mechanical[4a] and nmr[4b] relaxation data, and is due to local motions of the chain backbone. The small

(1) Address correspondence about this paper to W. H. Stockmayer at the Department of Chemistry, Dartmouth College, Hanover, N. H. 03755.

(2) M. E. Baur and W. H. Stockmayer, *J. Chem. Phys.*, **43**, 4319 (1965).

(3) G. Williams, *Trans. Faraday Soc.*, **61**, 1564 (1965).

(4) (a) B. E. Read, *Polymer*, **3**, 529 (1962); (b) T. M. Connor, D. J. Blears, and G. Allen, *Trans. Faraday Soc.*, **61**, 1097 (1965).

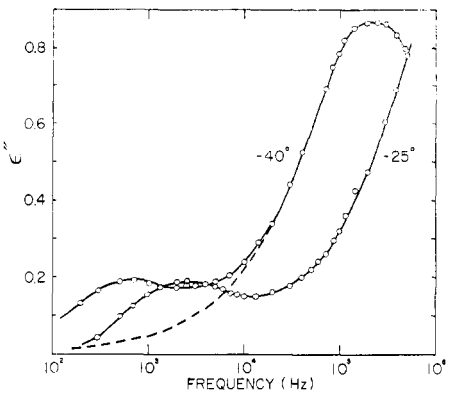

Figure 1. Dielectric loss factor ϵ'' as a function of frequency at two temperatures for branched polymer 11-400. The dashed curve emanating from the $-40°$ isotherm represents a smoothed extrapolation of the principal loss peak to lower frequencies.

secondary relaxation peak, which accounts for only 4–5% of the total dielectric polarization, occurs at lower frequencies which depend strongly on molecular weight. It reflects large-scale chain motions which are dielectrically active because of a small component of electric dipole moment parallel to the chain contour within each repeat unit of the structure. The observed frequency of maximum loss of this secondary dispersion can be quantitatively predicted[2] from the molecular weight and viscosity of the polymer by means of existing theory.[5,6]

In the present paper it is shown that rather similar and equally predictable dielectric behavior is found in branched poly(propylene oxides) with the trifunctional star structure

$$\begin{array}{l} CH_2(OCH_2CHR)_xOH \\ | \\ CH(OCH_2CHR)_yOH \\ | \\ CH_2(OCH_2CHR)_zOH \end{array}$$

where R is CH_3 and $x \simeq y \simeq z$. This work has already been mentioned elsewhere.[6]

Experimental Section

Dow Chemical Co. polyglycols 11-200 and 11-400 were the samples studied. These liquid atactic trifunctional star polymers had number-average molecular weights of 2600 and 4600, respectively, as calculated from the manufacturer's end group analysis (1.96 and 1.12% OH). The viscosity-average molecular weights were estimated from measured intrinsic viscosities in benzene at 25° (0.055 and 0.093 dl/g) by using the published[7] relationship with a factor $g^{1/2}$ of 0.88 for a trifunctional star,[8] the results being 2600 and 5800. Accordingly, we adopt 2600 and 5000 as the molecular weights in the calculation of relaxation times described below.

Viscosities of the polymeric liquids were measured over the temperature range 5–25°, and a manufacturer's figure is available at 100°F. These values were fitted to an equation of the Vogel-WLF type (eq 1) in which the constant 180°K

$$\log \eta = A(T - 180)^{-1} + B \qquad (1)$$

is the same as that employed[1] for linear poly(propylene oxides). With η in poise and T in °K, the constants are $A = 364$, $B = -2.52$ for polymer 11-200 and $A = 358$, $B = -2.23$ for polymer 11-400. Thus the temperature dependence of the viscosity is much the same as that of the viscosity of the linear polymers and that of the principal dielectric maximum loss frequency of the linear polymer.[3]

Dielectric measurements over the frequency range 50–6 × 10^5 Hz and the temperature range -45 to $+20°$ were performed with the Cole–Gross bridge[9] and cell previously employed,[2] and similar techniques were used throughout. All measurements were under atmospheric pressure. Sample results are given in Figure 1, where the dielectric loss factor ϵ'' for polymer 11-400 is shown as a function of frequency at two temperatures.

Results and Discussion

Static dielectric constants were not determined with high precision and are not reported here. It is worth remarking, however, that at a given temperature the static dielectric constant for all the atactic poly(propylene oxides) studied, both linear[2,3] and branched, is a smooth, almost linear function of hydroxyl content. Thus the values found for 11-200 and 11-400 are close to those for the linear samples 2025 and HMW studied previously.[2]

Frequencies of maximum loss for the principal dispersion peak are easy to obtain directly. The corresponding quantity for the secondary peak was obtained after subtracting an extrapolated smoothed loss curve for the principal peak from the experimentally determined curve which contains the secondary peak as a shoulder. The Fuoss–Kirkwood function[10]

$$\epsilon'' = A \operatorname{sech} [\alpha \log (f/f_{max})] \qquad (2)$$

is convenient for this purpose, and is adequate despite the rather asymmetric shape of the principal loss peak[2,3] because it is required only on the low-frequency side of the maximum. An example of this procedure is indicated in Figure 1. The maximum loss frequencies thus obtained were converted to the corresponding relaxation times by the relation

$$2\pi f_{max} = 1/\tau \qquad (3)$$

As remarked previously,[2] the total change in dielectric constant ϵ' on traversing the secondary dispersion region is small enough so that the values of τ obtained can safely be taken to be "molecular" relaxation times.

Results of the above treatment of the measurements are given in Table I, and some of these are shown in Figure 2. Attention is first directed to the relaxation times for the principal dispersion region, denoted by unflagged circles. It is seen that the figures for the two branched polymers are close to each other and to those for the linear polymers studied previously.[2] The dashed curve which passes among the points is drawn from the equation given by Williams[3] to correlate his measurements on a linear polymer of very high molecular weight ($M_w \sim 10^6$). It thus appears clear that the principal peak reflects a truly local mode

(5) W. H. Stockmayer and M. E. Baur, *J. Amer. Chem. Soc.*, **86**, 3485 (1964).
(6) W. H. Stockmayer, *Pure Appl. Chem.*, **15**, 539 (1967).
(7) J. Moacanin, *J. Appl. Polym. Sci.*, **1**, 272 (1959).
(8) B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, **37**, 19 (1959).
(9) R. H. Cole and P. M. Gross, *Rev. Sci. Instr.*, **20**, 252 (1949).
(10) R. M. Fuoss and J. G. Kirkwood, *J. Amer. Chem. Soc.*, **63**, 385 (1941).

TABLE I
COMMON LOGARITHMS OF DIELECTRIC RELAXATION TIMES FOR BRANCHED POLYPROPYLENE OXIDES

Temp, °C	Principal peak log τ_1, sec	Secondary peak log τ_2, sec
	Polymer 11-200	
−42.5	−5.3	−3.4
−38.0	−5.8	−3.8
−32.0	−6.4	−4.3
−25.0		−4.8
−20.0		−5.1
	Polymer 11-400	
−44.5	−5.4	
−42.5	−5.6	−3.1
−40.0	−6.2	−3.4
−35.0	−6.4	−3.8
−29.0		−4.0
−25.0		−4.1
−10.0		−5.1
0.0		−5.6
+20.0		−6.3

of motion of the chain backbone, independent of branching or of chain length. Detailed and realistic molecular theories of such motions have yet to be devised.

The secondary peak provides an opportunity for genuine prediction. For linear polymer 2025, it was shown[2] that the observed relaxation times τ_2 of the secondary peak are in very good agreement with relaxation times τ_2' calculated for the second normal relaxation mode of the chain,[11] free draining conditions being assumed as appropriate to the undiluted system.[12] The second rather than the first normal mode is the correct choice[5] because the polymers have the structure

$$H(OCHRCH_2)_xO(CH_2CHRO)_yH$$

where $x \simeq y$, so that the two ends of the chain must move in phase with each other and out of phase with the midpoint of the contour.

For the trifunctional star polymers of the present study, a glance at the structure shows that it is again the second normal mode which is congruent to the charge distribution produced by the parallel or "type A"[6] components of the repeat-unit dipoles: the three ends must each move just out of phase with the branch point. For a free-draining undiluted polymer the theoretical relaxation time corresponding to this nondegenerate mode is[5,13]

$$\tau_2' = 12M\eta/7\pi^2RT\rho \qquad (4)$$

where M is the molecular weight of the polymer and ρ is the density. From the measured molecular weights, densities and viscosities, the last extrapolated when necessary by means of eq 1, the theoretically calculated relaxation times based on the above equation are obtained as the full curves shown in Figure 2; the upper

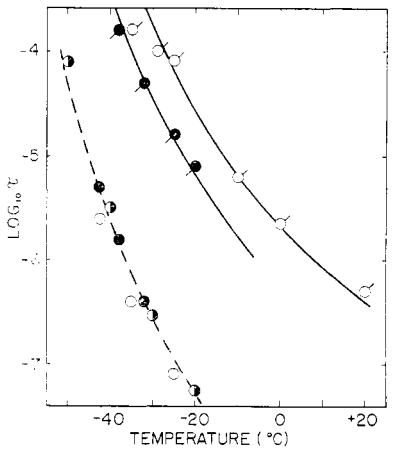

Figure 2. Relaxation times corresponding to frequencies of maximum loss for several propylene oxide polymers: ●, branched polymer 11-200; ○, branched polymer 11-400; ◑, linear polymer 2025 (ref 2); flagged circles are for the secondary dispersion, unflagged circles for the principal dispersion. The dashed curve through the points for the principal dispersion is drawn from the equation given by Williams (ref 3) for a high molecular weight linear polymer. The full curves for the secondary dispersions are theoretical predictions from eq 4.

curve is for sample 11-400 and the lower for 11-200. The experimental values, found as described earlier, are displayed as flagged circles. Since the uncertainty in evaluating log τ_2 from the data is of the order of at least ±0.1 unit, the prediction is spectacularly successful. It is also a bit lucky at the lower temperatures: the viscosity measurements stop above 0°, and the extrapolation is somewhat sensitive to the choice of the temperature parameter (where we have used 180°K) in eq 1. However, this remark cannot affect the excellent agreement at and above −20°.

The assumption of free-draining conditions in the bulk polymer liquid[12] is not rigorously established. At the other extreme, one might choose to apply the theory for nondraining molecules,[8,14] which would certainly be better in the case of dilute solutions. When this is done,[15] the predicted relaxation times are from three to five times longer than the experimental values. As an absolute prediction this can still be considered quite good, but empirically the free-draining equations give the better results. The bulk viscosity measurements also support the free-draining assumption. For example, by interpolating among the measured viscosities for linear poly(propylene oxides)[2] and applying the appropriate free-draining relation

$$\eta(\text{branched}) = g\eta(\text{linear}) = (7/9)\eta(\text{linear}) \qquad (5)$$

we predict bulk viscosities of 10.1 and 5.0 P for sample 11-200 at 10 and 20°, respectively; the measured values[15] are 10.4 and 4.95 P.

The magnitude of the parallel type A component of the dipole moment is not without interest. It is fortunately immaterial whether the Clausius–Mossotti or Onsager relation is used to calculate this part of the

(11) P. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1953).
(12) F. Bueche, *ibid.*, **20**, 1959 (1952).
(13) J. S. Ham, *ibid.*, **26**, 625 (1957). In addition to the second normal mode, all the higher "odd-even" modes, corresponding to $k = 6, 10, 14$, etc., must also contribute to the dielectric relaxation; but it is easy to show that over 80% of the peak is due to the mode with $k = 2$.
(14) B. H. Zimm, *ibid.*, **24**, 269 (1956).
(15) J. J. Burke, Jr., Ph.D. Thesis, M.I.T., 1962.

dipole moment, again because the total change of ϵ' through the secondary dispersion region is small. From either relation, and for each of the two branched polymers, it is found that the root-mean-square type A moment per repeat unit is 0.18 D. This numerical value is exactly the same as that found previously[2] for linear poly(propylene oxides), and compares well with the observed[16] moment of 0.22 D along the C–C bond of the ring in monomeric propylene oxide.

(16) J. D. Swalen and D. R. Herschbach, *J. Chem. Phys.*, 27, 100 (1957).

Acknowledgments. Most of this work was supported at M.I.T. (1959–1961) by the U. S. Army Research Office (Durham). Later support at Dartmouth College was from the NSF. The apparatus had been constructed earlier with the aid of grants from the American Chicle Co. and Dunlop of Canada, Ltd. Fellowship support of J. J. B. by Phi Kappa Pi, the American Cyanamid Co., and the NSF is gratefully recalled.

Toward a Statistical Theory of Superhelices. The Configurational Entropy of Cyclic Molecules with Random Loops

Homer Jacobson

Department of Chemistry, Brooklyn College of the City University of New York, Brooklyn, New York 11210. *Received June 25, 1969*

ABSTRACT: Expressions for the configurational entropy of superhelix-like molecules have been developed, using a random-walk cyclic model containing N rigid links of length b, with a minimum loop size of q links. Criterion of the configurational restriction into $t + 1$ loops is chain contact, within a volume $\pi r_e^2 b$, at t points, where r_e is an averaged closure radius. Application of ring-closing theory gives approximately $S(N,q,t) = k \ln [(2t!)^{-1} N^{t+5/2} (\mathrm{LCF})^t] + k\overline{I \ln I/\bar{I}}$, where $\mathrm{LCF} = (3/2)^{3/2}\pi^{-1/2}(r_e/b)^2$, and I is Π (from $i = 1$ to $t + 1$)$(m_i)^{-1/2}/m_1 m_{t+1}$, m_i being the size of the ith loop in the molecule. The indicated averaging was performed by Monte Carlo summation over a large sample of molecules with random m_i's, yielding a function approximately equal, for $\overline{I \ln I/\bar{I}}$, to $A - Bt$, for t above 2. Computations for a λ-phage–DNA-like model with $N = 200$, $q = 2$, and $\mathrm{LCF} = 10^{-4}$ at varied t show a monotonic decrease of S with t of an order slightly higher than linear, reaching $-965k$ eu for the maximally looped structure with $t = 99$. Expressions for distributions of t in ensembles with fixed net twist are derived; it is shown that reverse twists are unlikely in many loop molecules. Loop size distributions are also generable from expressions given by the theory; hydrodynamic variables are more properly calculated therefrom than from earlier simplified superhelix models.

Recent interest in superhelices stems from their discovery in viral and mammalian nucleic acids.[1–5] Mechanistic models have been produced[6,7] to account for their sedimentation and viscosity properties. This paper describes the start of a general configurational theory of the superhelix structure ensemble, as distributions of such configurations may be expected in response to the parameters affecting the ensemble. Its main thrust is the calculation of probabilities for the possible configurations in looped molecules, and by direct inference the distributions of loop numbers and sizes, and the entropy of specific collections of loops resulting from superhelix-generating chain twists.

The presence of multiple closed-end loops and contacts of crossed sections of the primary helix chain distinguishes a superhelix from an ordinary cyclic molecule. The latter may develop a small number of loops in random fashion, but the superhelix has an average excess of loops twisted in one direction. Figure 1 shows two possible models of superhelical chains, representing the twisted loop, or "interwound" model[2,8] considered here. We reject the "toroidal" model[2,8] as a physical reality, on the basis of experience with physical models of superhelix twist, which promptly close the opened loops, to assume the interwound configuration.

We define a loop index t to be the total number of chain contact crossings in either twist direction, leading to $t + 1$ loops. In Figures 1a and 1b, the twist directions are represented to be in the same direction. In fact t is a continuous variable, but here it will be considered discrete, as a convenience of theoretical analysis. We will also regard t as a *de facto* number holding for a particular configuration at a particular time, rather than as a time average, or as the quantity of potential chain twist which would just relieve the uncoiling of the primary helix. We are then free to consider the ensemble of possible looped molecules with any specific integral t, and to compute the entropy of the ensemble. Then any needed study of collections of configuration with various t's lumped together, or integrations over varied t, can be performed.

(1) J. Vinograd, J. Lebowitz, R. Radloff, R. Watson, and P. Laipis, *Proc. Nat. Acad. Sci. U. S.*, **53**, 1104 (1965).
(2) W. Bauer and J. Vinograd, *J. Mol. Biol.*, **33**, 141 (1968).
(3) H. S. Jansz and P. H. Pouwels, *Biochem. Biophys. Res. Commun.*, **18**, 589 (1965).
(4) L. V. Crawford, *J. Mol. Biol.*, **13**, 362 (1965).
(5) A. M. Kroon, P. Borst, E. F. J. Van Bruggen, and G. J. C. M. Ruttenberg, *Proc. Nat. Acad. Sci. U. S.*, **56**, 1836 (1966).
(6) V. A. Bloomfield, *ibid.*, **55**, 717 (1966).
(7) H. B. Gray, Jr., V. A. Bloomfield, and J. E. Hearst, *J. Chem. Phys.*, **46**, 1493 (1967).
(8) J. Vinograd, J. Lebowitz, and R. Watson, *J. Mol. Biol.*, **33**, 173 (1968).